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LITERARY HERITAGE

BIBLIOGRAPHY OF PROFESSOR D.Sc. IVELIN KULEFF

DEDICATED TO THE 70TH ANNIVERSARY OF PROF. Ivelin Veselinov Kuleff

Ivelin Veselinov Kuleff was born on July 5th, 1942 in Shumen. He is a graduate of the Faculty of Chemistry, “St. Kliment Ohrisdi” University of Sofia (1967). From the same year he has worked as a radiochemist at the Chair of General and Inorganic Chemistry. Later on Mr. Ivelin Kuleff successfully competed for the positions of Assistant Professor of Radiochemistry (1969), Senior Assistant (1973) and Chief Assistant (1979). In 1980 he defended a Ph.D. thesis in the field of radiochemistry (scientific consultant Prof. K. Kostadinov). During that early period of his career Dr. Kuleff lectured on “Radiometry” (1972–1979) and spent 17 months at the Technical University in Munich, Germany, on hot atoms chemistry (1971–1972) as a scholar of the International Atomic Agency (IAEA, Vienna).

In 1984 Dr. I. Kuleff moved to the Department of Analytical Chemistry and established there a “Laboratory of Radioanalytical Chemistry” (1984–2011), headed by him until his retirement in 2011. He has become Senior Research Associate on Analytical Chemistry (Radioanalytical Chemistry) (1989), Associate Professor of Analytical Chemistry (1996), and Full Professor of Analytical Chemistry (Radioanalytical Chemistry) (2002–2011). Dr. Kuleff defended a D.Sc. thesis on archaeometric studies by neutron activation analysis (NAA) in 1998.

Professor Kuleff has lectured in numerous courses on “Radiochemistry”, “Radioanalytical Chemistry”, “Radiometry and Radiometric Analysis”, “Nuclear Chemistry and

Prof. Kuleff has served as a Deputy Dean of the Faculty of Chemistry (2001–2004), a member of the Specialized Scientific Council on Inorganic and Analytical Chemistry (1997–2004), and a member (2004–2006) and Chairman (2007–2009) of the Commission on Chemical Sciences at the Supreme Attestation Commission at the Council of Ministers in the Republic of Bulgaria. Professor Kuleff is a member of the Union of Chemists in Bulgaria, Gesellschaft für Naturwissenschaftliche Archaeometrie (Germany), Bulgarian Society for the Chemistry Education and History and Philosophy of Chemistry (CE&HPC), and Fellow at the IUPAC, Inorganic Chemistry Division, Commission on Isotopic Abundances and Atomic Weights.

The scientific research of Professor Kuleff has been mailly in the field of analytical chemistry, radiochemistry, archaeometry and ecochemistry, with an emphasis on neutron activation analysis, gamma spectrometry, radiometry, X-ray fluorescence, sampling and chemomeric treatment of experimental data from multielement analytical techniques.

Complete bibliography of Professor Ivelin Kuleff, including 2 theses, 14 books/textbooks and book chapters and over 160 journal and conference papers has been compiled and given in chronological order below (in this issue). Titles of publications are given in their original language of publication and those published in Cyrillic (Bulgarian, Russian) are also translated in English.

**Theses**

1. **Кулев, И. В.** Неутронноактивационно определяне на съдържанието на уран в скали, минерали и природни води. Дисертация за научната степен “Кандидат на химическите науки” по 01.05.12 “Радиохимия”, Химически факултет, Софийски университет “Св. Климент Охридски”, С., 1980, 231 с.  

Books


Book Chapters


Textbooks


**Scientific Papers**


28. Тодоровски, Д., И. Кулеф, Д. Димова, Г. Чапкънова. Определение содержания уранила в тунисских фосфоритах, преработанных в Химкомбинате “Българо-съветска дружба”, гр. Димитровград и в продукты их преработки. Известия на КНТПВО, (бр.12), 1977, 191.


35. Петров, Й. Г., И. Кулеф, Д. Платиканов. Съдържание на неорганични йони в Лангмюир-Блоджетови мултислоеве: I. Двувалентни катиони в мултислоеве от арахинова киселина.


64. Цочев, С., **И. Кулев,** Г. Гьошев, Г. Стефанов. Относно радиоизотопния състав на течни радиоактивни отпадъци в АЕЦ. *Сб. докл. Нац. Съществе у Атоменерго–1000*, Варна, 1985, с. 46–56.


83. Джингова, Р., И. Кулев, И. Пенев. Химически профил на находки от сграфито керамика. II. Изследване на археологически находки от Калиакра, Каварна и Балчик (XII–XIV в.). Изв. Нар. музей Варна, 28 (43), 1992, 333–352.


88. Кулев, И., Р. Джингова, Г. Джингов, И. Пенев. Химически профил на находки от сграфито керамика. IV. Изследване на археологически находки от Велико Търново. Годишник на Музеите в Северна България, ХІІ, 1993, 131–158.


92. Кулев, И., Р. Джингова, Г. Джингов, И. Пенев. За химичния състав на стъклата от старите български столици Плиска и Преслав. Годишник на Музеите в Северна България, XX, 1994, 469–495.

93. Джингова, Р., И. Кулев, А. Вулгаропулос. Исследование загрязнения тяжелыми металлами в Софии (Болгарии) и Салониках (Греции) с применением Taraxacum officinale в качестве биомонитора. Экологическая химия, 4, 1995, 270–274.


117. **Кулеф, И. Защо измерваха динозаврите? или Как прецизният химичен анализ даде отговор на загадката. Химия, X (6), 2001, 409–423.**


139. Кулев, И. За имената на най-новите елементи в периодичната система. Химия, XIV (3), 2005, 196–203.

140. Кулев, И., Ст. Стоянов. Система от показатели за атестиране на университетските преподаватели в природните науки. Наука, XVI (2), 2006, 17–24.


159. Ivanova, S., **I. Kuleff.** Archaeological Amber from the Late Bronze and the Iron Age in the Territory of Ancient Thrace *Archaeologia Bulgarica, XIII* (3), 2009, 23–46.


170. Кулев И. Химия и археометрия. Наука, XXI (3), 2011, 12–17.

Kuleff, I. Chemistry and Archaeometry, Nauka (Sofia), XXI (3), 2011, 12–17 (in Bulg.).


Kuleff, I. Maria Sklodovska-Curie and the International Year of Chemistry, Khimiya, XX, 2011, 83–95 (in Bulg.).


173. Кулев, И. За Мария Склодовска-Кюри и радиоактивността. Наука, XXI (6), 2011, 17–21.

Kuleff, I. On Maria Sklodovska-Curie and Radioactivity, Nauka (Sofia), XXI (6), 2011, 17–21 (in Bulg.).


175. Кулев, И. Ароматите – в миналото и днес. Наука, XXII, (5), 2012 (in press).


MISCELLANEOUS PUBLICATIONS


186. *Kuleff, I.* Scientific Facts about the Shroud of Christ. *Orbita* (Sofia), (No. 19) (1130), 09.05.1992 (in Bulg.).

187. *Kuleff, I.* Bulgarian People ‘Eat’ about 3 Milligrams Uranium in One Year, *Demokratsia* (Sofia), No. 140 (2944), 02.06.1999 (in Bulg.).

188. *Kuleff, I.* How Dangerous is Depleted Uranium. *Demokratsia* (Sofia), No. 15 (3487), 19.01.2001 (in Bulg.).


197. **Кулев, И.** Пета Черноморска конференция по аналитична химия. Химия и индустрия, 80, 2009, 76–77.

**Kuleff, I.** 5th Black Sea Conference on Analytical Chemistry, Khimiya i Industriya, 80, 2009, 76–77 (in Bulg.).


**Kuleff, I.** 38th International Symposium on Archaeometry, Khimiya i Industriya, 82 (2), 2010, 65–66 (in Bulg.).

201. **Кулев, И.** Година на химията. Химия и индустрия, 82 (1–2), 2011, 2–4.


**Kuleff, I.** The Seminar of Conservators in Bulgaria, Khimiya i Industriya, 82, (1–2), 2011, 36–37 (in Bulg.).


**Kuleff, I.** Marieta Blau – Vienna and the Radioactivity. Homo Science, (Sofia), No. 5, 23.09.2011 (in Bulg.).


**Kuleff, I.** The demon-haunted world, a review, Nauka (Sofia), 21 (5), 2011, 82–83 (in Bulg.).

206. **Кулев, И.** Археометалургия в Европа – Трета конференция. Химия и индустрия, 82 (2), 2011, 67–68.

**Kuleff, I.** Archaeometallurgy in Europe – the 3rd Conference, Khimiya i Industriya, 82 (2) 2011, 67–68 (in Bulg.).

207. **Кулев, И.** Кой кой е в българската наука – рецензия. Химия и индустрия, 82, 2011, 84–85.

**Kuleff, I.** Who is Who in Bulgarian Science, a Review, Khimiya i Industriya, 82 (2), 2011, 84–85 (in Bulg.).
   Kuleff, I. Using of Copper in the Culture of “Bell Beaker”, a review, Bulgarian e-Journal for Archaeology, 1 (2), 2012, 83–90 (in Bulg.).


212. Кулев, И. Електрохимични методи в археометрията, консервацията и реставрацията — рецензия. Българско е-Списание за Археология, 1 (2), 2012, 137–140.

213. Кулев, И. За пигментите, използвани в археологията и художеството — рецензия. Българско е-Списание за Археология, 1 (2), 2012, 135–136 (in Bulg.).

214. Кулев, И. Археометрия като научна област, сн. Природа, 1 (1), 2012, 36–40
   Kuleff, I. Archaeometry as Scientific Field. Priroda (Sofia), 1 (1), 2012, 36–40 (in Bulg.).

Translations

Инструментален анализ, Крисчън, Г., Д. О’Рейли (ред.), превод от английски от Б. Желязкова,


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LITERARY HERITAGE

PROFESSOR D.Sc. NIKOLAY TYUTYULKOV

SCIENTIFIC PUBLICATIONS: 1993–2012

1993

1. Tyutyulkov, N., S. Karabunarliev, K. Müllen, M. Baumgarten. Band Structure of Quasi One-


1994


1995


1996


1997


1998


2000


2001


2002


72. Тютюлков, Н., Ф. Диетц. Органични полимери с феромагнитни свойства. Пленарен доклад. Материали на 15 Национален симпозиум “Полимери – 2002“, София, 3–5 Октомври, 2002

2003


78. Тютюлков, Н., Ф. Диетц. Молекулен магнетизм. Химия и Индустрия, 74 (2003), 1

79. Тютюлков, Н., Ф. Диетц. Молекулен магнетизм. Химия, 12, No 5 (2003), 383


2004


2005

86. Drebov, N., N. Tyutyulkov, S. Karabunarliev, F. Dietz. Photoswitching of redox potentials and spectroscopic properties in UV/Vis/NIR region. *Z. Naturforsch.*, 60b (2005), 75


**2006**


**2007**


**2008**


**2009**


**2010**


105. Тютюлков, Н. Приложение на симетрията в химията. *Химия и Индустрия*, 82 (2011), 9

2012

106. Тютюлков, Н. Полиметинови багрила. *Химия и Индустрия*, 82 (2011), 65

2013


МОНОГРАФИЯ

110. Тютюлков, Н., Ф. Дитц. Симетрия, Строеж и Свойства на Молекулите. Изкуство, София, 2011
In Memoriam: Assoc. Prof. DONKA CHRISTOVA NONOVA

1924–2012

Donka Christova Nonova was born on January 15th, 1924 in the Village of Podvis, District of Burgas, Bulgaria. She was a student in Chemistry at the Faculty of Natural Sciences, „St. Kliment Ohridski“ University of Sofia and graduated in 1947. Miss D. Nonova was elected an Assistant Professor of Analytical Chemistry in 1947 (working with M. Michoff and N. P. Pentchev), and was gradually promoted to the academic positions of Senior Assistant Professor (1953) and Chief Assistant Professor (1964). She was elected an Associate Professor of Analytical Chemistry in 1977. Miss D. Nonova specialized in Budapest (1964) and Brno (1972). Assoc. Prof. D. Nonova taught the main course of Analytical Chemistry and elective courses on (molecular) Spectrophotometry and Application of Organic Reagents in Analytical Chemistry. During the period of 1950–1984, D. Nonova published 44 research papers in Bulgarian, French, German and (mostly) in English (over one-half of them in international journals with impact factors), as well as one Bulgarian patent (‘Author’s Certificate’) in 1979, and one teaching aid on Qualitative Semimicroanalysis with four editions (1966, 1984, 1990, 2000). Her papers have been published in specialized journals such as Anal. Chim. Acta, Coll. Czech. Chem. Commun., Compt. Rend. Acad. Bulg. Sci., Fresenius’ Z. Anal. Chem., J. Inorg. Nucl. Chem., Mikrochim. Acta, Talanta, etc. Miss D. Nonova retired from the Faculty of Chemistry in 1984 but continued teaching for ten more years at the “Episkop Konstantin Preslavski” University of Shumen. During those over four decades, Miss D. Nonova has spent much efforts on higher education and research with numerous students and post graduates.

The main research field of D. Nonova was analytical chemistry, with an emphasis on qualitative semimicroanalysis, quantitative separations and enrichment by precipitation.
and liquid-liquid extraction, new organic reagents in spectrophotometry, complexometric titrations, metallochromic indicators, indirect methods for iodide, K, Te and thiocyanate, studies on complex formation in titrimetry and molecular spectrophotometry. Over 23 analytes and numerous organic reagents were involved in these in-depth studies. Efficient chemical reagents such as EDTA, 4-(2-pyridylazo)-resorcinol (PAR), 1-2(2-thiazolylazo)2-naphthol-3,4-disulphonic acid, 2-(5-bromo-2-piridylazo)-5-diethylaminophenol, Chrome Azurol S, long-chain quaternary ammonium salts (QAS), phenylfluorone, tri-n-octylamine, etc. were thoroughly studied. Representative selection of these papers by D. Nonova is given below.


Assoc. Prof. Donka Nonova has served for many years as an Editor of the journal “Annuaire de L’Universite de Sofia “St. Kliment Ohridski” Faculte de Chimie”.

For her long-term activities as an educator, scientist and editor, D. Nonova has been decorated with the Sign of Honor of the University of Sofia (2005), the Orders of Merit “Cyrill and Methodius” – Second Grade (1976) and First Grade (1984). The greatest recognition for her was the appreciation and love by her numerous colleagues, co-workers, and contributors to this journal.

Donka Christova Nonova died in Sofia on September 7th, 2012 at the age of 88.

SELECTED PUBLICATIONS

TEXTBOOKS


SELECTED SCIENTIFIC PAPERS


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SALT EFFECT ON THE RADICAL COPOLYMERIZATION OF 3-DIMETHYL(METHACRYLOXYETHYL)AMMONIUM PROPANE SULFONATE WITH N-VINYL-2-PYRROLIDONE IN WATER

I. KAMENOVA¹, E. KAMENSKA¹, G. GEORGIEV¹*

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Abstract. The copolymerization of 3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate (DMAPS) and N-vinyl-2-pyrrolidone (NVP), initiated by potassium persulfate (PPS), in water and in 1M NaCl at 43±1 °C under nitrogen atmosphere was studied. Copolymer composition was determined as a function of monomer feed. The relative monomer reactivity (DMAPS (M₁) and NVP (M₂)) were calculated: \( r_1 = 0.11±0.04; \) \( r_2 = 0.03±0.03 \) (copolymerization in water) and \( r_1 = 0.03±0.01; \) \( r_2 = 0.20 ± 0.02 \) (copolymerization in 1M NaCl aqueous solution). Salt effect is expressed in the change of \( r_1 \) and \( r_2 \) values in an opposite direction due to the increase of the π-electron delocalization ability in pure water in comparison with the same in 1M NaCl aqueous solution. Observable alternating tendency for this copolymerization in both solvents was indicated, which was attributed to the large difference between the e-parameters of both comonomers. The copolymers obtained with < 20 mol.% DMAPS concentration in monomer feed (\( M_{DMAPS} \)) are water-soluble – an important fact in overcoming the limited solubility of poly(DMAPS) in water.

Keywords: polyzwitterion, relative monomer reactivity, a donor-acceptor complex

INTRODUCTION

The poor solubility of polyzwitterion (PZ) in water limits their further studies such as thermal stability, viscometry, electrical conductivity etc. It was related to the formation of both intra- and inter- molecular dipole-dipole clusters (DDC) from opposite oriented
dipoles of zwitterionic (ZI) side groups, playing a role of physical nodes of the physical PZ network, see Figure 1 [1-8].

Several approaches are applied for increasing the PZ solubility in water: (i) addition of low–molecular salts [9-15]; (ii) temperature increase (PZ show an upper critical solution temperature) [12]; (iii) copolymerization of zwitterionic monomer with more hydrophilic monomer [16]. Having this in mind, in the present work the radical copolymerization of zwitterionic monomer (3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate) (DMAPS)) with N-vinyl-2-pyrrolidone (NVP) was studied.

![Figure 1. Dipole-dipole cluster of oppositely oriented dipoles of the zwitterionic side groups of PZ](image)

The main objectives were:

— Synthesis of new ZI copolymers - poly(3-dimethyl(methacryloyl-oxyethyl)ammonium propane sulfonate-co-N-vinyl-2-pyrrolidone) (poly(DMAPS-co-NVP)s) by radical copolymerization (RC) and their characterization.

— Determination of the copolymer composition and calculation of the relative monomer reactions.

— Statistical analysis of the microstructure of the poly(DMAPS-co-NVP)s obtained.

— The study of reaction rates of DMAPS and NVP radical copolymerization in aqueous solutions and the solubility of the copolymers in different solvents.

Having in mind the haemo- and biocompatibility of poly(NVP), NVP was regarded as suitable comonomer for our purpose. We expected that by varying copolymer composition, the self-assembling ability, hydrophilicity and solubility of the copolymers in water could be controlled.

EXPERIMENTAL

MATERIALS

NVP (Fluka Chemie AG, Switzerland) was vacuum distilled before use. DMAPS (Merck KGaA, Darmstadt, Germany, >98%) was used as obtained. Potassium persulfate (PPS) (Sigma-Aldrich Chemie GmbH, Munich, Germany, 99%) was purified by recrystallization from water. All copolymerizations were performed in distilled water and in 1M NaCl aqueous solutions. All other solvents were used as obtained.
COPOLYMERIZATION OF NVP AND DMAPS IN WATER AND IN 1M NaCl

The copolymerization of DMAPS and NVP (Figure 2) was performed in distilled water or 1M NaCl aqueous solution at 43 ± 1 °C with 1 wt.% PPS in nitrogen. The total monomer concentration was 1.5M. The ratio of DMAPS to NVP in the initial monomer feed were

Figure 2. Chemical structures of DMAPS and NVP.

10/90 (copolymer 1), 20/80 (copolymer 2, 2.1), 40/60 (copolymer 3), 50/50 (copolymer 4, 4.1), 70/30 (copolymer 5), 80/20 (copolymer 6, 6.1), 80/20 (copolymer 7) and 90/10 (copolymer 8) mol%/mol%. Relative monomer reactivity were determined under conversion (q) below 10%. The conversion (q) was determined gravimetrically. For removing residual unreacted monomers and initiator, the synthesized copolymers were purified by dialysis against distilled water for 10 days. After lyophilization and drying, white powders were obtained. The copolymer compositions were calculated from the elemental analysis data.

MEASUREMENTS

The copolymer compositions were determined by sulphur (S) analysis using Vario EL III elemental analyser (Elementar Analysensysteme GmbH, Hanau, Germany). The 1H-NMR spectra of DMAPS, NVP, their equimolar mixture and poly(DMAPS-co-NVP) were registered on Bruker 250 MHz spectrometer in D2O. The relative monomer reactivity ratios of DMAPS and NVP (r1 and r2) in both solutions were calculated by Ezrielev-Brochina-Roskin (EBR) [17] and Integral Tidwell-Mortimer (ITM) [18] methods. The calculation of the statistical distribution of monomer sequences M1-M1, M1-M2, and M2-M2 was performed for poly(DMAPS-co-NVP)s by both methods of Igarashi [19] and Markov chains [20, 21].

The 1H NMR spectra of DMAPS, NVP, their equimolar mixture and copolymer (the concentration of DMAPS monomer in copolymer composition M_{DMAPS} = 50 mol%) are prepared in D2O, δ ppm: (i) δ 6.2 ppm (s, 1H, CH3=C-CH3); 5.8 ppm (s, 1H, CH3=C-CH3); 4.6 ppm (t, 2H, COOCH2CH2); 3.52 ppm (m, 2H, COOCH2CH2); 3.41 ppm (t, 2H, N+(CH3)2-(CH2)2SO3–); 3.3 ppm (s, 6H, N+(CH3)2), 3.24 ppm (t, 2H, N+(CH3)2-(CH2)2-CH2-SO3–); 2.35 ppm (m, 2H, N+(CH3)2-CH2-CH2-CH2-SO3–) and 1.85 ppm (s, 3H, CH2=C-CH3) for DMAPS monomer; (ii) δ 2.10 ppm (t, 2H, CH3-CH2-C=O), 2.5 ppm (m, 2H, -CH2-C=O); 3.6 ppm (t, 2H, CH2-N), 4.6 ppm (m, 2H, CH3=CH-N) and 6.96 ppm (m, 1H, CH2=CH-N) for NVP monomer; (iii) for equimolar mixture of DMAPS and NVP: all signals for characteristic groups of the two monomers are present. The signals from DMAPS (3.41 ppm (t, 2H, N+(CH3)2-(CH2)2-CH2-SO3–), 3.52 ppm (m, 2H, COOCH2CH2), 4.6 ppm (m, 2H, CH3=CH-N),
COOCH$_2$) and from NVP (3.6 ppm (t, 2H, CH$_2$-N), 4.6 ppm (m, 2H, CH$_2$=CH-N)) are overlapped. (iv) for p(DMAPS-co-NVP) ($M_{DMAPS}$=50 mol%): the signals for characteristic groups of DMAPS and NVP are detected. The signals from DMAPS are: δ 4.6 ppm (m, 2H, COOCH$_2$); 3.9 ppm (m, 2H, COOCH$_2$-CH$_2$); 3.6 ppm (t, 2H, N′(CH$_3$)$_2$-CH$_2$-(CH$_2$)$_2$SO$_3^-$); 3.25 ppm (s, 6H, N′(CH$_3$)$_2$); 3.24 ppm (t, 2H, N′(CH$_3$)$_2$-(CH$_2$)$_2$-CH$_2$SO$_3^-$); 2.35 ppm (m, 2H, N′(CH$_3$)$_2$-CH$_2$-CH$_2$-CH$_2$SO$_3^-$); 1-1.3 ppm (m, 3H+2H, -CH$_3$-C(CH$_3$)COO). The signals from NVP are: δ 3.7 ppm (t, 2H, CH$_2$-N); 3.4 ppm (d, 1H, -CH$_2$-CH-N); 2 ppm (m, 2H+2H, CH$_2$-CH$_2$-C=O); 1.1 ppm (t, 2H, -CH$_2$-CH-N). The vinyl protons signals were missing in the 1H NMR spectrum of the analyzed copolymer which confirmed its well purification.

The copolymer solubility in different solvents was determined gravimetrically. After the stirring of the weighted copolymer sample in the fixed solvent at adjusted temperature for one day the rest sample was weighted again. If there is no change of the weight, the copolymer is regarded as unsolved in this solvent, if the weight of the rest sample is zero, the copolymer is solved in this solvent, and when the weight is more than zero, the copolymer is regarded as soluble partially in the solvent.

RESULTS AND DISCUSSION

POLY(DMAPS-co-NVP)S COMPOSITION

The plots DMAPS concentration in comonomers ($m_{DMAPS}$) as a function of DMAPS concentration in monomer feed ($M_{DMAPS}$), prepared in water and in 1M NaCl aqueous solution is presented in Figure 3. The results obtained show an alternating copolymerization tendency in both reaction media. In 1M NaCl solution however, this tendency is weaker than in water.

![Figure 3](image-url). Dependence of the DMAPS–NVP copolymer composition ($m_{DMAPS}$ – mole fraction of the DMAPS monomer units in copolymer) on the comonomer feed ($M_{DMAPS}$ – mole fraction of DMAPS in monomer feed). Total monomer concentration, 1.5 mol/L; initiator – PPS (1 wt.%); T = 43±1 °C; (curve 1 (■) – in pure water; curve 2(Δ) – in 1M NaCl aqueous solution)
RELATIVE MONOMER REACTIVITY

The products obtained and the relative monomer reactivity of DMAPS ($r_1$) and NVP ($r_2$) determined in both reaction media are presented in Table 1. As expected for alternating copolymerizations, both reactivity ratios are less than 1. The DMAPS $Q$– and $e$-parameters ($Q_1$ and $e_1$) were calculated [22] using $Q_{NVP} = 0.140$ and $e_{NVP} = -1.140$ [23] (Table 1). It should be pointed out that the $r_1$ value in 1M NaCl is lower than that in water, while for the $r_2$ values the effect is exactly opposite (Table 1). In this way, the considerable influence of low molecular salt (1M NaCl) on the microstructure of poly(DMAPS-co-NVP) mac-

Table 1. Calculated relative monomer reactivity ($r_1$, $r_2$), their product and $Q_1$ and $e_1$ values.

<table>
<thead>
<tr>
<th>Method</th>
<th>Solvent</th>
<th>Relative monomer reactivities</th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$r_1r_2$</th>
<th>$Q_1$</th>
<th>$e_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ezrielev-Brochina-</td>
<td>H$_2$O</td>
<td></td>
<td>0.109</td>
<td>0.030</td>
<td>0.003</td>
<td>0.302</td>
<td>1.250</td>
</tr>
<tr>
<td>Roskin (EBR)</td>
<td>1 M NaCl</td>
<td></td>
<td>0.026</td>
<td>0.198</td>
<td>0.005</td>
<td>0.052</td>
<td>1.158</td>
</tr>
<tr>
<td>Integral-Tidwell-</td>
<td>H$_2$O</td>
<td></td>
<td>0.145</td>
<td>0.034</td>
<td>0.005</td>
<td>0.297</td>
<td>1.165</td>
</tr>
<tr>
<td>Mortimer (ITM)</td>
<td>1 M NaCl</td>
<td></td>
<td>0.027</td>
<td>0.202</td>
<td>0.005</td>
<td>0.051</td>
<td>1.147</td>
</tr>
</tbody>
</table>

romulolices is established. For the explanation of this salt effect the possible electrostatic interaction (in pure water above all) between a partial negative charge of the carbonyl oxygen atom in DMAPS molecule and the positive charge of quaternary nitrogen atom might be accounted (Fig. 4).

What is more, the formation of such intramolecule complex in a DMAPS monomer molecule or in a DMAPS propagation radical provides an additional electrostatic interaction between of the positive charged quaternary nitrogen atom and the negative charged sulfo group, as it is shown on Fig. 4 also. The result of these electrostatic interactions is the increase of both polar ($e_{DMAPS}$) and resonance ($Q_{DMAPS}$) parameter values, in comparison with those when these interactions are modified because of the counterion screen effect.

Figure 4. Polar interaction between the positive charge of quaternary nitrogen atom and partially negative charges of sulfo and carbonyl groups.
in the aqueous 1M NaCl solution. However, the $Q_{\text{DMAPS}}$ augmentation is much greater (by a factor of 6) than $e_{\text{DMAPS}}$ (1.01 fold only) at a transition from aqueous 1M NaCl solution to pure water as a copolymerization medium (Table 1). This huge difference might be related to the distinction between the intramolecular complex (Fig. 4) effects (in pure water only) on the monomer and the propagation radical $\pi$-electron delocalization ($Q$ parameter) and polarization ($e$-parameter). Indeed, as it seen from the Fig. 4, the possibilities for a $\pi$-electron delocalization is much greater than in the DMAPS monomer and propagation radical with a disintegrated complex, as a result of the screen effect of the counter ion atmosphere in a salt aqueous solution. At the same time, both electrostatic interactions (>C=O$\rightarrow$$\rightarrow$N$^+<$$\rightarrow$SO$_3^-$) are in opposite directions (Fig. 4). Therefore, they are mutually compensated in the formation of partial negative charge on the carbonyl group, influencing the $e$-parameter value of the DMAPS. This compensation effect is just responsible for the mentioned above week growth of this parameter at the transition from the 1M NaCl aqueous solution to pure water (Table 1). Hence, the established change of $r_{\text{DMAPS}}$ and $r_{\text{NVP}}$ at the transition from pure water to 1 M NaCl aqueous solution is in the first place a result of the reduction of the delocalization space (resonance interaction) of the DMAPS $\pi$-electron system. Due to this factor $r_1 (r_{\text{DMAPS}})$ in pure water is greater than $r_2 (r_{\text{NVP}})$ and as a result of this the copolymer composition curve in pure water in coordinates $m_{\text{DMAPS}} – M_{\text{DMAPS}}$ is over the composition curve for copolymers, produced in 1M NaCl aqueous solution (Fig. 3). However, independently of this difference of the composition curves, the alternation tendency, estimated by the reactivity ratios product (Table 1), in both solvents is approximately the same. This is a result of the huge difference between the $e$-parameter values of the both monomers. Indeed, $e_{\text{NVP}} = -1.14$ (comonomer with high electron-donor ability) [23], while $e$-parameter values of DMAPS are $e_{\text{DMAPS}} = 1.165$ in pure water and $e_{\text{DMAPS}} = 1.147$ in 1M NaCl aqueous solution. This difference is provides a basis for a strong donor-acceptor interaction between comonomers and propagation radicals with alien monomer, responsible for a pronounced alternating tendency in the both solvents.

**MONOMER UNIT DISTRIBUTION IN POLY( DMAPS-co-NVP) MACROMOLECULES**

The effect of low molecular salt addition on $m_{\text{DMAPS}}$ and poly( DMAPS-co-NVP) monomer unit distribution were demonstrated by the calculation of the mole percentage of different monomer unit blocks in poly( DMAPS-co-NVP) and their average lengths using the Igarashi method [19]:

$$X = \Phi_1 - 2\Phi_1 (1 - \Phi_1) / \{1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1 (1 - \Phi_1)]^{1/2}\}$$  

(1)

$$Y = (1 - \Phi_1) - 2\Phi_1 (1 - \Phi_1) / \{1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1 (1 - \Phi_1)]^{1/2}\}$$  

(2)

$$Z = 4\Phi_1 (1 - \Phi_1) / \{1 + [(2\Phi_1 - 1)^2 + 4r_1r_2\Phi_1 (1 - \Phi_1)]^{1/2}\}$$  

(3)

where $X$, $Y$ and $Z$ are the fractions of $M_1$-$M_1$, $M_1$-$M_2$ and $M_2$-$M_2$ bond in copolymer molecule, $\Phi_1$ is the mole fraction of $M_1$ in the copolymer. The experimental data for product
\( r_1, r_2 \), calculated by EBR method are used in these calculations. The average lengths of homoblocks are calculated as follows:

\[
\mu_1 = \frac{1 + r_1[M_1]}{[M_2]} \tag{4}
\]

\[
\mu_2 = \frac{1 + r_2[M_2]}{[M_1]} \tag{5}
\]

The obtained results are summarized in Table 2. As can be seen, the heterodiad \((M_1-M_2)\) molar fractions of the copolymers, produced in pure water, range from 0.700 to 0.950 and exceed the homodiad \((M_1-M_1\) and \(M_2-M_2)\) molar fractions which values are from 0.001 to 0.180. This is in full correspondence with the discussed above alternating tendency of the DMAPS-NVP copolymerization in pure water. This tendency is confirmed by the large closeness of the homoblock lengths \((\mu_1\) and \(\mu_2\) values range from 1.02 to 1.19 only) to unity also. The alternating tendency is revealed for the copolymerization in 1 M \(\text{NaCl}\) (copolymers 2.1, 4.1, 6.1) too. In this case the molar fraction of the heterodiads \((M_1-M_2)\) is too large (its values range from 0.700 to 0.880) in comparison with those for the homodiads.

**Table 2.** Diad mole fractions and homoblock lengths \((\mu_1, \mu_2)\) in poly(DMAPS-co-NVP) macromolecules, produced in pure water and in 1M NaCl, and calculated by Igarashi (numbers without brackets) and Markov chain (the values are in brackets) models.

<table>
<thead>
<tr>
<th>No</th>
<th>(M_{\text{DMAPS}}) (mole fraction)</th>
<th>(m_{\text{DMAPS}}) (mole fraction)</th>
<th>Diad mole fractions</th>
<th>Block’s length</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.401</td>
<td>0.002 0.200 0.798</td>
<td>1.07 1.04</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.502</td>
<td>0.028 [0.015]</td>
<td>0.024 [0.057]</td>
</tr>
<tr>
<td>2.1</td>
<td>0.2</td>
<td>0.362</td>
<td>0.002 [0.004]</td>
<td>0.278 [0.092]</td>
</tr>
<tr>
<td>3</td>
<td>0.4</td>
<td>0.564</td>
<td>0.133 [0.004]</td>
<td>0.004 [0.004]</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.585</td>
<td>0.173 [0.052]</td>
<td>0.003 [0.014]</td>
</tr>
<tr>
<td>4.1</td>
<td>0.5</td>
<td>0.449</td>
<td>0.009 [0.014]</td>
<td>0.111 [0.092]</td>
</tr>
<tr>
<td>5</td>
<td>0.7</td>
<td>0.640</td>
<td>0.282 [0.176]</td>
<td>0.001 [0.003]</td>
</tr>
<tr>
<td>6</td>
<td>0.8</td>
<td>0.619</td>
<td>0.240 [0.166]</td>
<td>0.002 [0.024]</td>
</tr>
<tr>
<td>6.1</td>
<td>0.8</td>
<td>0.516</td>
<td>0.166 [0.046]</td>
<td>0.134 [0.024]</td>
</tr>
<tr>
<td>7</td>
<td>0.9</td>
<td>0.627</td>
<td>0.255 [0.176]</td>
<td>0.002 [0.003]</td>
</tr>
</tbody>
</table>

*\(^a\)Mole fractions are determined by an elemental (S) analyses; \(^b\)Calculated values, using the relative monomer reactions, determined by the EBR method; \(^c\)Copolymers, produced in 1M NaCl solution.*
(M$_{1}$-M$_{1}$ and M$_{2}$-M$_{2}$), which values are between 0.002 and 0.278, and the homoblock lengths are very close to unity (they range from 1.01 to 1.10) again. However, it is noteworthy that there are clear differences between the molar fractions of the both homodiads for the copolymers, produced in pure water (copolymers 2, 4, 6) and in 1 M NaCl (copolymers 2.1, 4.1, 6.1). Indeed, while the M$_{1}$-M$_{1}$ diad molar fraction values decrease considerably at the transition from pure water copolymerization medium to salt (1M NaCl aqueous solution) one, the M$_{2}$-M$_{2}$ molar fraction values change in opposite direction at the same medium transition. This result reflects the considerable salt effect on the monomer unit distribution in the copolymers with and without salt in copolymerization medium, and is in correspondence with the discussed above change of both monomer reactivity in the opposite directions at the same alteration of the copolymerization medium.

For confirmation of these conclusions, the dyad mole fractions and homoblock lengths are calculated by the Markov chain model [20, 21] also. The necessary to this aim transition probabilities $P_{11}$, $P_{12}$, $P_{21}$, $P_{22}$ were calculated by the following equations:

$$P_{21} = \frac{[M_1]r_2^{-1}}{([M_1]r_2^{-1} + [M_2])}$$ (6)

$$P_{12} = \frac{[M_2]r_1^{-1}}{([M_1] + [M_2]r_1^{-1})}$$ (7)

$$P_{11} = 1 - P_{12}$$ (8)

$$P_{22} = 1 - P_{21}$$ (9)

where $[M_1]$ and $[M_2]$ are the concentrations of the comonomers in the monomer feed, $r_1$ and $r_2$ are the relative monomer reactivity, calculated by EBR method. The average lengths of the homoblocks were calculated in this case as follows:

$$\mu_1 = \frac{1}{1 - P_{11}}$$ (10)

$$\mu_2 = \frac{1}{1 - P_{22}}$$ (11)

Some values (those of them underlining the salt effect), calculated by these relations, are included in Table 2 (the numbers in the brackets). It can be seen again the alteration of the homoblock mole fractions in opposite directions at the transition of the copolymerization in a pure water to the copolymerization in a 1M NaCl aqueous solution.

**KINETICS OF RC OF DMAPS AND NVP**

The conversion ($q$)–time ($t$) plots for different monomer feeds are shown in Figure 5. The initial copolymerization rate ($V_0$) for each monomer feed was estimated from the slope of these dependences. The dependence of $V_0$ of RC of DMAPS and NVP in water $M_{DMAPS}$ is presented in Figure 6. The plot $V_0/M_{DMAPS}$ exhibits a maximum in equimolar composition of the monomer feed ($M_{DMAPS} = 50$ mole %). This result is in good agreement with the expressed assumption for donor-acceptor alternating copolymerization. The presence and position of the maximum confirm the formation of intermediate equimolar complex between DMAPS and NVP and its participation in chain growth reactions.
Solubility of DMAPS, NVP and poly(DMAPS-co-NVP) prepared in water, is shown in Table 4. All copolymers are water-soluble in certain temperature ranges: copolymers

**Figure 5.** Kinetics of the RC of DMAPS – NVP radical polymerization in water: total monomer concentration 1.5 mol/L; [PPS] = 1 wt.%; \(T = 43\pm1^\circ\text{C}\); \(M_{\text{DMAPS}} = 0.1 \ (6); 0.2 \ (4); 0.4 \ (3); 0.5 \ (1); 0.7 \ (2); 0.8 \ (7); 0.9 \ (5)\).

**Figure 6.** Initial rate \((V_0)\) of the RC of DMAPS and NVP as a function of the DMAPS mole fraction in the monomer feed \((M_{\text{DMAPS}})\) in water; [PPS] = 1 wt.%; \(T = 43\pm1^\circ\text{C}\).  

**SOLUBILITY OF DMAPS, NVP AND P(DMAPS-co-NVP)**

Solubility of DMAPS, NVP and poly(DMAPS-co-NVP)s prepared in water, is shown in Table 4. All copolymers are water-soluble in certain temperature ranges: copolymers
1 and 2 at 25-30 °C, copolymers 3-7 at 50-60 °C. Copolymers 1-7 are partially soluble in CH₃OH, C₂H₅OH and insoluble in CH₃COCH₃, ether, DMF, THF, HCN, DMSO and CHCl₃. On the other hand, poly(DMAPS), prepared by the method already described, is soluble in water at 70-80 °C. Improving the water solubility of poly(DMAPS-co-NVP)s with higher \( m_{NVP} \) is an achievement of this work.

**Table 3.** Solubility of DMAPS, NVP and the p(DMAPS-co-NVP) in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DMAPS</th>
<th>NVP</th>
<th>poly(DMAPS-co-NVP)s*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>v</td>
<td>v</td>
<td>( v^a ) ( v^a ) ( v^b ) ( v^b ) ( v^b ) ( v^b )</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>v</td>
<td>v</td>
<td>o       o       o   o   o   o       o</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>o</td>
<td>v</td>
<td>o       o       o   o   o   o</td>
</tr>
<tr>
<td>Acetone</td>
<td>x</td>
<td>v</td>
<td>x       x       x   x   x   x   x   x</td>
</tr>
<tr>
<td>Ether</td>
<td>x</td>
<td>x</td>
<td>x       x       x   x   x   x   x   x   x</td>
</tr>
<tr>
<td>DMF</td>
<td>x</td>
<td>v</td>
<td>x       x       x   x   x   x   x</td>
</tr>
<tr>
<td>THF</td>
<td>x</td>
<td>x</td>
<td>x       x       x   x   x   x</td>
</tr>
<tr>
<td>HCN</td>
<td>x</td>
<td>x</td>
<td>x       x       x   x   x   x</td>
</tr>
<tr>
<td>DMSO</td>
<td>x</td>
<td>v</td>
<td>x       x       x   x   x   x   x</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>x</td>
<td>x</td>
<td>x       x       x   x   x   x   x</td>
</tr>
</tbody>
</table>

\( v^a \) - soluble at 25-30 °C, \( v^b \) - soluble at 50-60°C, o - slightly soluble, x – insoluble

* The numbers 1-7 relate to the copolymers, indicated in the Table 2.

**CONCLUSIONS**

New poly(DMAPS-co- NVP) copolymers were prepared at different monomer feeds via radical copolymerization in pure water and 1M NaCl solution. The alternating tendency, established in both solvents is a result of the large difference between \( \pi \)-electron polarizations of the both comonomers and propagation radicals. The alternating tendency is confirmed by the copolymer composition curves, closeness of \( r_1 \) and \( r_2 \) values to zero, the maximum copolymerization rate at the equimolar monomer feed, and the high percentage of heterodiads \( M_1-M_2 \) (94.8%) in copolymer macromolecules. The transition from pure water to 1M NaCl aqueous solution as copolymerization medium does not change the alternating tendency, but this transition changes the monomer reactivity in opposite directions. The latter is explained by the considerable alteration of the resonance parameter (Q value) of DMAPS, due to electrostatic interaction between positive change on the nitrogen atom with the negative charges on the carbonyl oxygen atom and sulfo group in pure water only. In a salt solution this interaction can not be realized because of the counter ion screenin effect. The salt effect is expressed also by the opposite influence of the mole fractions of homoblocs in the copolymer macromolecules. The solubility of the copolymers in different
solvents was determined and is established that in water copolymer solubility is higher than that of poly(DMAPS) homopolymer.

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REFERENCES


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IMMOBILIZATION OF OPTICALLY ACTIVE RHODIUM COMPLEX ON MCM-41. PART I. PREPARATION OF THE HETEROGENEOUS CATALYTIC SYSTEM

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Abstract: A new supported heterogeneous catalyst has been synthesized through the anchoring of 3,4-(R,R)-bis(diphenylphosphino)pyrrolidine rhodium complex to the surface of MCM-41 mesoporous material. The new catalytic system was characterized with X-ray diffraction, scanning electron microscopy (SEM), BET method for the surface area determination, IR spectra, $^{29}$Si MAS NMR, $^1$H NMR, $^{31}$P NMR, $^{13}$C NMR.

Key words: mesoporous materials, MCM-41, Rhodium complex, enantioselective catalyst, hydrogenation, cinnamic acid

INTRODUCTION

Hybrid catalysts prepared by immobilization of catalytically active organometallic complexes on inorganic supports or insoluble polymeric promise to combine high activity and selectivity of homogeneous catalysts and easy separation of reaction products from the catalyst. The incorporation of chiral ligand or catalysts on mesoporous silica materials for
asymmetric catalysis has attracted a great deal of interest due to its tunable pore dimensions, well-defined arrangement, relatively large specific surface area and pore volume. The large specific surface area and pore volume can enhance the loading amounts of the metal catalysts and increase its catalytic efficiency, while the tunable pore dimension and well-defined pore arrangement can avoid the aggregation of catalytic active species and maintain excellent stereocontrol performance. These mesoporous silica-supported chiral catalysts do not swell or dissolve in organic solvents. They also exhibit superior thermal and mechanical stability in catalytic process, indicating a potential application in industry [1]. Optically active MonoPhos [2, 3] and 1,2-diphenylethylenediamine (DPEN) [4, 5] are two important kinds of chiral ligand, which are used extensively to generate highly enantioselective catalysts for asymmetric hydrogenation of ketones. (R,R)-DPEN has been successfully incorporated onto various mesoporous materials [6, 7]. These works explore immobilized strategies for incorporation of chiral ligand or catalysts on mesoporous silica materials. Liu, G. et al. presented a facile approach to prepare mesoporous silica-support chiral Rh and Ru catalysts by directly anchoring the organometallic complexes onto SBA-15 which exhibited high catalytic activities and enantioselectivities during the asymmetric hydrogenation of various aromatic ketones [8].

Our research focused on the use of MCM-41 mesoporous materials as support for immobilization of [3,4-(R,R)-bis(diphenylphosphino)pyrrolidine-P,P'](1,5-cyclooctadiene) rhodium tetrafluoroborate.

EXPERIMENTAL PART

Synthesis of MCM-41

The MCM-41 support was synthesized using a method derived from the (below referenced) literature [9]. To 19 g of a solution of cetyltrimethylammonium hydroxide was added 1.65 g of NaAlO₂. The mixture was stirred at room temperature until the NaAlO₂ was dissolved. To this solution was added 40 g of tetramethylammonium (TMA) silicate solution (10% SiO₂), 10 g of HiSil, 200 g of water and 70 g of the auxiliary organic 1,3,5-trimethylbenzene. The resulting mixture was stirred carefully at room temperature for several minutes. The gel was then loaded into a stainless-steel autoclave and heated at 105°C for 68 h with stirring at 150 rpm. The resulting product was filtered and washed several times with warm (60–70°C) distilled water and with acetone. The air dried product was calcined to 540°C in N₂/air mixture and then held in air for about 10 h. The MCM-41 support was characterized by power-XRD, scanning electron micrograph, ²⁹Si MAS NMR and N₂ adsorption isotherm area.

Synthesis of Rh complex

[3,4-(R,R)-bis(diphenylphosphino)pyrrolidine-P,P'](1,5-cyclooctadien)rhodium tetrafluoroborate was synthesized as previously shown [10]. Bis(1,5-cyclooctadien)rhodium
tetrafluoroborate, [(cod)Rh]BF₄, (1 mol) reacted with 3,4-(R,R)-bis(diphenylphosphino) pyrrolidine (1 mol) in 30 ml CH₂Cl₂. After stirring for 24 h and vacuum evaporation a dry product was obtained to which glutaric acid anhydride (1 mol), dissolved in CH₂Cl₂, was added. The resulting oil product was washed with water and CH₂Cl₂, filtered off kieselgel and dried. The final product was determined by ¹H NMR, ³¹P NMR and ¹³C NMR.

The preparation of enantioselective rhodium complex follows the next steps:

\[
\text{Rh(cod)₂BF₄} + \text{HN} \begin{array}{c} \text{PPh₂} \\ \text{PPh₂} \end{array} \rightarrow \left[ \text{(cod)Rh} \begin{array}{c} \text{P} \\ \text{P} \\ \text{Ph₂} \\ \text{Ph₂} \end{array} \text{NH} \begin{array}{c} \text{N} \\ \text{O} \end{array} \right] \text{BF₄}
\]

\[
\text{O} \begin{array}{c} \text{O} \\ \text{O} \end{array} \rightarrow (\text{cod)Rh} \begin{array}{c} \text{P} \\ \text{P} \\ \text{Ph₂} \end{array} \text{N} \begin{array}{c} \text{C} \end{array} \text{-(CH₂)₃-CO-O} + \text{H₂N(CH₂)₃Si(OEt)₃}
\]

\[
\text{O} \begin{array}{c} \text{O} \end{array} \rightarrow (\text{cod)Rh} \begin{array}{c} \text{P} \\ \text{P} \\ \text{Ph₂} \end{array} \text{N} \begin{array}{c} \text{C} \end{array} \text{-(CH₂)₃-CNH-(CH₂)₃-Si(OEt)₃}
\]

**Preparation of hybrid catalyst**

Anchoring to the support was accomplished through reaction of rhodium complex with 1-amino-3-(triethoxysilyl)propan (0.48 g) in CH₂Cl₂. Rhodium complex 0.01 g (11.7 μmol) reacted with 1 g MCM-41 in CH₂Cl₂ at room temperature for 15 h. The bound complex was washed with MeOH for a few hours until the filtrates became colorless. To estimate the amount of fixed rhodium complex the combined filtrates were reduced to dryness in vacuo. The ¹H NMR signals of the phenylic protons in the spectrum was integrated and the rhodium content was calculated. The amount of the fixed rhodium complex was about 10 wt% (from weight of Rh complex). The rhodium complex reacted in CH₂Cl₂ with MCM-41 molecular sieve to give the catalyst:
RESULTS AND DISCUSSION

X-ray power diffraction and N\textsubscript{2} adsorption isotherm confirmed the high quality of prepared MCM-41 support used for subsequent hybrid catalyst preparation. The BET surface area was 1004 m\textsuperscript{2}/g and pore diameter was 6.5 nm (Fig. 1). The average particle size was about 5 -20 μm according to SEM (Fig. 2).

\textbf{Figure 1.} X-ray diffraction of MCM-41 mesoporous material.

\textbf{Figure 2.} SEM images of calcined MCM-41 mesoporous material.
$^{29}$Si MAS NMR spectra of MCM-41 show a band at –100 ppm which corresponds to ≡Si-OH groups (Fig. 3). The IR spectrum of MCM-41 shows band at 465 cm$^{-1}$ which is a typical for hexagonal prisms in faujasite structures (Fig. 4).

![Figure 3. $^{29}$Si MAS NMR spectra of MCM-41 mesoporous material.](image)

A signal at 953 cm$^{-1}$ assigned asymmetric stretching of Si–O bond neighbouring surface silanol groups. The band at 1084 cm$^{-1}$ indicates the presence of Si–O–Al bonds and the signal at 3418 cm$^{-1}$ is attributed to –OH groups.

The coupling between rhodium complex and MCM-41 support is a simple condensation of surface silanol hydroxy groups of the MCM-41 with the ethoxysilyl groups of complex and the rhodium side of the molecule remains cationic and solvated. The long and
flexible chain between MCM-41 surface and rhodium part against accessibility to the active center of the catalyst and higher optical purity of the resulting (S)-N-acetylphenylalanine.

CONCLUSIONS

A new hybrid catalyst was prepared by the anchoring of \([3,4-(R,R)\text{-bis(diphenylphosphino)}\text{pyrrolidine-}P,P']\text{(1,5-cyclooctadien)})\text{rhodium tetrafluoroborate}\) on mesoporous molecular sieve MCM-41. This catalytic system combines the catalytic properties of the rhodium complex with the possibility of heterogeneous catalysts for an easy isolation from the reaction mixture.

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REFERENCES


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IMMOBILIZATION OF OPTICALLY ACTIVE RHODIUM COMPLEX ON MCM-41 FOR HYDROGENATION OF $\alpha$-(ACETYLAMINO)CINNAMIC ACID. PART II. ENANTIOSELECTIVE CATALYTIC HYDROGENATION

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Abstract: A new supported heterogeneous catalyst has been synthesized through the anchoring of 3,4-(R,R)-bis(diphenylphosphino)pyrrolidine rhodium complex to the surface of MCM-41 mesoporous material. The catalyst showed to be highly active in the enantioselective hydrogenation of $\alpha$-(acetylamino)cinnamic acid.

Key words: mesoporous materials, MCM-41, Rhodium complex, enantioselective catalyst, hydrogenation, cinnamic acid

INTRODUCTION

The optically active rhodium complexes have been widely reported as efficient catalysts for a broad range of organic reactions [1, 2]. Rhodium complexes of 1,2-diphosphino ligands which have been used for asymmetric hydrogenation of N-acyldehydroamino acids have been known for 30 years. Brown [3] and Landis [4] have used either Dipamp:
(R,R)-1,2-ethanediylbis[(o-methoxyphenyl)phenylphosphine] [5] or Chiraphos: (S,S)-2,3-bis(diphenylphosphino)butane [6] complexes as catalysts for clarifying the mechanism of this reaction. Nagel [7] has synthesized new optically pure 3,4-bis(phosphanyl)pyrrolidine ligands. The rhodium complexes have been used as catalysts for the hydrogenation of cinamnic acid and its methyl ester and unfunctionalized ketones. Their catalytic activity strongly depends on the ligands structure: those bearing phenyl groups axial and methyl groups equatorial, give higher optical yields than their counterparts with methyl groups axial and phenyl groups equatorial.

With the success and diversity of chiral 3,4-bis(phosphanyl)pyrrolidine catalysts in enantioselective homogeneous phase, attention has also been turned to the development of heterogenized systems which may be of significant industrial interest. The problems associated with the recovery of homogeneous catalysts, their separation from the reaction products [8] and the difficulties associated with the recycling of the catalytic species have in part been addressed by immobilization on a heterogeneous solid support such as polymers or silicas [9]. Mesoporous material MCM-41 is suitable for use as catalyst support because it possesses large pores, controllable narrow pore-size distribution and high surface area. The pore size allows passage of large molecules such as organic reactants and metal complexes through the pore to react to the surface of the channel [10]. Crosman et al. realized a very straightforward for immobilizing rhodium diphosphine complexes on aluminated SBA-15. New heterogeneous chiral catalysts showed high activities and excellent chemo- and enantioselectivities during the hydrogenation of different prochiral olefins [11]. The immobilization of the rhodium complexes within sol-gel materials allows a better and easier separation of these catalysts from solution and facilitates their reuse, which greatly improves the productivity of the catalyst. Different mesoporous silica materials were used as support materials in order to adapt the catalyst to the substrate of the reaction [12, 13]. The hydrogenation of itacinic acid and its derivates was carried out with sol-gel building agent entrapped Rh/BPPM catalysts in methanol solutions. About 90–99% enantiomeric excess (e.e.) were achieved for the hydrogenation of itacinic acid to (S)-(−)+2-methyl succinic acid [14].

The research in this paper was focused on the use of immobilized 3,4-(R,R)-bis(diphenylphosphino)pyrrolidine rhodium complex for enantioselective hydrogenation of α-(acetylamino)cinnamic acid.

**EXPERIMENTAL PART**

In order to characterize the activity and stability of supported rhodium complex the experiments were performed in different conditions – a batch reactor and a stream reactor.

In the case when hydrogenation was carried out in a stream reactor, the catalyst was placed in a reactor in Ar atmosphere. H₂ pressure was 85 bar at room temperature, flow speed – 0.5 ml/min, substrate – 0.1 M α-(acetylamino)cinnamic acid in MeOH, catalyst – 1 g MCM-41 and 0.01 g rhodium complex. The experiment was carried out for 150 h.
A part of experiments were performed in a stainless-steel autoclave with a volume 80 ml as a batch reactor. The substrate (0.564g) dissolved in 40ml MeOH and the catalyst (1g MCM-41 and 2.43 μmol rhodium complex) were placed in the autoclave. The autoclave was closed, thoroughly evacuated and flushed at least three times with 1 atm of Ar to ensure a completely oxygen-free environment. The evacuated autoclave was filled with hydrogen (P(H₂) – 25 atm , temperature 25°C) and the reaction started with rapid stirring.

In all cases the quantitative hydrogenation was confirmed using a ¹H NMR spectrum. The products of reaction were analyzed by GC. The optical yield was determined by comparison with the specific rotations of the pure enantiomers [(S)-N-acetylphenylalanine, [α]_D^{22} = 47.4.

RESULTS AND DISCUSSION

The supported catalyst was tested for enantioselective hydrogenation of α-(acetylamino) cinnamic acid in methanolic solution to (S)-N-acetylphenylalanine (Scheme 1).

![Scheme 1](image)

**Scheme 1.** Enantioselective hydrogenation of α-(acetylamino)cinnamic acid to (S)-N-acetylphenylalanine over [3,4]-bis(diphenylphosphino)pyrrolidine-P,P’(1,5-cyclooctadien)rhodium complex – MCM-41

In the stream reactor, at the beginning of the reaction the conversion was about 95–96% and the optical yield was 93.04% enantiomeric excess (e.e.) (Figs. 1 and 2). During the hydrogenation conversion remained comparatively constant ~ 97% and the optical yield remained up to 94.0%.

![Figure 1](image)

**Figure 1.** Enaniomeric excess (%) of (S)-N-acetylphenylalanine
In the batch reactor up to 98.28 % e.e. was achieved. The catalyst was reused three times and after every run it was washed with MeOH and COD. The activity of the catalyst was preserved high during the runs (Table 1). A substrate/catalyst ratio of 1000:1 was used. In all cases MeOH was used as a solvent. Previous investigations have shown that MeOH is a better environment than CH₂Cl₂ for this reaction [15].

**Table 1.** Hydrogenation of α-(acetylamino)cinnamic acid.

<table>
<thead>
<tr>
<th>Catalyst Run</th>
<th>Turnover (%)</th>
<th>ee(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98.28</td>
<td>96.56</td>
</tr>
<tr>
<td>2-1</td>
<td>96.72</td>
<td>93.44</td>
</tr>
<tr>
<td>2-2</td>
<td>90.25</td>
<td>80.50</td>
</tr>
<tr>
<td>2-3</td>
<td>89.51</td>
<td>79.02</td>
</tr>
<tr>
<td>3-1</td>
<td>96.31</td>
<td>92.62</td>
</tr>
<tr>
<td>3-2</td>
<td>91.17</td>
<td>82.34</td>
</tr>
<tr>
<td>3-3</td>
<td>91.13</td>
<td>82.26</td>
</tr>
</tbody>
</table>

Solvent – MeOH 40 ml; p(H₂) = 25 atm.; T = 25°C; substrate α-(acetylamino)cinnamic acid; molar ratio substrate : catalyst = 1000 : 1.

In the rhodium complex of optically active diphosphines, the conformation of the chelating ligand determines the prevailing product configuration. Normally λ-chelate gives the (S)-enantiomer and a δ-chelate the (R)-enantiomer. Each phosphorous atom in the rhodium complex was attached with two phenyl groups. In the square-planar rhodium complex the equatorial phenyl groups control the stability of the diastereomeric substrate complexes. The axial groups have a little influence. In the octahedral dihydrido complex the axial phenyl groups dominate with their influence on the stereochemistry. The axial phenyl groups direct the reaction, during hydrogen activation, in the opposite sense com-
pared with that of the equatorial phenyl groups – substance equilibrium. This is expected because the handedness of the chiral array of the two axial groups is opposite to the array of the two equatorial groups.

CONCLUSIONS

The results obtained using the catalyst supported on MCM-41 indicate that the structure of the solid support does not influence the activity of the catalyst. The new supported catalyst possesses high catalytic activity for enantioselective hydrogenation of α-(acetylamino) cinnamic acid and we have demonstrated that it has a long life span, and it could be used more than once with good optical yields.

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REFERENCES


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A NEW CLASS OF POLYCONJUGATED $\pi$-SYSTEMS WITH DEGENERATE STATES

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DEDICATED TO PROFESSOR CORNELIUS WEISS
ON THE OCCASION OF HIS 70TH ANNIVERSARY

Abstract. The structure and magnetic properties of a new class of $\pi$-electron systems – molecules and 1-D polymers – are investigated by means of the many-electron band theory.

Keywords: 1-D polymers; energy spectra; degenerate states; organic ferromagnets.

INTRODUCTION

The presence of degenerate molecular orbitals (MOs) in a molecular system is an important requirement for the existence of high-spin states and non conventional magnetic materials [1-3].

The investigation of pure organic polymers with ferromagnetic ground states is focused mainly on non-classical (non-Kekulé) $\pi$-moleculare systems (see Ref. 1 and the references therein); a non-classical system – such one, to which no classical (valence) formula can be attributed [4].

In the case of alternant $\pi$-systems, the presence of degenerate non bonding MOs (NBMOS) are given by the theorem of Coulson-Rushbrooke-Longuet-Higgins (CRLH) [5-7]. For such systems there are:
\[ n = S^* - U^* \quad (1) \]

NBMOs, where \( S^* \) and \( U^* \) are the number of the starred and the unstarr\( \text{ed} \) \( \pi \)-centers, respectively, the starred being the larger set. Two examples are shown below:

\[ 4^* - 3^* = 1 \text{ NBMO} \quad 5^* - 3^* = 2 \text{ NBMOs} \]

The CRLH theorem has been generalized [8, 9] for some non-alternant and heteroatomic \( \pi \)-systems. In the generalized (ECRLH) theorem only the subset of the starred \( \pi \)-centers is responsible for the appearance of NBMOs. A conjugated system with \( M \) \( \pi \)-centers and a maximal set of \( S^* \) homonuclear disjoint \( \pi \)-centers must have at least:

\[ n = 2S^* - M \quad (2) \]

NBMOs.

The NBMOs are present even if the system is nonalternant and if the \( \pi \)-centers belonging to the nonstarred subset \( [U^*] \) are heteroatomic. Such radicals with NBMOs are:

\[ 2\times5^* - 8^* = 2 \text{ NBMOs} \quad 2\times7^* - 13^* = 1 \text{ NBMO} \]

The stable 2-aza-phenalenyl radical has been synthesized by Rubin and coworkers [10].

The ECRLH theorem is more general in comparison to the original variant. According to the CRLH theorem the biradical:

\[ \text{ has no NBMO. In accordance with the extended theorem, the system has two NBMOs:} \]

\[ 3^* - 3^0 = 0 \text{ NBMOs} \quad 2\times4^* - 6 = 2 \text{ NBMOs} \]

CRLH \quad \text{ECRLH}
The result obtained by means of the ECRLH method corresponds to the result following from the roots of the characteristic polynomial of the biradical:

\[ x^6 - 5x^4 + 4x^2 = 0 \]

The above theorems do not cover all possible \( \pi \)-systems with NBMOs either. For instance, the monoradical

![Monoradical](image)

has 1 NBMO, according to the Sachs theorem [11, 120] and to the numerical results.

The considered systems in the above-mentioned theorems are non-classical. The aim of the present work is to extend the class of systems with NBMOs for classical systems.

**STRUCTURAL PRINCIPLES OF THE CONSIDERED CLASSICAL SYSTEMS**

The MO energies of a cyclopolyene with ideal geometry – all bond-lengths equal, and \( N \) \( \pi \)-centers (\( N \) is even) is given by the expression [3] (in \( \beta \) units):

\[ e_k = 2\cos(2\pi k / N); \quad k = 0, \pm 1, \pm 2, \ldots \pm (N/2 - 1), N/2 \]  

(3)

Let us consider a cyclopolyene with ideal geometry, and \( N = 4 + 8n \) \( \pi \)-centers (\( n = 0, 1, 2, \ldots \)). Examples are shown in Fig. 1.

![Cyclopolyenes](image)

**Figure 1.** Cyclopolyenes with 4+8n \( \pi \)-centers;

The 4+8n cyclopolyenes are classical systems: Kekulé formulas can be associated with them (formula K in Fig.1).

In the 4 + 8n cyclopolyenes, which are alternant systems,

![Alternant system](image)

NBMOs are present even if the conditions of the CRLH and the extended theorems are not fulfilled.

The existence of two NBMOs for the 4 + 8n cyclopolyenes follows from Eq. (3):
\[ e_k = 2\cos(2\pi k/N) = 2\cos(2\pi k/(4 + 8n)) = 2\cos((\pi/2)k/(1 + 2n)) \]

If \( k = (1 + 2n) = N/4 \),

\[ e_k = 0. \]

The presence of NBMOs is a topological property of the \( 4 + 8n \) cyclopolyenes. Topological isomers (see Fig. 2) with different geometry and symmetry have identical energy spectra.

**Figure 2.** Topological isomers

The \( 4 + 8n \) cyclopolyenes are only theoretical models. They are typical Jahn-Teller systems [13]. The symmetry breaking is determined by the electron-vibrational interaction, as in the case of cyclobutadiene [14].

Here we consider a substituted cyclopolyene and two possible 1-D polymers based on it, shown in Fig. 3.

**Figure 3.** Investigated systems:

CHARACTERISTIC POLYNOMIALS REPRESENTATION

The characteristic polynomial, \( \varphi (G) \) of a molecule is the characteristic polynomial of its adjacency matrix [15, 16]:

\[ \varphi (G) = \varphi (G, x) = \det (xI - A) \]

(4)

The presence of the NBMOs in the \( 4 + 8n \) cyclopolyenes, and in the substituted analogues and their polymers, correspond to the result obtained with the characteristic polynomials, i.e. the polynomials representation is an indirect evidence for the presence of NBMOs.

The characteristic polynomial for cyclopolyene \( A \) (Fig. 1, \( n = 1 \)), has the form:

\[ \varphi (G) = x^{12} - 12x^{10} + 54x^8 - 112x^6 + 105x^4 - 36x^2 = 0 \]

(5)

The characteristic polynomial for the substituted cyclopolyene (Fig. 3) reads:
\[ x^{12} + hx^{11} - 12x^{10} - 10hx^9 + 54x^8 + 36hx^7 - 112x^6 - 56hx^5 + 105x^4 + 35hx^3 - 36x^2 - 6hx = 0 \]  

(6)

In Eqs. (6), \( h \) is the parameter of the Coulomb integral for the N atom. If \( h = 0 \), Eq. (6) is identical with Eq. (5).

The substituted cyclopolyene has one NBMO (see Fig. 4):

\[ \text{Figure 4. Frontier MOs of the substituted cyclopolyene (in } \beta \text{ units); } h = 1, \beta_{CN} = \beta_{CC} \]

For the polymer P-C the polynomial reads:

\[ x^{12} + hx^{11} - (12 + t^2)x^{10} - 10hx^9 + (54 + t^2)x^8 + 36hx^7 - (112 + 22t^2)x^6 - (56h - 4t \cos \omega)x^5 + (105 + 2ht \cos \omega)x^4 + (35h - 16t \cos \omega + 10ht^2)x^3 - (36 + 4ht \cos \omega + 9t^2)x^2 - (6h - 12t \cos \omega)x = 0 \]  

(7)

In Eq (7), \( t = \cos \theta \) (see Fig. 2). If \( t = 0 \), Eq. (7) is identical to Eq. (6). It follows from Eq. (7), that the polymer has one NBMO.

For the polymer P-D the polynomial reads:

\[ x^{12} + hx^{11} - (12 + t^2)x^{10} - (10h + ht^2)x^9 + (54 + 8t^2)x^8 + (36h + 6ht^2)x^7 - (112 + 22t^2)x^6 - (56h - 4t \cos \omega + 12ht^2)x^5 + (105 + 2ht \cos \omega + 24t^2)x^4 + (35h - 16t \cos \omega + 10ht^2)x^3 - (36 + 4ht \cos \omega + 9t^2)x^2 - (6h - 12t \cos \omega + 3ht^2)x + 2ht \cos \omega = 0 \]  

(8)

If \( t = 0 \), the polynomial (8) is identical to the polynomial for the substituted cyclopolyene (5).

The polynomials are obtained with ideal geometry for the cyclopolyene and the polymers – all bond-lengths equal.

The roots of the polynomials for the 1-D polymers correspond to the Hückel-Hubbard version of the Bloch running waves:

\[ \Psi(\kappa) = N^{-1/2} \sum_{\mu} \sum_{r} C_r(\kappa) \exp(-i\omega \mu)r,\mu > \]

\((k \in [-\pi, \pi])\) is the wave vector, \( \mu \) denotes the number of the elementary units (EU) and \( |r,\mu > \) is the r-th AO within the \( \mu \)-th EU; \( \omega = 2\pi k/N \).

SPIN-EXCHANGE INTERACTION IN THE HALF-FILLED BAND

In accordance with Anderson’s theory of magnetism [3], it was shown (see Ref.1 and the references therein) that the effective exchange integral, \( J_{\text{eff}} \), in the Heisenberg-Dirac-van Fleck Hamiltonian can be expressed as a sum of three contributions:
\[ J_{\text{eff}} = J - J_{\text{kin}} + J_{\text{ind}} \]  

(9)

\( J \) is the direct (Coulomb, Hund) exchange integral between the Wannier states localized at adjacent sites. \( J_{\text{kin}} \) (\( J_{\text{kin}} < 0 \)) is the kinetic exchange parameter representing the antiferromagnetic contribution to the spin exchange:

\[ J_{\text{kin}} = -\Delta \varepsilon^2 / 2U = \Delta \varepsilon^2 / 2(U_0 - U_1), \]  

(10)

where \( \Delta \varepsilon \) is the NBMO band width and \( U \) is the renormalized Hubbard parameter [17]. \( U_0 \) and \( U_1 \) are the Coulomb repulsion integrals of two electrons, residing in the same Wannier state or occupying adjacent Wannier states, respectively.

The term \( J_{\text{ind}} \) expresses the indirect exchange (super-exchange) via delocalized \( \pi \)-electrons in the filled energy bands. The sign of \( J_{\text{ind}} \) is determined by the structure and the interaction between the EUs. The terms can be calculated using a formalism described in Ref. 18.

The exchange parameters in Eq. (9) were calculated by means of the Mataga-Nishimoto potential [19] for the two-centre Coulomb atomic integrals:

\[ \gamma_{rs} (M) = e^2/(a + DR_{rs}), \]  

(11)

where \( D \) is the screening constants. The results obtained by means of the Ohno potential [20] did not differ substantially from the results calculated using the Mataga-Nishimoto approximation. Standard values for the one-center integrals: \( \gamma_C = 10.84 \text{ eV}, \gamma_N = 12.28 \text{ eV} \) were used [1].

**NUMERICAL RESULTS AND DISCUSSION**

The numerical results for the magnetic characteristics, which should be considered as quantitative illustration of qualitatively correct results, are given for the polymer \( \text{P-C} \).

The band structure of the investigated polymer is characterized by a large gap in which the two frontiers half-filled bands (HFBs) are situated. An example is shown in Fig. 5.

![Figure 5](image.png)

**Figure 5.** Frontier bands of the polymer \( \text{P-C} \) \((\theta = 45^\circ)\) with: ferromagnetically (6-th band), and antiferromagnetically (7-th band) coupled electrons.

Tables 1–2 collect the numerical results for the calculated values of the components of the effective exchange integral between the electrons in the HFBs for the polymer \( \text{P-D} \). The results for the polymer \( \text{P-C} \) are qualitatively similar. The geometry of the polymers is optimised by means of the extended Su-Schrieffer-Heeger method [22].

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CONCLUSIONS

The character of the ground state in the 1-D $\pi$-systems with one half-filled band is determined only by the magnetic coupling of the electrons within the band: The ground state is ferromagnetic, when all spins have identical orientation, and anti-ferromagnetic, if the spins belong to two sublattices of opposite orientation with compensated magnetic moments of the two spin lattices. If in the latter case the spins are uncompensated, the state is a ferrimagnetic one.

The magnetic coupling of the electrons within the two frontier HFBs of the considered poly-mer is different: ferromagnetic, $J_{\text{eff}} > 0$, in one of them and antiferromagnetic, $J_{\text{eff}} < 0$, in the other, with different values of the components of the effective exchange integral. The character of the ground state is not a sum of the components of the effective exchange integrals. The character depends significantly on the electron interaction of the two HFBs.

Investigations of such cooperative phenomena are in progress.

REFERENCES

2. Itoh, K., M. Kinoshita. Molecular Magnetism, Kodansha, Tokio, 2000

Table 1. Calculated values of the components of the effective exchange integral of the 6-th band (see Fig. 5) of the polymer P-D. The results are obtained by means of the Mataga-Nishimoto potential– Eq. (11), with different screening constants D, and different values of the dihedral angle $Q$ (all entries are in meV).

<table>
<thead>
<tr>
<th>$\theta^\circ$</th>
<th>D</th>
<th>J</th>
<th>$-J_{\text{kin}}$</th>
<th>$J_{\text{ind}}$</th>
<th>$J_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>1</td>
<td>155</td>
<td>~0</td>
<td>-5</td>
<td>150</td>
</tr>
<tr>
<td>45</td>
<td>2</td>
<td>123</td>
<td>~0</td>
<td>-11</td>
<td>112</td>
</tr>
<tr>
<td>45</td>
<td>10*</td>
<td>78</td>
<td>~0</td>
<td>-18</td>
<td>60</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>118</td>
<td>~0</td>
<td>-7</td>
<td>111</td>
</tr>
</tbody>
</table>

* Dielectric constant of graphite [23].

Table 2. Calculated values of the components of the effective exchange integral of the 7-th band of the polymer P-D.

<table>
<thead>
<tr>
<th>$\theta^\circ$</th>
<th>D</th>
<th>J</th>
<th>$J_{\text{kin}}$</th>
<th>$J_{\text{ind}}$</th>
<th>$J_{\text{eff}}$</th>
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<tbody>
<tr>
<td>45</td>
<td>1</td>
<td>125</td>
<td>58</td>
<td>-58</td>
<td>9</td>
</tr>
<tr>
<td>45</td>
<td>2</td>
<td>97</td>
<td>58</td>
<td>-66</td>
<td>-27</td>
</tr>
<tr>
<td>45</td>
<td>10</td>
<td>60</td>
<td>58</td>
<td>-72</td>
<td>-70</td>
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<tr>
<td>50</td>
<td>1</td>
<td>94</td>
<td>44</td>
<td>-60</td>
<td>-10</td>
</tr>
</tbody>
</table>

* Dielectric constant of graphite [23].

CONCLUSIONS

The character of the ground state in the 1-D $\pi$-systems with one half-filled band is determined only by the magnetic coupling of the electrons within the band: The ground state is ferromagnetic, when all spins have identical orientation, and anti-ferromagnetic, if the spins belong to two sublattices of opposite orientation with compensated magnetic moments of the two spin lattices. If in the latter case the spins are uncompensated, the state is a ferrimagnetic one.

The magnetic coupling of the electrons within the two frontier HFBs of the considered poly-mer is different: ferromagnetic, $J_{\text{eff}} > 0$, in one of them and antiferromagnetic, $J_{\text{eff}} < 0$, in the other, with different values of the components of the effective exchange integral. The character of the ground state is not a sum of the components of the effective exchange integrals. The character depends significantly on the electron interaction of the two HFBs.

Investigations of such cooperative phenomena are in progress.

REFERENCES

2. Itoh, K., M. Kinoshita. Molecular Magnetism, Kodansha, Tokio, 2000

69
17. Tyutyulkov, N., D. Bonchev, editors. Graph Theory, Nauka, Sofia, 1987

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SPIN POLARIZATION EFFECT ON THE 2-HYDROXYETHYL METHACRYLATE ATOM TRANSFER RADICAL POLYMERIZATION IN METHYL ALCOHOL

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Abstract: Pulsatile magnetic field accelerates 2-hydroxyethyl methacrylate (HEMA) atom transfer radical polymerization (ATRP) in methanol, though the control efficiency on the molecular weight distribution on the polymer produced decreases slightly. These effects depend on the magnetic field characteristics, magnetic induction, B, and pulsatile coefficient, P. They are the most significant at B = 0.15 T and P = 32%. These extremal dependencies are explained by the influence of the pulsatile magnetic field on the spin evolution of the radical pairs (RP) producing after the breaking of the carbon-bromide bond in the frame of the intermediate complex of the equilibrium D↔A. Two complementary mechanisms of the energy exchange between the complex components and RP spin polarization are proposed and compared. The preference of the Förster inductive-resonance energy transfer mechanism is given.

Key words: Spin polarization, pulsatile magnetic field, pulsatile coefficient, exchange interaction, inductive-resonance energy transfer.

INTRODUCTION

In our previous work [1] the pulsatile magnetic field effect on the HEMA ATRP in methyl alcohol was proved. The polymerization rate at the same conditions increases in comparison with that of ATRP without magnetic field or under a constant magnetic field. It is
noteworthy that together with this acceleration the polydispersity increases as well, namely the molecular weight distribution control decreases. The partial explanation of these experimental results is presented. It is constructed on the assumption that the magnetic field changes the population ratio between the triplet \((U_{T\Sigma})\) and singlet \((U_{S})\) levels of the radical pair (RP), produced as a result of the homolytic destruction of the carbon-halogen bond in the dormant (D) propagation end. This change is in the direction of the \(U_{T\Sigma}\) increase at the expense of \(U_{S}\) as a result of which the RP triplet polarization \((P_{T\Sigma} = (U_{T\Sigma} - U_{S}) / (U_{T\Sigma} + U_{S}))\) under a magnetic field is higher than that without a magnetic field \([2, 3]\). The effect of this spin polarization is the increase of the escape (EP) and scavenge (SP) product yields at the expense of the cage product (CP) one (Fig. 1).

**Figure 1.** Reaction paths for RP evolution of its initial electron spin state in a cage (i.e [RP: S, T\(_{\alpha}\), T\(_{\beta}\), T\(_{-}\)]) to the both final states: \(f_1[S \rightarrow CP]\) defining the CP yield produced by the RP recombination in a S state, and \(f_2[(S, T\(_{\alpha}\), T\(_{\beta}\), T\(_{-}\)]\) defining EP and SP yields, produced by the RP radical reaction with the radical scavengers after the RP cage escape at an absent \((B=0, \text{ double dashed lines})\) and under an applied (black lines) magnetic field. The vector lengths corresponds to the yield of the both types of the products obtained.

In the concrete example the EP and SP yield augmentation designates the realization of the halogenphilicity of \(\text{Cu}^{(0)}\) \([4]\) (oxidation of \(\text{Cu}^{(i)}\) to \(\text{Cu}^{(0)}\)), as well as a transition from a dormant (D) to an active (A) state of the propagation chain. This means a shift of the general ATRP equilibrium (D\(\rightleftharpoons\)A) to A, which explains the experimentally established growth both the polymerization rate and the polydispersity index \([1]\). However, the unclear problems in this work are why the \(P_{T\Sigma}\) increases and why the discussed equilibrium D\(\rightleftharpoons\)A is shifted to the right (to A) remarkably when the constant magnetic field is changed by the pulsatile one? The essential peculiarity for the registered polymerization acceleration and the growth of the polydispersity index of the produced poly(hydroxyethylmethacrylate) (PHEMA) is the low pulsation frequency (150 Hz) of the magnetic field applied. For the clarification of this intriguing problem in the work presented the distinction between of the influences of the pulsatile and constant magnetic field on ATRP of HEMA is studied. The important contribution to achieve this object is the established formation of the excited intermediate complex between \(\text{Cu}^{(i)}/\text{L}\) and the initiator or D during ATRP \([5]\).
The existence of such an intermediate complex is an additional precondition for the low frequency magnetic field influence on both $P_T$ value and on the mentioned above equilibrium ($D\leftrightarrow A$). This possibility is developed in the work presented assuming exciton mechanism for the energy exchange interaction between the mentioned above excited intermediate complexes, which was proposed by Förster [12] for the excitation energy transfer between the porphyrin complexes of the photosynthetic schemes.

**EXPERIMENTAL**

**Materials.** Ethyl-2-bromoisobutyrate (EBIB), 2,2′-bipyridine (Bipy) and copper(I) bromide (CuBr) (Merck) are used without any additional purification. HEMA is purified by the method discussed in [6].

**Apparatus.** The constant magnetic field with a magnetic induction $B = 0.15$ T is produced by the solenoid inductor, supplied with an asymmetrical Larionov’s bridge, which produces nonfiltered direct current with monopolar pulsatile component with a frequency 150 Hz [7]. The used electrical scheme allows to control the value of the superimposed on the constant magnetic field impulse component by the incorporation in the scheme proper reactive (inductive and capacitive) resistancies. As a quantitative measure of the impulse component value the pulsatile coefficient ($P$) is used. It is defined as a ratio between the effective value of the impulse current ($I_{imp,ef}$) through the inductor to the direct constituent of the current ($I_{const}$), providing $B = 0.15$ T. It is expressed in percents: $P = (I_{imp,ef}/I_{const})10^2$ [8].

**Polymerization.** In a practical example EBIB ($2.3 \times 10^{-4}$ mol) is dissolved in 2.25 mL equivolume (1/1) HEMA/methanol solution, placed in a glass ampules. After the gas release from the obtained solutions the ligand (44 mg; $2.36 \times 10^{-4}$ mol Bipy) and after that the catalysts (16 mg; $1.13 \times 10^{-4}$ mol CuBr) are added. In view of the fact that the polymerization begins instantly (at 20°C) the closed ampules are subjected under the magnetic field influence immediately. The polymerization conversion ($q$) is determined gravimetrically. To this aim the produced after a determined period PHEMA is precipitated in a diethyl ether and dried under vacuum at 50°C. An additional purification of produced PHEMA is performed chromatographically by the transport of the polymer solution in an equivolume.

\[
\begin{align*}
\sim R-X + Cu^{III}/L &\stackrel{kp, M}{\leftrightarrow} \sim R\cdots X\cdots Cu^{III}/L^* \stackrel{\sim R^- + X-Cu^{III}/L}{\leftrightarrow} \sim R-R^- \\
&\text{or} \sim R^- + \sim R^+ 
\end{align*}
\]
methanol/water mixed solvent through the columns with silica. After the freeze-drying of the PHEMA colorless solutions, the pure white powdered PHEMA is produced. PHEMA molecular weight and molecular weight distribution (MWD) are determined by a size-exclusion chromatography (SEC) (Waters 510) with linear Shodex OHpakSB-800 HQ columns, packing with poly(hydroxyethyl methacrylate) gel with pore size 1000, 500 and 200 Å, connected with Waters 410 differential refractometer and Waters M490 UV (λ = 230nm) detectors. SEC measurements are performed using methanol/water (60/40 v/v) eluent and eluation rate 1 mL/min at 30°C. For the calibration the PEG standards (MW from 10⁶ to 2.2×10⁴ Da) and PEO (MW from 2×10⁴ to 10⁶ Da) (Polymer Laboratories) are used.

For the evaluation of the magnetic field effect on the polymerization kinetics the determined Mn and Mw/Mn of the PHEMA samples, produced without and under magnetic field with B = 0.05, 0.10, 0.15, 0.20 and 0.25T at P = 0, 32 and 133%, are compared. The results at P = 0% corresponds to the nonpulsatile (constant) magnetic field.

RESULTS

The conversional dependencies of Mₙ and Mₚ/Mₙ of the PHEMA samples, produced by ATRP of HEMA in methanol under a magnetic field with P = 0.15 T, are presented in Table 1. The linear Mₙ growth with q and the fact that for all of the samples Mₚ/Mₙ < 1.3 are good proofs for an effective control of MWD of the produced by ATRP under magnetic field PHEMA.

<table>
<thead>
<tr>
<th>q</th>
<th>Mₑ ¹⁰⁻³(g/mol)</th>
<th>Mₚ/Mₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>3.08</td>
<td>1.28</td>
</tr>
<tr>
<td>0.35</td>
<td>3.85</td>
<td>1.24</td>
</tr>
<tr>
<td>0.52</td>
<td>5.46</td>
<td>1.18</td>
</tr>
<tr>
<td>0.60</td>
<td>5.92</td>
<td>1.16</td>
</tr>
<tr>
<td>0.67</td>
<td>6.85</td>
<td>1.14</td>
</tr>
<tr>
<td>0.75</td>
<td>7.77</td>
<td>1.12</td>
</tr>
</tbody>
</table>

From the presented on Fig. 2 results it is clear that the ATRP rate of HEMA depends on the magnetic induction (B) of the applied magnetic field. The ATRP rate has a maximum at B = 0.15 T. The extreme dependence of ATRP rate can be related to the discussed in the introduction section spin polarization of RP produced after the breakage of the R–X bond, depending on B as well [2, 3]. The dominating factor for the character of these dependencies is a mechanism of the spin evolution of the forming RP. According to two of
them $P_{\tau\Sigma}$ (so the ATRP rate according to the discussion in the introduction section) passes through the maximum with the B growth if: i. The exchange interaction between the the RP components as well as between them and medium ones (J-effects) dominates; ii. The combination of the superfine interaction of the RP unpaired electrons with the paramagnetic cores around them (hfc-mechanism) with a possible interaction of both RP spins with different g-factors ($\Delta g$-mechanism) [9]. By this way, two alternative mechanisms can be responsible for the extremal $P_{\tau\Sigma}$ run, and consequently, for the similar extreme ATRP rate dependence as a function of P: J-mechanism and ($\Delta g$ + hfc)-mechanism. Since the RP is formed at ~R–X (D) bond breaking when ~R·····X·····Cu(1)/L exciplex (Scheme 1), the J-mechanism looks reasonable and acceptable. However, the formation of this complex is not to be a prerequisite for a considerable hfc-interaction between X and Cu(1)/L because of the Cu(1)/L diamagnetic properties. The difference in g-values of the RP-components (~C and X) is a possible reason for a $\Delta g$-mechanism for a $P_{\tau\Sigma}$ polarization. However, this mechanism does not provide extremal (with maximum) dependence of $P_{\tau\Sigma}$ on B, and consequently the similar relationship between the established experimentally HEMA ATRP rate on B. To verify the fairness of the assumption for the domination of the J-mechanism for the $P_{\tau\Sigma}$ spin polarization, raised from the discussed above results, the kinetic and MWD effects of the constant and pulsatile with different pulsatile coefficients (32 and 133%) are compared (Table 2).

It seems that P influences both the HEMA ATRP rate and $M_n$ and $M_w/M_n$ of the PHEMA produced. More impressive is the fact that this effect is the most considerable at $P=32\%$. This extremum confirms assumption for an effective J-mechanism for the spin $P_{\tau\Sigma}$ polarization of the RP discussed. From the “gold rule” [10] it follows that the rate constant

![Figure 2. Dependence of the ATRP rate of HEMA under magnetic field ($V_B$) and without such field ($V_0$) as a function of B; T=20°C; [HEMA]_o = 50% (w/v); [EBIB]:[CuBr]:[Bipy] =1:1:2.5.](image)
for the transition between initial $<i,m>$ and terminal $|f,n>$ states of this system is not zero if only the external impact energy is equal to the difference $E_{i,m} - E_{f,n}$ (2).

$$k_{if} = \frac{2\pi}{\hbar} \sum_m p_m \sum_n \langle i,m|H|f,n\rangle^2 \delta(E_{i,m} - E_{f,n})$$

That fact that top ATRP rate (maximum $P_{T\Sigma}$ polarization) is observed at $P = 32\%$ and so low-frequency pulsatile magnetic field, evidences, according to this rule, probably for very close standing vibrational RP levels. It appears that a spin evolution, namely $P_{T\Sigma}$ polarization, in a pulsatile magnetic field has resonance character. The resonance $P_{T\Sigma}$ polarization is a result of the simultaneous pulsatile magnetic field effect both on the settlement of the initial RP states ($p_m$ in Eqn. (2)) and on the determinant intensity of the transition dipole moment ($\langle i,m|H|f,n\rangle$ in Eqn. (2)), more exactly on the relaxation component of the Hamiltonian (H). The RP inclusion in the exciplex (1) is a possible reason both for a little value of the difference $E_{i,m} - E_{f,n}$ and for an intensive exchange interaction between the RP components.

In the literature on the ATRP mechanism [4], this exchange interaction is expressed by the electron transfer through the internal part of the complex formed. According to the P. Anderson’s model [11] the dominating component of the exchange interaction in the similar to (1) exciplexes is indirect (superexchange) component whose value is determined by ambient both spins ions and dipoles, namely the components of the internal complex sphere (1).

However, the resonance character of $P_{T\Sigma}$ polarization can also be a consequence of one or more types of the exchange resonance interaction also, such as induction resonance energy transfer by the exitone Förster mechanism [12–14]. The precondition for its realization is the excimer formation again. By this mechanism the exciplex can transfer its excitation energy to other similar complexes as well as to such complexes in an unexcited state. At first sight this exchange does not open thermodynamic possibilities for the $P_{T\Sigma}$ increase. However, in reality, the excitation of the new complexes expands the multitude of the exitones with different local environments. It means that the probability for the production of the RP with $P_{T\Sigma}$ polarization increases since the exitones with a specific, favourable type of a local environment can only produce RP with $P_{T\Sigma}$ spin polarization.

<table>
<thead>
<tr>
<th>B (G)</th>
<th>P (%)</th>
<th>q</th>
<th>$V_{b}/V_{e}$</th>
<th>$M_n$ (g/mol)</th>
<th>$M_L/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>–</td>
<td>0.261</td>
<td>1.0</td>
<td>6450</td>
<td>1.21</td>
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<tr>
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<td>2.2</td>
<td>3630</td>
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</tr>
<tr>
<td>1500</td>
<td>133</td>
<td>0.258</td>
<td>1.6</td>
<td>4520</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Table 2. The change of the ratio between the initial ATRP rates without ($V_o$) and under ($V_B$) magnetic field ($V_{b}/V_{e}$), $M_n$ and $M_L/M_n$ PHEMA, produced without and under constant ($P = 0\%$) and pulsatile ($P + 32$, $133\%$) magnetic fields with $B = 0.15$ T; [HEMA] = 50\% (w/v) in methanol; [EBIB]:[CuBr]:[Bipy] = 1:1:2.5; Pulsatile frequency 150 Hz.
The complexes with such environment are indicated on Fig. 3 by an additional (double) circumferencies. Contribution to $P_{\Gamma\Sigma}$ spin polarization have only these complexes (with a favourable environment) if they are in an excited state. Without excitation energy transition by the Förster mechanism, such contribution in $P_{\Gamma\Sigma}$ is possible only for complexes with favourable environment after its direct excitation, the central complex of the first row on Fig. 3a and 3b. If the Förster energy migration from the excited complex is possible (the horizontal arrows in Fig. 3b), including the excited complexes with an unfavourable environment (Fig. 3b), the complexes with such environment can be excited and provide an effective $P_{\Gamma\Sigma}$ yield (Fig. 3b) by the complexes which initial state is not excited, though the environment is favourable.

**Figure 3.** Comparison between contributions to $P_{\Gamma\Sigma}$ by a ineffective (3a) and an effective (3b) inductive resonance transition of the excitation energy to the complexes between a dormant state of the propagation chain and Cu(1)/L. The complexes with a favourable environment are denoted by an additional (double) circumference, while the complexes without such environment are denoted with a single circle (circumference). The complexes in an initial excited state are denoted by the black circles. The induction resonance energy migration are denoted by horizontal wave arrows, while the vertical arrows – the effective RP $P_{\Gamma\Sigma}$ polarization, produced through the complex destruction with an initial excited state (black vertical arrow) and with a acquired excited state (thick vertical arrow).

In the frame of the nonadiabatic chemical reaction theory [15] the discussed energy exchange reduces to the augmentation of the transition coefficient in the relationship for the rate constant of the transition from the dormant to the active states of the propagation state, namely the activation rate constant. Furthermore, the greater increase of this constant the closer potential surfaces between which the nonadiabatic exchange takes place. The same requirement is in force for the Förster inductive resonance exchange. The formation of the complex between $\sim R-X$ and Cu(1)/L (1) is a crucial precondition for the satisfaction of this common condition. The closeness of the vibration levels of this complex in the ground (white cycles on Fig. 3) and excited (black cycles on Fig. 3) states provides the necessary correspondence between the complexes taking part in the energy exchange. It is noteworthy that the complex components do not provide such closeness by no means separately.

The suppositions and conclusions made so far are based on the experimental results of the ATRP rate at $B = 0.15T$ (Fig. 2) and $P = 32\%$ (Table 2). It is interesting to check
whether the $M_n$ and $M_w/M_n$ relationships on B and P (Table 2) are in correspondence with these suppositions and conclusions. From the Table 2 it is seen that at $P = 32\%$ $M_n$ value is the least, while the value of the polydispersity index ($M_w/M_n$) is the greatest. According to the theory [16] at a small conversion and in the absence of the additional ATRP initiation, the average number degree of polymerization

$$P_n = \frac{q[M]_0}{[I]_0(1 - e^{-k_{act}t})},$$

while the polydispersity index

$$\frac{M_w}{M_n} = 1 + \frac{1}{P_n} + \frac{8}{3k_{act}t},$$

where $q$ is a conversion, $[M]_0$ and $[I]_0$ are the monomer and initiator concentrations accordingly, and $k_{act}$ can be accepted with some approximation as a rate constant of the initiator activation, as well as of the dormant state also. The general conclusion from the results discussed above is that resonance $P_{\text{TRP}}$ growth at $B = 0.15\, \text{T}$ and $P = 32\%$ is a result of a spin evolution through the specific for ATRP exchange mechanism (J-effect). It means higher $k_{act}$ values at these B and P. From the Eqn. (3) it follows that $k_{act}$ growth at $P = 32\%$ would be so considerable that the exponent term in the denominator can provide 1.78, 1.64 and 1.24 times $M_n$ ($P_n$) reduction for the PHEMA samples, produced in the absence and under an applied constant and pulsatile ($P = 133\%$) magnetic fields, correspondingly. Furthermore, it follows that $k_{act}$ growth at $P = 32\%$ should compensate the time reduction for the achievement of the approximately the same conversions in other synthesis, running with greater rates (column 4 of the Table 2).

From the presented in the Table 2 $M_w/M_n$ values and from the Eqn. (4), the conclusion deduced is that the polydispersity index variation is a result of the $P_n$ change. Indeed, from the presented in the Table 2 experimental $M_n$ values it is clear that $28 \leq P_n \leq 50$, namely $0.02 \leq P_n^{-1} \leq 0.036$. This variation of the second term of the Eqn. (4) is too narrow in the comparison with the interval of the $M_w/M_n$ change (Table 2). It means that for the $M_w/M_n$ deviation from unity, the third term of the relation (4) is responsible. At the same time the variation of this term is small also. It seems that the admission for a relative constancy of this term is a result of the compensation behaviour of the multipliers in the product $k_{act}t$.

CONCLUSION

The formation of the intermediate complex between $\text{Cu^{(I)}}/L$ and D is a premise for an effective exchange interaction between both complex components and different complexes in a contact. The energy exchange is a reason for an extremal run of both the spin evolution of RPs (produced after the complex destruction) and spin polarization as a function of the magnetic induction ($B$) and on the the pulsatile coefficient ($P$) of the pulsatile magnet field. These dependencies are used for the explanation of the obtained for the first time
extremal effects of the effects of the pulsatile magnetic field on the ATRP rate and molecular weight characteristics of PHEMA produced.

The complement mechanisms for the exchange interaction are proposed. According to the first one the exchange interaction is between the complex components, the most probably, between components of RP, forming after the complex destruction. The other one is the proposed by Förster induction-resonance energy transport between the excited state of the complex and the complex in the ground state, but with a favourable for the $P_{\Sigma}$ polarization local environment. From the “golden rule” relation for the rate constant (Eqn. (2)), it follows that the intensity of this exchange and $P_{\Sigma}$ polarization are determined by the Hamiltonian relaxation component. Another essential multiplier of this relation is the Dirac operator, predetermining the resonance character of the spin $S\rightarrow T$ evolution rate constant. The fact that such extremal change takes place at so low pulse frequency (150 Hz) evidences for very close disposed energy levels (probably vibrational) between which the exchange takes place. This is an additional argument for the Förster induction-resonance exchange mechanism.

It is shown also that the molecular mass reduction of PHEMA samples produced, and the alteration of their MWD under a pulsatile magnetic field are in full correspondence with the popular theoretical relationship (Eqns. (3) and (4)), and are the result of the growth of the activation rate constant ($k_{act}$), namely the $D \rightarrow A$ transition.

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REFERENCES


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EFFECTS OF THE MAGNETIC FIELD AND VISIBLE LIGHT ON THE INITIATED BY 10-I-3 IODANES ALTERNATING MALEIC ANHYDRIDE COPOLYMERIZATION WITH VINYL ESTER OF 2,2,4-TRIMETHYLHEPTANE ACID

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Abstract: It is shown that diacetoxyiodbenzene (DAIB) initiates the donor-acceptor copolymerization of maleic anhydride (MA) with vinyl ester of 2,2,4-trimethylheptane acid (VH) at room temperatures or higher in darkness and under irradiation with visible light. The determined mono-mer’s reactivity are in correspondence both with this assertion and with the increase of the alternating tendency under the irradiation with visible light as well as magnetic field. The augmentation of this alternating tendency is related to the contribution of the specific, bounded covalently radical pairs (RP, introduced by J. Hall) in the chain propagation reaction. These RP’s are produced from the donor-acceptor comonomer complexes and their triplet polarization depends on the light and magnetic irradiation. The dependencies of the copolymerization rate on the induction and pulsation component amplitude of the applied magnetic field is related by the Förster exchange mechanism of the RP spin evolution. This mechanism is in keeping with nonadiabatic character of the established magnetokinetiks effects on the copolymerization discussed.

Key words: Alternating copolymerization, donor-acceptor complex, radical pair, spin polarization magnetokinetic effect.

INTRODUCTION

The primary products of DAIB destruction under thermal and light influences are acyl and iodanyl radicals:
The latter are responsible for DAIB photo-initiating and thermo-initiating ability of the radical polymerization [1-3]. Since a negative superconjugation and partial ionization of the I-O bond the iodanyl radical has a partial stability and displays the iniferter properties at methyl methacrylate radical polymerization, forming “dormant” propagation ends [3-6]. This gives reason to check a possibility for DAIB initiated alternating copolymerization of MA with VH, the subject of this work.

The spin evolution of the produced after a DAIB destruction RPs (Eqn (1)) depends on the applied magnetic field induction [7]. As it was shown in our previous work [7], the RP triplet polarization \( P_T = U_T/(U_T + U_S) \); \( U_T, U_S \) – the numbers of the RP in triplet and singlet states, correspondingly) increases under a magnetic field, as a result of which the augmentation of the yields of the products of the radical interaction with their scavengers or with the medium components takes place [8]. In practice, it means the growth of the initiation efficiency of the radical polymerization [9]. That is why, the influence of the magnetic field on the donor-acceptor MA-VH copolymerization rate and on the alternating copolymerization tendency of the copolymer monomer units is investigated in the work presented.

However, there is one more type of RP, produced during the donor-acceptor MA-VH alternating copolymerization. Be speaking of RPs, obtained from the destruction of the donor-acceptor complex (C) by the Hall scheme (2) [10-13].

\[
\text{(C)} \quad \text{(RP)}
\]

where \( \equiv A \) and \( \equiv D \) are the electron donor (MA in this case) and electron acceptor (VH) comonomers. The spin evolution of the triplet polarization (PT) of this type RP also depends on the magnetic field, and can influence not only on copolymerization initiation, but also the propagation of copolymer chain. The analysis of the possible contributions of these two types RPs on the magnetokinetic effects of the donor-acceptor alternating copolymerization is the general subject of the work presented.

**EXPERIMENTAL**

**Materials.** VH (Shell) and dioxan (solvent) were dried and distilled just before the usage. MA was also purified by sublimation in a nitrogen atmosphere before the application also. The initiator, DAIB (Merk), was used without further purification.
Apparatus. The device for generation of permanent and pulsatile magnetic fields (nonsinusoidal nonopolar pulses with a frequency 150 Hz) with a required magnetic induction was described in our previous works [9]. The source of the visible light was a 450W electrical lamp. The dark experiments were performed in ampules, coated in a black textile.

Copolymerization. The copolymerizations in dioxan were performed under nitrogen in sealed glassed ampules, containing solvent, comonomers (the total comonomer concentrations were 2.9M, while the MA mole fractions in the monomer feed were 0.35, 0.50, 0.70 and 0.90) and DAIB (the initiator concentration was 0.5M) and heating at the desired temperatures. The temperatures (20°, 30°, 35°, 50°, 70°C) were kept within the limits ± 0.2 °C. The polymerization conversion (0.07 ≤ q ≤ 0.70) is determined gravimetrically. To this aim the produced after a determined period copolymers were precipitated in a mixed ethanol/water solvent (2/1 volume ratio). After drying of the purified copolymers (at temperature 45°C under vacuum) they were analyzed. The copolymer compositions were determined by titration of the carboxyl groups in the samples dissolved in acetone.

RESULTS

At first, it is shown that in dioxane solution at 20°C the initiated by DAIB VH (50%, wt) homopolymerization does not pass both without and under visible light. Probably, the VH reactivity to the iodanyl and acyl (methyl) radicals, produced after the homolytic DAIB degradation (Eqn.1) is not enough or the concentration of these radicals is less than necessary for the VH homopolymerization. However, the latter should be excluded as at the same conditions DAIB initiates the VH-MA copolymerization with a rate enough to enrich the conversion from 7 to 50% for 2 hours, depending on the composition of the initial monomer feed. Therefore, the forced assumption is that the reactivity of the complex, formed, probably, between MA (a strong electron acceptor with e = 2.25) and VH (a outlined electron donor with e = −0.53) [14, 15] is much greater than that of VH, and that it is enough at these conditions both for an interaction with the radical products of the DAIB destruction (Eqn. 1) and for a participation in the chain propagation reaction. To verify this supposition the MA-VH copolymerization as a function of the monomer feed composition is studied. The results of the kinetic investigations are presented on Fig. 2. As it can be seen from this figure, the copolymerization rate has a maximum at an equimole composition of the monomer feed, one of the peculiarities of the alternating copolymerization [16]. It is also kept if the copolymerization is performed at a higher temperature, 35°C (the curves 2 and 3). What is more, at this temperature the copolymerization proceeds both without irradiation with visible light (curve 2 of the Fig. 2) and under such irradiation (curve 3 of the Fig. 1).

The maximal conversion enriched at 35°C, M_{MA} = 0.50 for 2 hours is 70%. It proves that homolytic degradation of DAIB (Eqn. 1) can be both photo- and thermo-induced. The closeness of the curves 2 and 3 on Fig. 1 is a proof for an effective thermo-initiated MA-VN copolymerization at 35°C. Earlier the possibility for the thermo-initiated with DAIB
radical homopolymerization was established [17]. The curve 2 of the Fig. 1 expands the applicability of this statement to the radical copolymerization.

It is noteworthy that the difference between the copolymerization rates with (curve 3) and without (curve 2) an irradiation with a visible light is the most considerable at an equimole comonomer composition, when the alternating tendency is the most powerful. At the same equimole monomer feed composition, the discussed difference increases with a temperature higher than 35°C (Fig. 2). It is seen that at T > 35°C the copolymerization rate under a visible light continues to rise (curve 2 on Fig. 2), though not so impetuously as in the interval from 20 to 35°C, while, without the similar irradiation (in a dark, curve 1 on Fig. 2), the copolymerization rate begins to decrease. In spite of this, the copolymerization rate even at 70°C remains higher than that at 20°C, the difference between the curves 2 and 1 on Fig. 2 increases considerably with a temperature. One possible explanation of this difference is connected with a decrease the concentration of the donor-acceptor complex (C) between MA and VH with a temperature growth above 35°C. If the copolymerization runs in darkness (without a visible light) the decrease of the C concentration leads to the reduction of the copolymerization rate (curve 1 on Fig. 2). When the copolymerization takes place under a light (under an irradiation with a visible light) this effect is compensated with a higher degree of the degradation of C to the covalent-bound radical pairs (RP) through the scheme of Hall [12] [Eqn. (2)]. RPs can have an additional contribution in the copolymerization initiation, which is a possible reason for the copolymerization rate growth.
mentioned above at T>35°C. This explanation is in a correspondence with a supposition for the alternating MA-VH copolymerization at these conditions.

Another possible explanation of the difference under a discussion (the difference between the curves 1 and 2 on Fig. 2) is a supposition [4-6] for effective photo-stimulated degradation of the iodanyl (Eqn (1)) and propagation radicals, representing peculiar dormant states of the propagation chain. At higher temperatures there are other possible paths for the destruction of these dormant propagation states, which is confirmed by the fact that the reaction medium is colored, probably as a result of the iodine formation. At the copolymerization under light, there is not such colorization because of the transition of the dormant into active states, which accelerates the copolymerization.

For an additional verification of the assumption that the MA-VH copolymerization is an alternating one, the copolymer compositions are determined as a function of the monomer feed composition. The compositions of the copolymers produced are presented in Table 1. It is visible that the synthesized at 20°C (under an irradiation with a visible light) and at 35°C (in a dark) copolymers are have very close to equimolecular compositions, independently from the composition of the initial monomer feed. This is the second indicator for the truthfulness that the investigated copolymerization is alternating one [16]. The calculated monomer reactivity from the presented in the Table 1 relationships between the copolymer compositions as a function of the monomer feed compositions is: \( r_{MA} = 0.019 \) and \( r_{VH} = 0.022 \) if the copolymerization is performed at 20°C and under an irradiation with a visible light and \( r_{MA} = 0.024 \) and \( r_{VH} = 0.032 \) if the copolymerization is run at T=35°C without a visible light [18]. As it could be expected from the copolymer
composition relationships the relative monomer reactivity is very close to zero, another strong indication for the alternating character of the copolymerization discussed.

Table 1. Dependence of the MA–VH copolymer composition (MA mole fraction in a copolymer, \( m_{MA} \)) on the monomer feed composition (MA mole fraction in an initial monomer feed, \( M_{MA} \)), produced by the MA-VH copolymerization, initiated by DAIB at 20°C under an irradiation with a visible light, at 35°C in a dark and at 20°C under an irradiation with a visible light and with an applied magnetic field with \( B = 0.15 \) T.

<table>
<thead>
<tr>
<th>( M_{MA} )</th>
<th>( m_{MA} ) ( T = 20^\circ C), visible light</th>
<th>( m_{MA} ) ( T = 35^\circ C), without light</th>
<th>( m_{MA} ) ( T = 20^\circ C), visible light, Magn. field with ( B = 0.15 ) T</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.478</td>
<td>0.471</td>
<td>0.480</td>
</tr>
<tr>
<td>0.33</td>
<td>0.496</td>
<td>0.489</td>
<td>0.497</td>
</tr>
<tr>
<td>0.50</td>
<td>0.499</td>
<td>0.496</td>
<td>0.501</td>
</tr>
<tr>
<td>0.65</td>
<td>0.508</td>
<td>0.509</td>
<td>0.505</td>
</tr>
<tr>
<td>0.80</td>
<td>0.515</td>
<td>0.521</td>
<td>0.511</td>
</tr>
</tbody>
</table>

It is noteworthy that for the copolymerization at \( T=20^\circ C \) with an applied pulsatile magnetic field the values of the relative monomer reactivity are smaller (\( r_{MA}=0.014 \) and \( r_{VH}=0.018 \)). This is additional evidence for the above formulated assumption regarding the enhanced alternating tendency if the MA-VN copolymerization is run under the pulsatile

**Figure 3.** Dependence of the ratio between the copolymerization rates under \((V_B)\) and without \((V_0)\) magnetic field on the magnetic induction \((B)\). Solvent – dioxane, equimole initial monomer ratio, monomer concentration: 50% (wt), \( T=20^\circ C \), initiator [DAIB] = 0.4% (wt).
magnetic field. For a clearer reviling of this possibility, the dependencies of the copolymerization rate on the magnetic induction (B) (Fig. 3) and pulsatile coefficients (Table 2) are determined.

The curve on Fig. 3 demonstrates a rate maximum at B=0.15T. From the theory of the alternating copolymerization [16, 19] it follows that the effect of the magnetic field on the alternating tendency is the most significant. However, from the discussion in the introduction it follows that the greater the P_r RP polarization under magnetic field the more considerable the magnetostimulated kinetics effect [8]. There are two cases when P_r runs through the maximum as a function of B [20, 21]. The first one is realized when the exchange interaction between the spins of both RP components is greater than the superfine interaction of these spins and those of the environment core magnetic moments (J-mechanism of the spin evolution). The second one takes place when the dominating factors for the spin evolution are both the difference between g-factors of RP spins (\(\Delta g\)-mechanism) and the mentioned above superfine interaction (hfc-mechanism) simultaneously, namely (\(\Delta g+hfc\))-mechanism. Spin evolution through the \(\Delta g\)- or hfc-mechanisms separately does not provide extreme P_r dependence on B, and hence the experimental curve on Fig. 4 [22].

RP produced by the DAIB (initiator) degradation through the reaction (1) comprises of the iodanyl radical (AcOI\'Ar with a strong d-resonance interaction between non-paired electron on the iodine atom and aromatic \(\pi\)-electrons [23, 24]) and acyloxide radical (CH_3COO\'). Although the difference between the g-factors of both radicals is negligible, the mentioned above d-resonance interaction in the frame of the iodanyl radical can be reason to expect a spin evolution of this RP through the (\(\Delta g+hfc\))-mechanism. Therefore, the treatment of the demonstrated on Fig. 4 extreme dependence as a result of the P_r-polarization of RP, produced by the DAIB degradation (Eqn (1)) through the (\(\Delta g+hfc\))-mechanism looks reasonable and substantiated. However, this spin polarization explains only the acceleration of the copolymerization under the subjected magnetic field. It is not possible to explain the augmentation of the alternating tendency of the MA-VH copolymerization, which is outlined in the comparison of the demonstrated on Fig. 1 curves, the copolymer compositions (Table 1) and the calculated relative monomer reactivity for the copolymerization performed without and under magnetic field. Indeed, the P_r polarization of the discussed RP influences the copolymerization rate through initiation efficiency, as it was discussed in the introduction section. However, in a common case, the initiation rate does not influence the alternating tendency [16, 19].

The possibility for the explanation of the simultaneous changes of the copolymerization rate and the alternating tendency with P_r opens the participation in the copolymerization of the RPs, produced by the Hall’s scheme (Eqn 2) [12-14]. Essential characteristic of this RP is the consistency of both spin components. It is a precondition for a more considerable exchange interaction between spins, which, as it was shown above, explains the demonstrated on Fig. 4 extreme copolymerization rate dependence on magnetic induction B. More important in this case is that this exchange interaction provides chain reproduction of this type RP by the Förster mechanism [26-28], proposed at first for the explanation of the excited energy migration in the photosynthetic schemes [29, 30].
This mechanism is named inductive-resonance or vibration-relaxation one. The reason for the second one is that the interaction is between induced dipoles of the molecules or the molecular associates with equal or very close vibration energy levels. For the first one it follows from the fact that the energy exchange is a result of the resonance energy transfer from the energy donor to the energy acceptor and the latter gets in its excited state. The produced by the scheme (2) RPs can perform the part of the energy donors, which is in the full correspondence with the original scheme of Huisgen [31], called these RPs high energy RPs. On the scheme (3) these RPs are denoted with RP☼. After the interaction of these RPs with the donor-acceptor complexes (C on the scheme (3)) they are recovered. However, the composition of such RPs is equimole, which is other their peculiarity, besides the mentioned above their consistency. Hence, the participation of these RPs in the initiation, as well as in the chain propagation of the donor-acceptor copolymerization, explains the contribution of the discussed exchange interaction in the registered alternating tendency under the applied magnetic field. In this way, the applied magnetic field furthers the triplet polarization (Pₜ) of the specific (equimole composition and component binding) RPs, while the exchange interaction through the Förster mechanism provides the regeneration of these RPs, and their participation in copolymerization initiation and propagation increases the alternating tendency. The RP reproduction from the donor-acceptor complex (C) by the scheme (3) is an original expansion of the established by Huisgen [31] and Hall [10-12] formation of RPs of this type and their participation in the spontaneous initiation. The essential peculiarity of this expansion is the participation of such RPs not only in the initiation, but also in the participation of the propagation chain, which just provides their contribution in the enhanced alternating tendency under the applied magnetic field.

The discussed induction-resonance mechanism allows to explain the established magneto-kinetics effects, in spite of the small field contribution on the activation energy of the chemical reactions. According to its physical essence, the realization of this mechanism is possible only for nonadiabatic chemical reactions, for which the change of the rate constant is possible not only through the change of the activation energy, but by the alteration of the transmission coefficient (α) also. The α increase is in proportion to the likelihood for the transition between the potential surfaces of the reaction paths [32]. This probability is inversely proportional to the energy difference between the exchange potential surfaces [33, 34]. Hence, the closeness between vibrational levels of RP and C, between which the resonance exchange takes place, is a precondition not only for the energy exchange by the Förster mechanism, but for the more considerable magneto-kinetics effect too.

The result of the comparative analysis of both discussed mechanisms for the spin evolution ((Δg+hfc)-mechanism for RP, produced by the DAIB degradation, and the
exchange mechanism for RP, forming as a result of the interaction between the electron-donor and electron-acceptor monomers), explaining the extreme dependence on Fig. 4, is that the second one is more preferable as:

- It is in accordance not only with the pointed out on Fig. 4 extreme dependence.
- It explains more considerable tendency of alternating under a magnetic field.
- It allows to understand the observable magneto-kinetics effect as a result of the nonadiabatic character of the spin evolution of the bounded covalently RPs.

It is clear the closeness of the energy levels of the exchanging energy RP and donor-acceptor complex (C) is a precondition for a more considerable augmentation of the transmission coefficient (not only through the reduction of the activation energy) in a classical relationship for the rate constant \( k_{if} \). By the “golden rule” relationship \([22,35]\) this requirement is outlined clearly by the Dirac term \( \delta(E_{i,m} - E_{f,n}) \), selecting transitions between isoelectronic levels of the initial \( <i,m| \) and final \( |f,n> \) states of the reaction system:

\[
k_{if} = \frac{2\pi}{\hbar} \sum_{m} p_m \sum_{n} \langle i,m | H | f,n \rangle^2 \delta(E_{i,m} - E_{f,n})
\]  

Hamiltonian \( (H) \) defines intensity of the dipole transition moment \( \langle i, m | H | f, n \rangle \) through which the magnetic moment is expressed in this case by the perturbation term \( (H_{st}) \), constituted from stationary \( (H_{st}) \) and relaxation \( (H_{rel}) \) parts. \( H_{rel} \) is responsible for the relaxation transitions between the mentioned above close energy levels. This relaxation part of \( H \) is just of special interest, as it points to the experimental verification of the uninvestigated until now influence of the pulsatile magnetic field on the rate of chemical reactions, in particular on the rate of the investigated alternating MA-VH copolymerization.

The admission for a considerable closeness of the energy levels, between which the energy exchange takes place by the Förster mechanism, puts on the forefront the investigation of the influence of the low frequency magnetic field on the rate of the alternating MA-VH copolymerization. In addition, if such influence is effective, it would be a strong confirmation of the justice of the preference of the exchange mechanism for the spin evolution of the discussed RPs to \( (\Delta g + hfc) \)-mechanism. Indeed, in contrast to the expected influence of the low frequency magnetic field on the exchange interaction between RP and C, a similar impact on the spin evolution by the \( (\Delta g + hfc) \)-mechanism is unlikely, as such field should not influence the values of the g-factors, as well as the constant of the superfine interaction of the unpaired electrons with ambient paramagnetic cores.

The results, presented in Table 2, demonstrate the acceleration of the donor-acceptor MA-VH copolymerization with pulsation coefficient \( (P) \). The copolymerization rates at \( P=32 \), \( 133\% \) are 1.20 and 1.12 times higher than that under a constant magnetic field with \( B=0.15T \). These results are in correspondence with an expected effect of the pulsatile magnetic field and confirm the proposed by Hall [10-12] assumption for an exchange mechanism of the magnetic field effect on the spin evolution of RPs taking part in the chain propagation. The low frequency of the pulsatile magnetic field component at \( P>0 \) might be considered as an experimental confirmation of the assumption that a spin evolution runs through the Förster undiction-resonance energy transfer mechanism between
Table 2. Dependence of the donor-acceptor MA-VH copolymerization rate in dioxane at equimole monomer ratio under a magnetic field with $B = 0.15\, T$ ($V_{0.15}$) related to the rate of the same copolymerization without such field ($V_0$) as a function of the pulsation coefficient $P$. The full monomer concentration is 50% (wt), initiator is DAIB with a concentration 0.4% (wt) and $T = 20^\circ\text{C}$. The copolymerization is performed under irradiation with visible light.

<table>
<thead>
<tr>
<th>$P$ (%)</th>
<th>0</th>
<th>32</th>
<th>133</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{0.15}/V_0$</td>
<td>1.23</td>
<td>1.47</td>
<td>1.38</td>
</tr>
</tbody>
</table>

the close situated energy levels of the initial (i) and terminal (f) products (Eqn. (4)) of the reaction (3). Other strong confirmation of this assumption is the established extreme of the copolymerization rate acceleration on the $P$ value (Table 2). The maximum acceleration is at $P = 32\%$. With allowance that the relaxation component of the Hamiltonian in the expression for $k_{if}$ (Eqn. (4)) influences not only on the relaxations between close situated energy levels, but on the their coupling in time [22], the discussed extreme dependence evidences the resonance effect of the pulsatile component of the applied magnetic field. This resonance effect differs from the described in literature [36] by both the pulsatile frequency component and by the orientation of the latter toward the stationary magnetic field. It could be conditionally called $P$-resonance. Its rigorous theoretical treatment is in store. It is established for the first time for this donor-acceptor copolymerization. It is an additional confirmation of the Förster exchange energy mechanism of the spin evolution of the covalently bound RPs (Eqn. (3)), produced by the interaction of A with D (Eqn (2)).

**CONCLUSION**

In the work presented it is shown that DAIB initiates the radical MA-VH copolymerization both at room and a bit higher up temperatures. The copolymerization is alternating as the copolymerization rate has a maximum at an equimole monomer composition (Fig. 1), the copolymer composition is close to the equimole (Table 1) and depends slightly on the monomer composition, and the relative monomer reactivities is very close to zero. It is shown for the first time that the copolymerization rate and copolymer composition depend on both the visible light and on the applied magnetic field (constant and pulsatile). The effects of the external impacts on the formation and spin evolution of RP, produced by destruction of both the DAIB and comonomer MA-VH donor-acceptor complex (C) through the Hall’s scheme [10-12] is proved.. The effect of the magnetic field on the alternating tendency records the participation of the Hall’s covalent bounded RPs not only in the initiation, but in the chain propagation. Triplet polarization of these RP is a precondition for the established enhancement of the alternating tendency. It appears that the copolymerization rate depends on magnetic field induction also, and the rate augmentation is the most considerable at $B = 0.15\, T$. This extreme dependence is explained by nonadiabatic exchange mechanism for the singlet-triplet RP evolution. The exchange interaction between RP and
comonomer donor-acceptor complexes through the inductive-resonance Förster mechanism is a part of this explanation. Its realization is in correspondence with the established for the first time magnetic field pulsatile coefficient (P) effect on the copolymerization rate. This P-resonance mechanism of the magneto-kinetics effect is different from the known magnetic resonance effect on the chemical reaction yields, and is at hand to be investigated and grounded theoretically.

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REFERENCES


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COMPARISON OF THERMAL FLUCTUATIONS IN FOAM FILMS AND BILAYER STRUCTURES

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Abstract: In the frames of the DLVO theory the root mean square amplitude and correlation length of capillary waves in thin liquid films are calculated. Their dependences on some important physical parameters are studied. Two models are considered here: A) films with classical interfaces and B) films between two lipid bilayers. The performed numerical analysis demonstrates essential differences in their behavior, which are due to different elastic properties of the film surfaces in the models.

INTRODUCTION

Thin liquid films (TLFs) bounded by simple interfaces, insoluble monolayers and membranes are in the scientific focus for many years [1]. The interest to these nanothin structures is promoted by specific phenomena, taking place in TLFs, and their large application in technology. An important aspect in the practical application is the stability of TLFs [2–4], which is decisive for many processes in flotation [5], colloidal coagulation [6], food industry [7] and other disperse systems [8]. In literature, TLF stability is described as a result of competition between the van der Waals disjoining pressure and the stabilizing effect of capillary and electrostatic forces (DLVO theory). A linear hydrodynamic theory of the kinetics of hole or black spot formation is developed [9–11] which provides calculation of the films’ lifetime and critical thickness. This theory accounts for many interfacial processes such as adsorption, surface and bulk diffusion of surfactants, Marangoni effect, etc. The basic restriction of the linear theory is the small parameter expansion over the ratio $\zeta/h$ between the amplitude $\zeta$ of the surface corrugations and the average film thickness $h$. 

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Since at the point of the film’s rupture they are of equal order, such a presumption is not justified. However, the linear theory results are very important for interpretation of light scattering experiments [12-15].

An interesting effect on the TLF’s stability is the coupling of the film’s drainage and the unstable modes due to non-linear TLF hydrodynamics [16, 17]. Its theoretical description requires correct calculation of the drainage rate, which depends substantially on the shape of the film’s interfaces. Usually, a dimple is formed [11, 18-21] and the corresponding law of thinning [22, 23] differs from the classical Reynolds expression first applied to TLF by Scheludko. During the last few decades, some attempts to take into account the influence of non-linear effects on TLF’s stability have been made. Some authors [24-26] have reported analytical-numerical calculations based on the Navier-Stokes equations. These theories further continue some usual ideas of hydrodynamic stability without considering fluctuations. Other authors [27] have accounted for the influence of the thermo-convection in a non-linear flow by means of temperature dependence of viscosity. The main non-linear effects are due to two factors: the non-linear hydrodynamic terms in the Navier-Stokes equations and the non-linear dependence of the disjoining pressure from the film’s thickness. In pure form, the first effect takes place at capillary-gravity waves on infinitely deep liquids where the disjoining pressure is missing. In this case, the interfacial kinematics is described by a Korteweg-de Vries equation of fifth degree [28]. The dependence of the disjoining pressure from the film’s thickness is a problem, which has been an object of intensive investigations. Abreast of now becoming classical van der Waals and electrostatic components, a number of new interesting effects of macroscopic interaction were observed [29]. Here we can mention non-DLVO hydrophobic, hydration, protrusion and other forces [30]. In the case of surfactant concentration above CMC, the disjoining pressure isotherm exhibits periodic behavior, which is responsible for the film’s stratification [31]. Similar periodic behavior but with smaller characteristic length could be expected as a consequence of the discrete molecular structure of the matter [32].

The picture in membrane multilamellar structures is additionally complicated by the low value of surface tension leading to large out of plane deviations of membranes. For this reason, the steric interaction between the two membranes bordering the film becomes important and leads to the so-called undulation forces [33]. This interaction depends substantially by the membrane’s elasticity κ, which can be conveniently measured by ellipsometry and X-ray scattering [34, 35]. Membranes are soft and easily flexible bilayer structures, which possess freedom for fluctuations onto a membrane plane [36]. The scale of these fluctuations grows up close to the intra-membrane phase transitions [37, 38]. The mechanical properties of membranes, even if composed by two or more monolayers of insoluble surfactants, are far from those of the latter [39, 40]. The internal behavior of bilayers is well studied using methods based on diffraction and scattering of light [41, 42], X-rays [43] and neutrons [44, 45], and some interesting phase transitions are observed as result of the phase state of the lyophobic parts of surfactant molecules [46, 47]. They play an important role not only in the membrane’s transport, elastic properties and secondary quasi-crystalline arrangement of the membrane incorporations, but also in the biological
functions. Additional complications could arise from the existence of membrane proteins, which interact with each other by potential and curvature-induced surface forces [21, 48, 49]. Due to the Brownian motion those membrane proteins migrate and create a secondary crystalline structure, which changes properties of the whole membrane [50]. The problem of rupture of TLF, bounded by biomembranes, is relevant to coalescence of biological cells, fusion of colloids in cells, stability of vesicles and lamellar structures and other life-important processes. Both linear [51] and non-linear [52] theories were applied to the multilamellar membrane structure stability. A quasi-thermodynamic theory for rupture of bilayers and Newton black films was proposed [53], which explains the phenomenon by appearance of holes with a critical size.

FLUCTUATING HYDRODYNAMICS OF THIN LIQUID FILMS

Local fluctuations of the thickness of a thin liquid film are the major factor responsible for the film’s stability. Usually the thin liquid films behave rheologically as a Newtonian fluid and they can be described on the base of the classical hydrodynamics, coupled with the fluctuation theory. In the frames of the well-known lubrication approximation the TLF’s hydrodynamics obeys the following Navier-Stokes-Reynolds equations

\[ \begin{align*}
\hat{\partial}_x p &= \eta \hat{\partial}_{zz} v_x \\
\hat{\partial}_y p &= \eta \hat{\partial}_{zz} v_y \\
\hat{\partial}_z v_x &= \partial_x v_x + \partial_y v_y + \partial_z v_z = 0
\end{align*} \tag{1,2,3} \]

where the \( z \)-axis is normal on the film’s surface, \( p \) is the hydrodynamic pressure including fluctuations, \( v_x, v_y \) and \( v_z \) are the components of the hydrodynamic velocity, and \( \eta \) is the dynamic viscosity of the liquid in the film. Since the symmetric modes of local film thickness changes, the so-called squeezing modes [13], are only responsible for the film’s rupture, the lateral boundary conditions read

\[ \begin{align*}
v_x(z = \pm H/2) &= 0 \\
v_y(z = \pm H/2) &= 0
\end{align*} \tag{4} \]

which imply films with tangentially immobile surfaces; \( H(x,y,t) \) is the local film thickness. According to Eq. (2), the pressure does not change normally along the film, which allows a direct integration of Eqs. (1). The corresponding results are

\[ \begin{align*}
2\eta v_x &= (z^2 - H^2/4)\hat{\partial}_x p \\
2\eta v_y &= (z^2 - H^2/4)\hat{\partial}_y p
\end{align*} \tag{5} \]

which account for the boundary conditions (4). Introducing Eqs. (5) into the continuity equation (3) and integrating once under the obvious symmetry condition \( v_z(z = 0) = 0 \) yield an explicite expression for the normal component of the hydrodynamic velocity

\[ 6\eta v_z = \hat{\partial}_x [z(3H^2/4 - z^2)\hat{\partial}_x p] + \hat{\partial}_y [z(3H^2/4 - z^2)\hat{\partial}_y p] \tag{6} \]

Finally, combining the kinematic relations for the film surfaces
\[ \partial_t H + v_x(z = \pm H/2)\partial_x H + v_y(z = \pm H/2)\partial_y H = v_z(z = H/2) - v_z(z = -H/2) \]

with Eqs. (5) and (6), the following equation governing the evolution of the local film thickness \( H \) is derived

\[ 12\eta \partial_t H = \partial_x (H^3 \partial_x p) + \partial_y (H^3 \partial_y p) \quad (7) \]

In general, the local film thickness can be split into the mean value \( h \equiv <H> \) and the local fluctuation \( \zeta \equiv H - h \). In the frames of the considered non-draining flat films, the mean thickness does not depend on the position at the film and is constant in time. A realistic model for such a film is the soap bubble. The rigorous theory of the stability of films requires solution of the nonlinear equation (7). Unfortunately, contemporary mathematics does not supply methods for a rigorous solution. For this reason, all considerations which follow are limited in the frames of a linear model where \( \zeta \ll h^2 \). Hence, the linearized version of Eq. (7) for the present films reads

\[ 12\eta \partial_t \zeta = h^3 \Delta p \quad (8) \]

Here a two-dimensional Laplace operator \( \Delta \equiv \partial_{xx} + \partial_{yy} \) is introduced for convenience. Equation (8) is not complete and requires appropriate expression of the hydrodynamic pressure on the local film thickness. According to linear TLF thermodynamics the normal force balance on the film’s surface takes the form

\[ p = -(\sigma/2)\Delta \zeta + (\kappa/2)\Delta \Delta \zeta - \Pi' \zeta + \delta P \quad (9) \]

where the reference pressure in the gas phase is taken to be equal to the disjoining pressure \( \Pi(h) \) which is the necessary condition for stationary of the film’s average thickness. The first term on the right hand side of Eq. (9) represents the local capillary pressure, where \( \sigma \) is surface tension. The second term accounts for elastic deformations of the film surfaces with elasticity modulus \( \kappa \) of the interfaces. \( \Pi' \) is the first derivative in respect to \( h \) of the total disjoining pressure, being a sum of all existing components, and \( \delta P \) represents the pressure fluctuations due to the thermal motion of the matter.

By introducing Eq. (9) in Eq. (8) one yields the following basic equation

\[ (24\eta/h^3)\partial_t \zeta + \sigma \Delta \zeta - \kappa \Delta \Delta \zeta + 2\Pi' \Delta \zeta = 2\Delta P \]

describing the fluctuation dynamics of the surface waves. A useful tool for analysis of this stochastic equation is the Fourier transform in respect to the spatial coordinates. After its application the equation above changes to

\[ (24\eta/q^3 h^3)\partial_t \zeta_q + (\sigma q^2 + \kappa q^4 - 2\Pi') \zeta_q = 2\delta P_q \quad (10) \]

Where \( q \) is the modulus of the wave vector and the new indicated quantities are the Fourier images of the original ones. One can recognize immediately the destabilizing role of the negative components of disjoining pressure on the film waves. They can lead to a negative harmonic force in Eq. (10) which is an indication for divergent solutions. It is...
important to note the stabilizing effect of the surface tension and film’s surface elasticity.

From Eq. (10) it is possible to obtain the spatial spectral density of the thermal non-

homogeneity of the film thickness which is defined via the relation [17]

\[ C_{\zeta \zeta}(q,t) \equiv \langle \zeta_q \zeta^*_q \rangle \equiv \frac{1}{K_{\zeta \zeta}(pR,t)}J_0(qpR)2\rho dp \] (11)

Where \( K_{\zeta \zeta} \) is the spatial autocorrelation of the waves, \( R \) is the film radius and \( J_0 \) is Bessel function of first kind and zero order. The integral presentation in Eq. (11) employs the assumption for spatial uniformity of the film and for this reason the autocorrelation depends only on the distance between the two points of interest. By multiplying Eq. (10) by the complex conjugated Fourier component \( \zeta^*_q \), taking average value of the result and using definition (11), one yields the following equation

\[ (12\eta/q^2h^3)\partial_t C_{\zeta \zeta} + (\sigma q^2 + \kappa q^4 - 2\Pi')C_{\zeta \zeta} = -2\langle \zeta^*_q \delta P_q \rangle \] (12)

To close this equation an appropriate modeling of the last statistical model is required. It can be obtained from the classical theory of thermodynamic fluctuations. According to this theory the mean value of the product of any fluctuation’s quantity and its thermodynamic conjugation (i.e. the partial derivative in respect to this quantity of the minimal work necessary to disturb the system equilibrium) is equal to \( k_B T \), where \( k_B \) is the Boltzmann constant and \( T \) is temperature. In the present case the work of the fluctuation forces is equal to

\[ \delta W = -\int \zeta \delta P dx dy = -\pi R^2 \sum_q \zeta^*_q \delta P_q \] (13)

where the last equality expresses a well-known theorem relating the integral sums of the originals and their Fourier images. One can conclude from Eq. (13) that the thermodynamically conjugated quantity of \( \delta P_q \) is \( -\pi R^2 \zeta^*_q \). Hence, according to the principle cited above, the following relation \( < \zeta^*_q \delta P_q > = -k_B T/\pi R^2 \) holds. Consequently, Eq. (12) acquires the form

\[ (12\eta/q^2h^3)\partial_t C_{\zeta \zeta} + (\sigma q^2 + \kappa q^4 - 2\Pi')C_{\zeta \zeta} = 2k_B T/\pi R^2 \] (14)

To obtain the solution of Eq. (14) it is necessary to know the initial condition. The assumption, that initially, the film has been in a state of infinitely deep liquid where the disjoining pressure vanishes, is plausible from the viewpoint of the film’s history. Hence, one can model the initial spectral density as one corresponding to an infinitely thick film at equilibrium

\[ C_{\zeta \zeta}(q,0) = 2k_B T/\pi R^2(\sigma q^2 + \kappa q^4) \] (15)

Thus, the solution of Eq. (14) with initial condition (15) reads

\[ C_{\zeta \zeta}(q,t) = \frac{2k_B T}{\pi R^2(\sigma q^2 + \kappa q^4)} \frac{2\Pi' \exp\left[\left(q^2h^3/12\eta\right)(2\Pi' - \sigma q^2 - \kappa q^4)t\right] - \sigma q^2 - \kappa q^4}{2\Pi' - \sigma q^2 - \kappa q^4} \] (16)
This fundamental result contains the well-known quantitative criterion for the film’s stability. It is easy to recognize from Eq. (16) that the surface waves become unstable \((C(q,t\to\infty)\to\infty)\) if the inequality \(2\Pi' > \sigma q^2 + \kappa q^4\) is fulfilled. The corresponding equality defines a critical wave number

\[
q_{cr} = \sqrt{\left(\sigma^2 + 8\kappa\Pi' - \sigma\right)/2\kappa}
\]

below in which the waves are not stable and their amplitudes grow exponentially. In the case of negligible elastic modulus \(\kappa\) this criterion reduces to the well-known result \(q_{cr} = \sqrt{2\Pi'}/\sigma\) first derived by Scheludko. The other extreme case of negligible surface tension is appropriate for lamellar membrane structures and the corresponding critical wave number is \(q_{cr} = \sqrt[4]{2\Pi'}/\kappa\). These relations show again that unstable films are those with positive first derivative \(2\Pi' > 0\) of the disjoining pressure.

From Eq. (16) one can derive the value of the wave vector corresponding to the most rapid fluctuation mode, which is an important characteristic of the linear theory [11]. It follows from Eq. (16) the following expression for the decrement of the growth of the waves

\[
\alpha \equiv \lim_{t\to\infty} \ln\left[\frac{C(q,t)}{t}\right] = (2\Pi' - \sigma q^2 - \kappa q^4)q^2h^3/12\eta
\]

As seen, the antagonism between the destabilizing effect of the viscous friction and the stabilizing effect of the interfacial elasticity leads to a maximum in the dependence of the decrement of wave growth on the wave vector. At this point the derivative of \(\alpha\) becomes zero

\[
\frac{\partial}{\partial q} \alpha = (2\Pi' - 2\sigma q^2 - 3\kappa q^4)q^3h^3/6\eta = 0
\]

The solution of this equation is the wave number of the most rapid Fourier mode

\[
q_{mq} = \sqrt{\left(\sigma^2 + 6\kappa\Pi' - \sigma\right)/3\kappa}
\]

It is easy to show that the most rapid wave is unstable since \(q_{mq} < q_{cr}\). For the two cases previously discussed the corresponding values of the wave numbers of the most rapid waves are equal to \(q_{mq} = \sqrt{\Pi'}/\sigma\) and \(q_{mq} = \sqrt[4]{2\Pi'}/\kappa\), respectively.

**STATISTICAL PROPERTIES OF THE FLUCTUATION WAVES**

As was clearly demonstrated in the introduction, one of the most important actors in the dynamics of the TLF fluctuation waves is the disjoining pressure. Many publications have considered the van der Waals component as the main force leading to rupture of symmetric films. The most simple and relatively good expression for this component of the disjoining pressure is given by the following formula \(\Pi_{VW} = -K_{VW}/h^3\), where \(K_{VW}\) is a specific constant for the film matter. The negative value of \(\Pi_{VW}\) corresponds to a tendency for film thinning, which determines the destabilizing effect of this force. The present paper will consider DLVO forces only as a first attempt to complete description of the fluctuation picture in the
film. For this reason, an adequate expression of the electrostatic component of the disjoining pressure is required. For the sake of convenience, the following well-known formula $\Pi_{EL} = 64k_BT N_A C \exp(-h/D)$ is employed, which is valid for relatively large surface potentials [1]. Here $N_A$ is the Avogadro number, $C$ is the concentration of a monovalent electrolyte in the film, and $D$ is the Debye length of the counter ion atmosphere. The latter is given by the expression $D^2 = \varepsilon_0 \varepsilon N_A k_B T/2F^2 C$, where $\varepsilon_0$ and $\varepsilon$ are the dielectric permittivity of vacuum and matter of the film, and $F$ is the Faraday constant. After these assumptions the total disjoining pressure is a sum of the two components described above

$$\Pi = -K_{yw} / h^3 + 64N_A k_B T C \exp(-\sqrt{2C / \varepsilon_0 \varepsilon N_A k_B T F h})$$

As was pointed out, in the frames of the linear theory the basic parameter, accounting for the specific interactions in the film, is the first derivative of the disjoining pressure in respect to the film’s thickness. For the present case it takes the form

$$\Pi' = 3K_{yw} / h^4 - 64C F \sqrt{2N_A k_B T C / \varepsilon_0 \varepsilon} \exp(-\sqrt{2C / \varepsilon_0 \varepsilon N_A k_B T F h})$$

(17)

![Figure 1](image.png)

**Figure 1.** The dependence of $\Pi'$ on the electrolyte concentration and the film’s thickness

In the Figure 1 the isotherm of $\Pi'$ is presented for aqueous films with specific constants $K_{yw} = 6.25$ meV, $\varepsilon_0 \varepsilon = 0.5$ nF/m and $T = 300$ K. Here, the film’s thickness is presented in nanometers and the concentration of electrolytes is in mol/l. It is clear from this figure that the increase of electrolytes leads to the appearance of a positive derivative of the disjoining pressure. The latter corresponds to film instability, which is the explanation for the destabilising role of electrolytes in the colloid coagulation. A more detailed analysis shows that there are two values of the concentration $C$ where the derivative $\Pi'$ is zero. It is well known that the lower one corresponds to a maximum of $\Pi$ while the upper value corresponds to a minimum of the disjoining pressure. The part of $\Pi$, being after the minimum, does not have effect for the stability analysis of the film even if the derivative $\Pi'$ is positive. This fact is due to the appearance of the maximum at lower thickness, which in the frame of a non-linear theory corresponds to a stable state. The real instability will be detected for film thickness smaller than that corresponding of the maximum. For the
present case the transition between stable and unstable film takes place in the range of electrolyte concentrations lower than $C = 10$ mM.

The spatial spectral density of the waves can be obtained from Eq. (16) completed by Eq. (17). The evolution of $C_{\omega}(q,t)$ in time is presented below at different electrolyte concentrations. In the present paper two sets of specific constants are considered: model A for a film with fluid phase surfaces and model B for a film restricted by two membranes. In both cases the bulk fluid is water and for this reason the bulk specific and geometric characteristics of the films are equal: $T = 300$ K; $\varepsilon_0\varepsilon = 0.5$ nF/m; $K_{VW} = 6.25$ meV; $\eta = 1$ mPa s; $h = 30$ nm; $R = 0.1$ mm. The only difference is in the characteristic properties of the film interfaces. A typical value of the surface tension for the model A is $\sigma = 50$ mN/m while the elastic modulus is negligible and for this reason $\kappa$ is accepted to be zero. Figure 2 presents the evolution of the spectral density $C_{\omega}(q,t)$ for the model A (the time is in seconds) as a function of the electrolyte concentration. As seen, the film is unstable for electrolyte concentration of 0.000 mM and its amplitude grows in time. In this case the electrostatic disjoining pressure is zero. At concentration 10 µM the film is stable and the spectral density of the waves corresponds to that of an infinite liquid. Films with concentration 2 µM are unstable but in the considered time interval the effects of van der Waals and electrostatic forces are commensurable. For this reason, the resulting picture is a combination of the other two. From the figures above it is easy to conclude that the wave vector of the most rapid mode $q_{mq}$ is about 250 mm$^{-1}$, which corresponds well to the theoretical prescribed value of $q_{mq} = \sqrt{\Pi'/\sigma} = 272$ mm$^{-1}$. The wave number of the critical wave $q_{cr} = \sqrt{2\Pi'/\sigma} = 385$ mm$^{-1}$ is also underlined in the first two figures.

![Figure 2](image-url)

**Figure 2.** The evolution of the spectral density for model A at $C = 0$, 2 and 10 µM
The thin liquid films between lipid bilayers possess surface tension many times lower than the foam films but their interfacial elasticity modulus is large. A typical value of $\kappa$ is 0.5 pJ, while $\sigma$ can be considered to be zero. In Figure 3 the evolution of the spectral density for model B is presented in different electrolyte concentrations. The dependence of the spectral density on the electrolyte concentration is analogical to that of the model A. From the figures it is easy to determine the wave vectors of the most rapid and critical modes, which correspond well to the expectations $q_{mq} = \sqrt{2\Pi'/3\kappa} = 265$ mm$^{-1}$ and $q_{cr} = \sqrt{2\Pi'/\kappa} = 345$ mm$^{-1}$, respectively.

Figure 3. The evolution of the spectral density for model B at $C = 0, 1$ and 10 µM

Knowing the spectral density one is able to calculate several important statistical characteristics of the fluctuation waves. For the stability analysis the most important are the root mean square amplitude of the waves $A$ and the number of uncorrelated subdomains $N$. They are defined via the relations [17]

$$A^2(t) \equiv <\zeta^2> = \sum_{i=1}^{\infty} C_{iq}^2(q = \lambda_i / R, t) / J_1^2(\lambda_i)$$

$$N(t) = A^4 / \sum_{i=1}^{\infty} C_{iq}^2(q = \lambda_i / R, t) / J_1^2(\lambda_i)$$

where $\{\lambda_i\}$ is the set of all zeros of the Bessel function of zero order, i.e. $J_0(\lambda_i) = 0$, and $J_1(\cdot)$ is Bessel function of first class and first order. Since the analytical expressions for the sums above are not possible, they have to be calculated numerically. In the present paper only the first one hundred zeros $\{\lambda_i\}$ of the Bessel function are used in the calculations. A restriction on the number of zeros is allowed since the unstable modes are those with wave
numbers smaller than $q_{cr}$. In all the cases here $\lambda_{100} \approx 313$ is at least two times larger than the critical value $q_{cr} R$. In Figure 4 the calculated mean square amplitude $A$ and number of uncorrelated domains $N$ for model A are presented as a function of the electrolyte concentration. The first figure demonstrates the exponential growth of the amplitude of the surface waves in time after the stable-unstable film phase transition with decreasing electrolyte concentration. More interesting is the second figure, which demonstrates breakdown of the film to many uncorrelated subdomains at the transition state. As was demonstrated in previous investigations [54, 55], the evolution of $N$ in time passes through a maximum, which is due to a rearrangement of the wave spectrum.

![Figure 4](image1.png)

**Figure 4.** The evolution of the amplitude $A(t,C)$ in nm and number of domains $N(t,C)$ for model A

![Figure 5](image2.png)

**Figure 5.** The evolution of the amplitude $A(t,C)$ in nm and number of domains $N(t,C)$ for model B

Analogical calculations for the model B are presented in Figure 5. The amplitude of the waves and the number of uncorrelated subdomains exhibits nearly analogical behavior like those of model A. The basic difference is the relatively lower number of uncorrelated subdomains in model B. It is not surprising, however, since the wave vector dependence of the elastic term is on forth power, while the surface tension multiplies only by the second power of $q$. This leads to a sharper dependence of the spectral density on the wave vector at the model B, hence to a decrease of the number of the existing unstable modes. The latter reflects in a decreased number of uncorrelated subdomains $N$. It is important to note the relative retardation of the spectrum rearrangement at model B as compared to the model A.

In order to discriminate the influence of different factors on the stability of TLFs, the dependences of $A$ and $N$ on the surface tension $\sigma$ (standard value 50 mN/m for model A), elasticity $\kappa$ (standard value 0.5 pJ for model B), film thickness $h$ (standard value 30 nm),
viscosity $\eta$ (standard value 1 mPa s) and film radius $R$ (standard value 0.1 mm) will be considered for both models. The electrolyte concentration is fixed equal to $C = 1$ mM. Let us start with the dependence on the surface tension. As expected the amplitude of the thickness of waves increases strongly with decreasing surface tension. The latter is an important factor for stabilization of films and its decrease is reflected by the appearance of unstable waves and increase of the number of uncorrelated subdomains:

Let us see now the effect of elasticity on the film’s stability. Calculations show that moderate changes in $\kappa$ do not affect the behavior of films for model A. This could be easily explained by the fact that the unstable modes correspond to lower values of the wave vector and for this reason the effect of the surface tension is emphasized. On Figure 7 the effect of $\kappa$ in pJ is studied on model B.

The first plot demonstrates the expected effect of suppression of the waves by increasing elasticity, analogical to the effect of $\sigma$. More interesting is the second plot, where the number of uncorrelated subdomains increases at smaller $\kappa$. The effect is, however, weaker than that of the surface tension in model A, which can be attributed to the forth root in $q_{cr}(\kappa) = \sqrt[4]{\Pi'/\kappa}$ as compared to the second root in $q_{cr}(\sigma) = \sqrt{2\Pi'/\sigma}$ for model A.

Another important parameter for the dynamics of the film’s fluctuations is the mean film thickness, which is responsible for three effects. First, with decrease of $h$ the derivative $\Pi'_{FW}$ increases, thus leading to film destabilization. Second, with decrease of $h$ the derivative $\Pi'_{EL}$ decreases, which is a stabilizing effect. And third, the decrease of $h$ strongly
increases the friction coefficient of the fluctuations, which slows down their evolution. Because of the interplay of these effects complicated dependences of $A$ and $N$ on $h$ are to be expected. Moreover, the decrement $\alpha$ could demonstrate affinity to some values of $h$.

**Figure 8.** The evolution of the amplitude $A(t,h)$ in nm and number of domains $A(t,h)$ for models A and B

The plots of the root mean square amplitude clearly show the accelerated evolution of the unstable modes at thinner films. Moreover, the number of uncorrelated subdomains also grows as a consequence of the increase in value of the critical wave vector. Note that again the evolution of $N$ demonstrates a larger latent period for model B, after which it grows tremendously. According to Eq. (16) the role of the film viscosity is to slow down the evolution of the waves. Since the values of the critical and most rapid wave vectors do not depend on the viscosity, the latter should not affect strongly the number of uncorrelated subdomains, which is evident from the calculations presented in Figure 9.

The most interesting behavior is demonstrated by $A$ and $N$ as functions of the film radius. Since both quantities are sums of Fourier components, the role of $R$ consists in modulation of the spectra of the steady state waves present on the film surface. Obviously, due to the discrete spectra it is expected to see some resonances reflecting coincidence of a steady state wave with the theoretical most rapid wave with $q_{mq}$. As is seen the amplitude of the waves decreases with increase of the film radius but the dependence is not a monotonous one. Such a periodic behavior corresponds well to our expectations for a resonant dependence on $R$. The other two plots, presenting the evolution of $N$, also demonstrate a resonant effect. Additionally, an increase on the number of uncorrelated domains is observed, which is in accordance with the idea for a finite correlation length of the waves. The latter insists a linear growth of $N$ on the area of the film, which is easily
recognized on the figures above. A quantitative measure of the periodicity on \( R \) could be made as follows. It is known that the zeros of the Bessel functions are almost regularly distributed and the mean distance between them is about 3. On the other hand, the most important wave vector for the evolution of the surface waves is the most rapid \( q_{mq} \). Hence, one could propose the following estimate for the period on minima and maxima shown in Figure 10, \( \delta R = 3/q_{mq} \approx 0.01 \text{ mm} \). In the calculation of the latter, the previous estimates

**Figure 9.** The evolution of the amplitude \( A(t,\eta) \) in nm and number of domains \( N(t,\eta) \) for models A and B

**Figure 10.** The evolution of the amplitude \( A(t,R) \) in nm and number of domains \( N(t,R) \) for models A and B
of $q_{max}$ are employed, which seem to be similar for both models A and B. Comparing this result with the calculations above confirms our conclusion that the periodicity of $A$ and $N$ on $R$ is a result of the discrete nature of the steady state wave spectrum. Of course, the imposed by us boundary conditions on the film rim are quite idealized. For this reason, the effect described above could be strongly depressed in real TLFs.

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REFERENCES

1. A. Scheludko, Colloid Chemistry, Mir, Moscow, 1984
5. H.J. Schulze, Physicochemical Elementary Processes in Flotation, Elsevier, Amsterdam, 1984
11. B. Radoev, A. Scheludko and E. Manev, J. Colloid Interface Sci. 95 (1983) 254
24. A. Sharma and E. Ruckenstein, J. Colloid Interface Sci. 113 (1986) 456

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INVERSION OF THE MAGNETIC FIELD EFFECT ON THE RADICAL METHYL METHACRYLATE HOMOPOLYMERIZATION IN BULK AT A TRANSITION FROM A CONSTANT TO PULSATILE MAGNETIC FIELD

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Abstract. Original results on the pulsatile external magnetic field effects on both the bulk methyl methacrylate radical polymerization kinetics and the tacticity of the obtained polymers are presented. It is established an inversion of the magnetokinetic effects at a transition from a constant to pulsatile magnetic field. The opposite change of the polymerization rate under a pulsatile (the rate decreases) and under a constant (the rate increases) magnetic fields is explained by the broadening of the energy levels of the singlet and triplet radical pair states, produced by the degradation of the initiator molecules. As a result of this broadening there is an increase the exchange interaction not only between the radical pair components, but between the radical pairs with different relaxation times for the transition from one to another energy state. The result from this exchange interaction is not only mentioned above inversion, but an occurrence of the polymerization rate minimum as a function of the magnetic field induction. For the first time it is shown also, that the pulsatile magnetic field reduces the probability for a mesoaddition at the expense of the racemic addition in this bulk homopolymerization.

Key words: Radical pair, singlet state, triplet state, exchange interaction, polymers tacticity, configurational diade, configurational triade

INTRODUCTION

Two radicals, at a distance less than necessary for the situation of molecules of other components of the medium between them, form a radical pair (RP) [1, 2]. It is proved
that value of the magnetokinetic effects on number of chemical reactions, including the polymerization, depends on the RP’s fortune [1, 5]. The recombination of both radicals, forming RP, produces a cage product (CP). This appellation is a consequence of the fact that the region which the RP components occupy is assumed to be referred to as cage. The recombination is possible if only the RP is in a singlet (S) state. When the RP is in a triplet (T) state it can convert back in S or the both radicals to move apart (to leave the cage) and to interact with the medium’s components (the products are named escape products, EP), or with the radical’s traps (these products are named scavenger products, SP). By this way the produced from RP products (CP, EP, SP) are obtained selectively: CP – from the RPs in S state, and EP or SP from the RPs in T state. The singlet and triplet energy level populations change dynamically and this process is called spin evolution. The latter depends on many factors, but under an external magnetic field the direction and the intensity of the spin evolution can be more monitored. In a magnetic field the three triplete energy levels (T_0, T_+, T_) differentiate and their general population (n_{T_0} + n_{T_+} + n_{T_-}) increases at the expense of the singlet state (n_S) population. From this fact it follows that the CP yield decreases, while those of EP and SP increase. Just by these yield changes of the RP products under a magnetic field, the magnetostimulation of all of the investigated up to now homo- and copolymerizations were explained [6–29]. The main subject of this investigation is the comparison between the spin evolutions of RPs, produced during the homolytic degradation of the initiator molecule without and under a magnetic field. The decrease of the CP yield under a magnetic field is a result of the reduction of the probability for a cage recombination of the primary radicals – the RP’s components. The result of the augmentation of the EP and SP yields in this case is the increase of the probability for the interaction of the primary radicals with monomer, namely, the higher initiation efficiency (f). By this way, the change of the spin evolution of the RPs, produced as a result of the initiator degradation before and after the constant magnetic field application results in the f increase under a magnetic field, and hence – the higher initiation and polymerization rates.

It is noteworthy that all polymerization accelerations [6–29] are established under a constant magnetic field, and they are explained by mentioned above spin evolution change of the RPs discussed. However the magnetokinetic effect of the pulsatile magnetic field on the radical polymerization is of considerable scientific and applied interest. The latter is a result of not only the fact that a similar effect is not studied up to now. Other stimulation for such interest is the RP formation during the each act of the propagation reaction as a result of the double bond cleavage. In contrast to the mentioned above RP (produced during the homolytic degradation of the initiator molecule) this new type of RPs are subjected always to the effect of the variable magnetic field, produced by the rotation of the unpaired electron of the propagation radical, together with the substituents around the last and before last chemical bonds of the propagation chain. The effect of this variable magnetic effect can be both kinetic and configurational - the space order of the monomer units. In the present work the results of the first experiments in this direction are presented. Magnetokinetic effect of the magnetic field with the pulsatile component on the radical homopolymerization of methyl methacrylate (MM) in bulk, as well as the influence of the same field on the tacticity of the obtained poly(methyl methacrylate) (pMM) are determined.
EXPERIMENTAL

The MM (Fluka) and the solvents (acetone, methanol and doixane) are purified by common methods for drying and distillation before use. Azoisobutiridinitrole (AIBN) (Fluka, 0.2 wt.%) is used as an initiator. Before the application it is precrystallized from ethanol solution.

The apparatus for a constant with necessary magnetic induction (B) and pulsatile (with nonsinusoidal unipolar impulses and frequency 150 Hz) magnetic fields is described in our earlier work [30]. As a quantitative measure for the impulsive component amplitude is accepted an pulsatile coefficient (P) [31], defined as a ratio between the effective value ($I_{ef}$) of the current generated from the pulsatile component and this of the direct current ($I_{const}$), ensuring a magnetic field with induction B, i.e. $P(\%) = \frac{I_{ef}}{I_{const}} \times 10^2$.

The MM homopolymerization in bulk is accomplished in glass ampoules, nitrogen atmosphere, initiator 0.2 wt.% and temperature 60°C. The polymerization rate is determined gravimetrically. To this aim the obtained pMM samples are dried under vacuum at temperature 45°C to a constant weight. Then they are weighted to determine the achieved conversion. After that these samples are used for the viscosity determination of their 1% (wt.) dioxane solutions in Ubellode viscometer, as well as for determination of the pMM tacticity by $^1$H-NMR spectroscopy. The spectra are registered at 400 MHz (Bruker WP 80) at 25°C in CD$_3$Cl and TMS as inner standard. The molar parts of the configurational triads are calculated using the peaks, related to the α-CH$_3$ groups in the macromolecules at 0.90 ppm (for the syndiotriads), 1.05 ppm (for the atactic triads) and 1.25 ppm (for the isotactic triads) [32–34].

The magnetic effects are estimated by the comparison of the initial homopolymerization rates and the pMM examples tacticities registered without and under magnetic field with different B and P values. The homopolymerizations under magnetic field are accomplished in glass ampoules with monomer and initiator, situated in a carrier, inserted in the oil-bath with a temperature control (±0.2°C) in the interior of the inductor, producing magnetic field with suitable B and P values.

RESULTS AND DISCUSSIONS

OPPOSITE MAGNETOKINETIC EFFECTS OF THE CONSTANT AND PULSATILE MAGNETIC FIELDS ON THE RADICAL MM POLYMERIZATION RATE

On Fig. 1 the MM homopolymerization kinetics curves in bulk without (curve 1) and under a constant ($B = 0.15$ T – curve 7) and pulsatile ($P = 133 \%$, $B = 0.05$ T – curve 2; $B = 0.10$ T – curve 3; $B = 0.15$ T – curve 4; $B = 0.20$ T – curve 5 and $B = 0.25$ T – curve 6) magnetic fields are compared. The most-intriguing consequence of this comparison is the inversion of the kinetic effects of the permanent (curve 7) and pulsatile (curves 2–6) magnetic fields in relation to the homopolymerization rate without magnetic field (curve 1). Under
Figure 1. MM homopolymerization kinetics without (curve 1) and under a constant ($B = 0.15$ T, curve 7) and pulsatile with $P = 133\%$ and $B = 0.05$ T (curve 2); $B = 0.10$ T (curve 3); $B = 0.15$ T (curve 4); $B = 0.20$ T (curve 5) and $B = 0.25$ T (curve 6) magnetic fields. Temperature: 60°C. Initiator: AIBN (0.2% wt.).

Figure 2. Dependence of the initial MM homopolimerization rates in bulk ($V_o$) on the induction (B) of the pulsatile magnetic field applied with $P = 133\%$ (black points). $V_o$ under a constant magnetic field and $B = 0.15$ T is presented as a white point A. The opposite arrows show the opposite directions of the $V_o$ change under a constant (point A) and pulsatile (point B) magnetic fields in relation to the polymerization rate without magnetic field (line CD). Temperature: 60°C. Initiator: AIBN (0.2% wt.)
a constant magnetic field with $B = 0.15$ T (curve 7) the homopolymerization rate is higher than that without applied field (curve 1). The essence of the inversion is expressed by the opposite signs of the differences between the polymerization rates without (curve 1) and under a constant (curve 7, negative sign) or pulsatile with $P = 133\%$ (positive sign, curves 2–6 for $0.5 \, \text{T} \leq B \leq 0.25 \, \text{T}$). More-clearly the inversion is outlined by the change of the initial homopolymerization rates ($V'_0$) at the transition from constant to pulsatile magnetic fields, presented on Fig. 2. The opposite directions of the arrows on this figure show the directions of the rate alteration under a constant (up direction) and pulsatile (down direction) in relation to the rate without magnetic field influence on the homopolymerization. In Table 1 these alterations are presented as ratios of initial rates under magnetic field ($V_{o,B}$) to that without such field ($V'_0$). For a constant magnetic field $V_{o,B}/V'_0 = 1.52$, while for the pulsatile one with $P = 133\%$, this ratio is less than unity for all of the $B$ values.

**Table 1.** The ratio of the initial polymerization rates under a magnetic field with different inductions ($V_{o,B}$) and that without such field ($V'_0$). ($T = 60^\circ\text{C}$; Initiator: AIBN; 0.2\% wt.).

<table>
<thead>
<tr>
<th>$B$, T</th>
<th>$P$, %</th>
<th>$V_{o,B}/V'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0</td>
<td>1.51</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.05</td>
<td>133</td>
<td>0.86</td>
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<tr>
<td>0.10</td>
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</tr>
<tr>
<td>0.15</td>
<td>133</td>
<td>0.54</td>
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<tr>
<td>0.20</td>
<td>133</td>
<td>0.71</td>
</tr>
<tr>
<td>0.26</td>
<td>133</td>
<td>0.81</td>
</tr>
</tbody>
</table>

The discussed inversion is established for the first time. Therefore, the reasons for this phenomenon are of great interest. The challenge becomes even more considerable if the lack of any other information for a negative magnetoochemical effect on MM homopolymerization [6–23] is accounted, together with an extreme run of the initial polymerization rate as a function of $B$ (the curve with minimum on Fig. 2). The explanation of the inversion reasons is in principle, the clarification of the precondition for the decrease of the probability for the transition from singlet (S) to triplet (T) states ($^3\text{P}_T$) of the RP (produced during the initiator molecule destruction) at the transformation of the constant to pulsatile magnetic field. It is noteworthy that the RP concentration in S state should not only increase in comparison to that under a constant magnetic field, but to become more than that, produced without magnetic field. Only at this precondition the initiation efficiency under a magnetic field will be less than that without such field, the result which is in correspondence with the MM homopolymerization rate values at these conditions.

The broadening of the S and T energy levels as a result of the pulsatile component of the magnetic field can be related to the effect of the pulsatile frequency and intensity on the superfine spin-core interaction [2]. This broadening accounts to the Zeeman energy
level cleavage as a function of \( B \) and is presented on Fig. 3. It is seen the larger broadening
the longer of the \( B \) interval in which the S and T- energy levels are overlapped. Just in this
interval of \( B \) the probability for exchange interaction between S and T_ RPs is the most
considerable. From the analysis of this effect, using the analytical (or numerical) decision
of the stohastic Liouville’s equation for the electron-nuclear matrix spin density [35, 36]
(the most powerful mathematical approach for the description of the RP spin evolution) it
is follows: i. The transition from S to the T RPs retards significantly [37, 38]. This means,
that the produced at the AIBN molecule degradation primary radicals ((CH\(_3\))\(_2\)C \( \cdot \) CRCN)
recombine under a pulsatile magnetic field more considerably than under constant one.
The consequences of this are less initiation efficiency and rate, which are in correspondence
with the established experimentally reduction of the MM homopolymerization rate
velocity (Fig. 2, Tabl. 1); ii. RPs subdivision (clustering) according to their relaxation time
values for reversible S–T transitions and their ability for direct outlet from the “cage”. This
is a preposition for an exchange interaction between the RPs with equal or different spin
multiplicity, but with different relaxation times [39–45]. Significant part of the models,
developed on the mentioned above Liouvile’s stohastic equation for the RPs spin evolution,
are adequate and significant [46–53] due to their ability to account the mentioned
above RP heterogenety and the possibilities for an exchange interaction between RPs with
different relaxation times and abilities for outlets from the “cage”. By this way it can be
deduced the unexpected conclusion that the raised by the magnetic field broadening of
the energy levels of the different RP spin states is a dominant factor for the exchange in-
teraction between RPs with different relaxation times and probabilities for the outlet from
the “cage”. It is noteworthy also that the exchange interaction in this case between RPs
with an unspecified type is possible: between covalently bounded and nonbounded RPs, as well as between RPs with equal and different in nature components also. Specification of the RPs under a magnetic field is based on another criterion – relaxation times of the transition from one to another RP spin states, which are determined by the energy level broadening of these states.

The relationship between the pulsatile component of the external magnetic field and RP exchange interaction, substantiated qualitatively above, is imminent to be proved quantitatively also. An interest in this direction represents the dependencies between the exchange interaction characteristics and those of the pulsatile magnetic field, such as frequency, amplitude and signal form. However, even on the basis of this qualitative level of argumentation the discussed relationship allows to explain the extreme \( V_o - B \) dependence with minimum, shown on Fig. 2. Indeed, according to the general classification of the magnetokinetic effects of the external magnetic field as a function of its induction \((B)\) [54, 55], a similar dependence with a minimum is a result of the dominating exchange interaction between RPs. In addition to this qualitative explanation of \( V_o - B \) dependence (Fig. 2), the discussed relationship allows to prove the established inversion of the constant and pulsatile magnetic fields on \( V_o \) (the opposite arrows on Fig. 2). Under a constant magnetic field the magnetokinetic effect is realized by the general, described in the introduction, mechanism for RP transition from S to T states [6–29], as a result of which there is an increase of the radical’s out"er from the “cage” and increasing both the initiation efficiency and the polymerization rate too. Under a pulsatile magnetic field the magnetokinetic effect changes drastically. The caused by the pulsatile magnetic field energy level broadening of the RP spin states is the reason for an effective interaction between RPs with different relaxation times for the transition from one to another spin states. This exchange interaction characterizes just with the shown on Fig. 2 extreme curve with minimum for \( V_o - B \) dependence. In general, the reason for the inversion established (the opposite arrows on Fig. 2) is the switching over from one to other mechanism of the magnetokinetic effects at the transition from the constant to pulsatile magnetic fields. Under a constant magnetic field the mechanism of the magnetic influence is the superfine interaction between the electron and nuclear spins (hfc mechanism), while under a pulsatile magnetic field the magnetic influence mechanism is the exchange interaction between RPs with different relaxation times between the RP spin states.

Dependence of the specific viscosity of the pMM dioxane solutions (1%, wt.) as a function of the magnetic induction is presented on Fig. 4. As could be expected it is anti-symmetric to that, presented on Fig. 2 because of the inversely proportional relationship between \( V_{pol} \) and \( P = (k_p C_M)^2/k_{1pol} \) where \( P \) is a degree of polymerization; \( k_p \) and \( k_1 \) are propagation and termination rate constants, respectively; \( C_M \) is monomer (MM) concentration; \( V_{pol} \) is the homopolymerization rate). It is seen that the position of the maximum of this curve (Fig. 4) is the same (0.15T) as of the minimum position of the “\( V_o - B \)” curve (Fig. 2). By this way, these two mutual complementary dependencies prove the discussed inversion of the magnetokinetic effects of the constant and pulsatile magnetic fields on the MM homopolymerization. In addition, they are a general substantiation of the conception
that this inversion is a result of the change of the mechanism of the RP (produced by the thermal initiator degradation) spin evolution from the superfine interaction under a constant magnetic field to the exchange interaction between RPs with different relaxation times through the Förster mechanism.

If the pulsatile component of the magnetic field and the caused by it broadening of the energy levels of the RP spin states are really so effective for the change of the RP spin evolution mechanism, then a more general question about the influence of this broadening on the radical polymerization as a whole is appeared. More precisely, it is necessary to check the possibility for the control of the propagation reaction of the radical polymerization under a pulsatile magnetic field as: i. In each step of this reaction the covalent bounded RP is formed as a result of the π-electron double bond degradation of the joining monomer molecule; ii. The energy levels of these RP spin states can be strongly broadened by both the external pulsatile magnetic field and the local one, originated by the rotation of the unpaired electron around the last and next to the last bonds of the propagation chain – the propagation radical virtually (Fig. 5).

The complex dynamic behaviour of the propagation radical unpaired electron generates a local pulsatile magnetic field, which independently or in a combination with an external pulsatile magnetic field applied should influence spin evolution of RPs, formed during the interaction of the propagation radical with the monomer molecule at each propagation step. This influence is in fact the possible magneto-kinetic effect on the propagation rate constant. According to the available literature, a similar magnetokinetic effect on the

**Figure 4.** Dependence between the specific viscosity ($\eta_{sp}$) on magnetic induction ($B$) at $T = 20^\circ C$ of the 1.0% (wt.) dioxane solutions of pMM, produced by MM homopolymerization in bulk for 40 min under pulsatile magnetic field with pulsatile coefficient $P = 133\%$. Initiator: AIBN (0.2% wt.); Temperature: 60°C.
radical polymerization processes was not studied up to now. All investigated until now magnetokinetic effects on the radical polymerization are related to the polymerization initiation [6-29]. In the next part of this communication, the first results of the verification of the possible magnetokinetic effect on the propagation reaction of the MM radical polymerization are presented.

PULSATILE MAGNETIC FIELD EFFECT ON THE TACTICITY OF PMM, PRODUCED BY MM HOMOPOLYMERIZATION IN BULK

More clear and full representations of the rotation of the last carbon atom of the propagation chain around the next before the last C–C σ-bond (with angle frequency $\omega_{t-1}$) and its substituents (H and Y), together with a semi-occupied π-orbital with the unpaired electron around the last σ-bond (with angle frequency $\omega_t$) are presented on Fig. 6.

Figure 5. Rotation of the propagation radical unpaired electron at the radical polymerization of the α-olefinic monomer (CH$_2$=CHY) around the last (with an angle frequency $\omega_t$) and next before the last (with an angle frequency $\omega_{t-1}$) propagation chain σ-bonds. By the doted point line the orbit (circumference) of the unpaired electron around the bond before the last is denoted. By interrupted lines the possible overlapping (exchange interaction) between π-orbitals of forming from the joining monomer RP and unpaired electron of the propagation radical is presented also.

Figure 6. The rotation of the last carbon atom around the next before last bond (with an angle frequency $\omega_{t-1}$) and its substituents (H and Y) around the last bond (with an angle frequency $\omega_t$) at the moment of the connection of the propagation radical with the monomer molecule, forming RP during this act. The new forming bond and breaking one as a result of the π-electron overlapping, are presented through the interrupted lines.
The rotation of the unpaired electron (propagation radical), situated on the last carbon atom, produces a magnetic moment, different from electron orbital and spin magnetic moments. There is not any information in the literature about the influence of this magnetic moment on the propagation rate constant. The same for the effect of the external magnetic field on the electron rotation and produced magnetic moment. The clearance of these problems could be achieved by means of the molecular dynamics or the stochastic Liouvil’s equation decision [35, 36]. The absence of the theoretical basis and developed analytical approaches in this direction, and the complex combination of the effects of the magnetic moment components are maybe a part of the reasons for a set at a defiance of the effect of the external magnetic field on the propagation reaction. It can be expected, that these difficulties will be overcome in near future, and the external magnetic field influence on this reaction will be clearly outlined.

The rotation around the last C–C σ-bond with an angular frequency $\omega_t$ (rotation along the upper circle on Fig. 6) of the substituents H and Y of the last carbon atom of the propagation chain is of crucial importance for the tacticity of the polymer obtained. If the monomer incorporation to the propagation radical takes place at such rotation around the last C–C σ-bond that the substituents H and Y are situated by the manner shown on Fig. 6, then the configuration of these substituents around the new-forming pseudoasymmetric carbon atom is “YHC” – the substituents at the tetrahedron basis, hatched on the Fig. 7a. If the monomer joining is accomplished at a rotation angle at which the substituents Y and H (Fig. 6) change their positions, then the upper configuration around the pseudoasymmetric carbon atom will be “HYC” (Fig. 7b).

Both configurations are mirror-image one to another and forms a full set. That’s way, if the new forming configuration coincides with that of the previous pseudoasymmetric carbon atom, then the monomer incorporation is mesoincorporation (m). If these configurations are different (opposite in this case) then the incorporation is racemic (r). The conclusion is that m and r diad formation, i.e. the polymer tacticity, is determined by the substituent H and Y rotation angle around the last C–C σ-bond. Therefore, the problem for the possible magnetic field influence on the polymer tacticity reduces to the field influence on this
rotation angle. If the field (permanent or pulsatile) influences this rotation angle and there are preferred rotation angles, then the field could be an effective factor for the control of the obtained polymer tacticity. If the rotation angle is independent on the magnetic field characteristics, then the field is not such ruling factor. There is not information in the literature both for a theoretical analysis and for any experimental results in this direction. That’s way, the experimental verification of the possibility for an effective influence of the pulsatile magnetic field on pMM tacticity is estimated as reasonable.

The different configurational triad values (iso – $m_i$, sindio – $m_s$, and atactic – $m_a$) estimated from $^1$H-NMR spectra of pMM samples (Fig. 8), synthesized in absence and under magnetic field with $P = 133\%$ and different B are included in Table 2. It is seen that under a magnetic field at all of the B values the $m_s$ mole fraction is higher than that for the sample, obtained without a magnetic field. The increase is from 1 to 3\%, depending

![Figure 8](image)

**Figure 8.** $^1$H-NMR spectra in CDCl$_3$ of the poly(methyl methacrylate) ($\alpha$-CH$_3$ ragion), produced by radical polymerization (AIBN, 0.2\% wt) in bulk at 60°С under a pulsatile magnetic field ($B = 0.15$ Т, $P = 133\%$). I – isotactic-, A – atactic- and S – syndio-triads
on the the $B$ value. It is at the cost of the atactic ($m_a$) and above all of the isotactic ($m_i$) triads. Though the deviations of the $m_s$ values from that of the comparative sample, produced without the magnetic field influence, are systematic, they are too small to make the definitely conclusion about the effective influence of the magnetic effect on the tacticity of pMM. Nevertheless, these data could be considered as the first positive confirmation of such possibility. Rather these data should be regarded as stimulation for a further investigation under magnetic fields with broader set of $B$- and $P$-values and a frequency (not only the amplitude) of the pulsatile component. Part of the results included in Table 2 support this statement. The triad mole fractions at $B = 0.15$ T are different from those at other B values. It is noteworthy this peculiarity is at the same B where it is registered the minimal value of the homopolymerization rate (Fig. 2) and maximum viscosity of the pMM solutions in dioxane (Fig. 4). Local extremes (maximum for the $m_i$, and $m_a$ and minimum for $m_s$) characterize the pMM tacticity, generated at this B. Unlikely these peculiarities at $B = 0.15$ T is accidentally. At the moment it is impossible to substantiate rigorously the logic relationship between the peculiarities shown on the Figs. 2, 4 and Table 2. However, the coincidence is important as the first two peculiarities (the extremes on Figs. 2 and 4) prove the magnetic field influence on the MM homopolymerization, from which it is followed that their coincidence with the mentioned in the Table 2 peculiarities at $B = 0.15$ T indicates the pulsatile magnetic field influence on the polymer tacticity too.

The mole fractions of the both dyads (meso – m and racemic – r), calculated from the experimental $m_i$ ($m^2 = m_i$) and $m_s$ ($r^2 = m_s$) values, are presented in the Table 3. As could be expected, the mesodyad values ($m$) of all the polymer samples, produced under a magnetic field obtained are less than those produced without a magnetic field. The opposite statement is valid for the racemic diad ($r$) mole fractions. The common conclusion which could be deduced is that under a pulsatile magnetic field the racemic incorporation dominates. The local extremes for the sample, produced at $B = 0.15$ T, are on hand again. It is interesting that the sum of the mole fractions of both diads (the last column of the Table 3) for the sample, produced without magnetic field, is higher than 100%, while for the

<table>
<thead>
<tr>
<th>Magnetic field induction, B(T)</th>
<th>Configurational triades mole fractions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m_i$</td>
</tr>
<tr>
<td>0(without a magnetic field)</td>
<td>5.69</td>
</tr>
<tr>
<td>0.05</td>
<td>4.03</td>
</tr>
<tr>
<td>0.10</td>
<td>3.81</td>
</tr>
<tr>
<td>0.15</td>
<td>5.19</td>
</tr>
<tr>
<td>0.20</td>
<td>4.34</td>
</tr>
</tbody>
</table>

Table 2. Configurational triad mole fractions (iso-$m_i$, syndio-$m_s$ and atactic-$m_a$) of pMM, produced by radical polymerization in bulk without and under a magnetic field with $P = 133\%$, as a function of the magnetic field induction ($B$). Mole fraction values are determined from $^1$H-NMR spectra. Temperature: 60°C; [AIBN]: 0.2% (wt).
samples under a magnetic field (with the exception of the sample, produced at $B = 0.15$ T again) this sum is less than 100%. If the deviation from 100% is accepted as an indicator for a deviation from the Bernoullian scheme for the configurational dyad formation, it is clear that the magnetic field influence on this deviation is different from that, which takes place without such field. This is the next peculiarity, supporting the magnetic field influence on the polymer tacticity.

The differences between the experimentally determined atactic triad values ($(m_a)_{exp}$, Table 2) and calculated through the diad mole fractions ($(m_a)_{calc}$, Tabl. 3) support this conclusion: $(m_a)_{exp} - (m_a)_{calc} = 2.63\%; -2.62\%; -3.24\%; 1.44\%$ and $-1.21\%$ for polymers produced at $B = 0$ T; 0.05 T; 0.10 T; 0.15 T and 0.20 T, respectively. That’s way, in spite of the justice of the affirmation that an unambiguous conclusion about the magnetic field influence on the polymer tacticity is early to be made, the results discussed provoke the verification of this hypothesis.

**CONCLUSION**

It is established, that a constant and pulsatile magnetic fields have opposite magnetokinetic effects on the MM radical homopolymerization in bulk (Figures 1, 2 and Table 3). Under a constant magnetic field the polymerization rate increases, which is in agreement with all of the performed up to now investigations on the radical polymerization kinetics under a constant magnetic field [6–29]. The effect of the pulsatile magnetic field (with frequency 150 Hz and pulsatile coefficient 133%) is opposite, and the polymerization rate is less than that without a magnetic field. This inversion at a transition from constant to pulsatile magnetic fields is of interest not only that it is established for the first time, but because of the dependence of the polymerization rate on the pulsatile magnetic runs through the minimum at $B = 0.15$ T (Figure 2). The viscosity of the polymer solutions in dioxane as a function of the magnetic induction is a curve with maximum at the same $B$ (0.15 T).
It is proposed an original explanation of these two mutual complementary dependencies, as well as of the mentioned above magnetoikinetic effect inversion. It is based on the broadening of the energy levels of the singlet and triplet states of the radical pairs, produced by the initiator molecule degradation under a pulsatile magnetic field. This broadening is the initial cause for the exchange interaction between both the components of a given radical pair and the radical pairs with different relaxation times for the transition from singlet to triplet states. Just this exchange interaction is a reason for the extremums observed (Figures 2 and 4) [54, 55].

The possibility for an external pulsatile magnetic field influence on the poly(methyl methacrylate) tacticity is verified for the first time. The stimulation for this part of the work is the fact that in each propagation step the intermediate radical pair is formed, which energy levels can be broadened under both an external pulsatile magnetic field and pulsatile magnetic field originated by the rotation of the unpaired electron of the propagation radical. It is established, that this effect is expressed by the increase of the probability for a racemic incorporation at the cost of the mesoincorporation (Tables 2 and 3). The results obtained are not so considerable to make a definitive conclusion about this effect (probably because of the limitations of the magnetic induction, frequency and pulsatile coefficient used), and generate the challenge to check this possibility rigorously.

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REFERENCES


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ANTIFEEDANT ACTIVITY OF STEM EXTRACTS FROM SPECIES OF *Genus Scutellaria* L. AGAINST COLORADO POTATO BEETLE LARVAE

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*Abstract*: Extracts from eight species of genus *Scutellaria* (*Labiatae*) were screened for their action as feeding suppressors and deterrents against *Leptinotarsa decemlineata* (Say). Treatment of potato leaf disks with small amounts of extracts (concentration 10 000, 1 000 and 100 ppm, which is dose of 333,33 µg/cm², 33,33 µg/cm² and 3,33 µg/cm², respectively), resulted from good to very good antifeedant activity. The extract from *Scutellaria albida* showed the strongest feeding inhibition than the rest and exhibit significant effect at concentration 100 ppm. Activity was established by calculating, at different time intervals, the feeding ratio (FR) between the consumed areas of treated disks (CTD) and control disks (CCD). For comparison goals was established FR50, the ratio determined when 50% of the CD in every dishes has been consumed (CCD50). These results support the previously investigation on antifeedant properties of other plants which contain neo-clerodane diterpenoids and confirm that plant extracts may have role as control agents of Colorado potato beetle population.

*Key words*: *Scutellaria*; *Labiatae*; neo-clerodane diterpenes; *Leptinotarsa decemlineata* (Say), antifeedants.

*INTRODUCTION*

To retrench the damage in agriculture caused by Colorado potato beetle (*Leptinotarsa decemlineata* Say) are in use major chemical control of its population. This insect quickly develop resistance to many synthetic insecticides [1,2], which stimulate the search for knew
insect pest control agents which are biodegradable and demonstrate low impact on the environment. Some natural products, mainly alkaloids and diterpenoids, show relevant activity as antifeedants that could be successfully used like source of new control agents [3-5].

The neo-clerodane diterpenoids have attracted interest on account of their varied biological activities, especially as feeding suppressors and deterrents against some economically important insect pests as *Leptinotarsa decemlineata* (Say) [6,7]. The neo-clerodanes are bicyclic diterpenoids with basic neo-clerodane skeleton 1. The genus *Scutellaria* was proved a rich source of these compounds [8-11]. From *S. woronowii* has been isolated two neo-clerodane diterpenoids: jodrellin A (2) and jodrellin B (3). Both demonstrate better antifeedant properties than clerodin (4) and the 3 is the most potent clerodane antifeedant known to date [12]. Lately jodrellin B has been found in the species of genus *Scutellaria: galericulata, albida, polyodon* [13-15].

In Bulgaria this genus is represented with eight species. The studying of the plants, for availability of neo-clerodane diterpenoids, started in 1993 year with isolation of scutalpin A from *S. alpina* [16]. I report here on the receiving of plant extract from species of genus *Scutellaria* and investigation on the feeding restrain of the Colorado potato beetle larvae.

**EXPERIMENTAL**

*Insects*

Newly emerged fourth instar larvae of Colorado potato beetle used for bioassays were collected from potato fields located around Plovdiv (Bulgaria).

*Extracts*

Plant materials were collected from May to August 2012 as follows: In May *S. orientalis* around Sliven and *S. columnae* in adjacencies of Dolnoslav near Asenovgrad; In June *S.*
altissima in Bachkovo, S. hastifolia around Yambol, S. velenovskyi between Pester and Batak and S. albida in the forest of Topolovo not far from Asenovgrad; S. galericulata was gathered in July at the swamps of Osam river after Lovech. Finally, stems of S. alpina were picked up in August at the Pirin Mountains in the region of hut Vichren.

Dried and finely powdered aerial parts of the species (30 g) were extracted with Me₂CO (3×150 ml) at room temperature for a week. After filtration, the solvent was evaporated to dryness under reduced pressure and low temperature (45°C) yielding gums (about 600 mg). 33.3 mg from each total extracts were dissolved in 1 mL Me₂CO to obtain work solutions.

Antifeeding bioassays. Summary.

The choice feeding bioassay was carried out in petri dishes (15×85 mm), with covered bottom with filter paper, using potato leaf disks with 2.0 cm² area. The upper surface of the disks was treated with 20 µL acetone solution of the test extracts with dose 333.33 µg/cm² (10 000 ppm) with a microsyringe and after evaporation of the solvents received treated disks (TD). After ten and a hundred multiple dilution with acetone were prepared solutions for testing of compounds with dose 1 000 ppm (33.33 µg/cm²) and 100 ppm (3.33 µg/cm²), respectively. The control disks (CD) were manipulate analogously with pure solvent. In each petri dish alternatively were placed three treated and three control disks. The newly emerged fourth instar larvae were starved for 5 h and placed four in each dish, where they were allowed to feed. At regular intervals (20 min) during 4–6 h were simultaneously measured consumed areas of treated disks (CTD) and those of control disks (CCD), to calculate the relevant feeding ratio FR = CTD/CCD. To receive comparative results we used FR₅₀, the ratio when 50% of the control disks areas in every dishes has been consumed (CCD₅₀). Bioassays were performed under the same temperature, humidity conditions and constant darkness.

Experiments were terminated, when 75% of the control potato disks area has been consumed in each petri dish.

RESULTS AND DISCUSSION

The antifeedant activity of the extracts produced by species of genus Scutellaria was assigned to the neo-clerodane diterpenoids they contain. It considers that the activity of neo-clerodanes depend on some structural features of these compounds. Kojima and Kato underlined that the presence in the molecule of the substructures tetra- or hexahydrofurofuran at C-9 is accountable site for significant activity (Fig. 1) [17]. The other authors assign the activity of clerodanes to the decalin ring with C-4-C-18 spiroepoxide and two acetate groups at C-6 and C-19 positions (Fig. 2) [6, 18-19].

Among the tested plants in S. hastifolia, and S. orientalis have not found compounds which to contain tetra- or hexahydrofurofuran moiety, while in the rest present constituents with such substructures.
Table 1. Feeding ratios of test extracts

<table>
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<th>Extracts</th>
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<th>FR_{75}±SE</th>
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<tbody>
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<td></td>
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<td></td>
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<td>S. alpina</td>
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<td>6</td>
<td>0.13±0.01</td>
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<tr>
<td></td>
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<td>0.16±0.02</td>
<td>0.21±0.02</td>
</tr>
<tr>
<td></td>
<td>100</td>
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</tr>
<tr>
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<td>10 000</td>
<td>6</td>
<td>0.08±0.01</td>
<td>0.12±0.02</td>
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<td>S. galericulata</td>
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<td>5</td>
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<td>6</td>
<td>0.08±0.01</td>
<td>0.10±0.03</td>
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<tr>
<td>S. altissima</td>
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N - number of replications; SE - standard error; FR - feeding ratios; FR = CTD/CCD (where CTD and CCD represent consumed areas of treated disks and control disks, respectively.)
The results of the bioassay (shown in Table 1) for the antifeedant activity of eight plant extracts assessed by presenting them on potato discs to larvae of *Leptinotarsa decemlineata*, indicate that the most of the studied natural substances exhibited good to very good action. As seen, low antifeedant activity was found for the extract of *S. hastifolia* (FR\(_{50} = 0.36\) by dose 10 000 ppm) which is probably due to the very small contents of neoclerodanes in this species and the lack of tetrahydrofurofuran or hexahydrofurofuran substructures, as stated above. The maximum depression of feeding was shown by extract of by *S. albida* (FR\(_{50} = 0.00\)), followed *S. altissima* and *S. galericulata* (FR\(_{50} = 0.08\)), *S. alpina* (FR\(_{50} = 0.13\)), according to the quantity of diterpenes in separate species. *S. columnae* (FR\(_{50} = 0.19\)) and *S. velenovskyi* (FR\(_{50} = 0.21\)) exhibited moderate effect. It is interesting that the extract from *S. alpina* did not show full inhibition of feeding at 10 000 ppm, but preserved high activity at 1 000 and 100 ppm. That may be explained with the bigger quantity of neo-clerodane diterpenoids in this species.

Comparison of the data achieved in this study with previous results is problematic. First, the chemical constituents of the plants change in accordance with climatic and environmental conditions of the region they were gathered and the sort of the soil where species had growth. Secondly, the reported publications on antifeedant activity concern properties of pure neo-clerodane diterpenoids. So in the literature missed comprehensive data by bioassay of extracts from species of genus *Scutellaria*.

This preliminary investigation provide promising results to be continued work with testing antifeedant activity of neo-clerodane diterpenoids isolated from plants belonging of genus *Scutellaria*.

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**REFERENCES**


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