

RECENT ADVANCES IN SYNTHESIS OF MONOSUBSTITUTED ACETYLENE POLYMERS

RAZVOJ NA PODROČJU SINTEZE MONOSUBSTITUIRANIH ACETILENSKIH POLIMEROV

JIRÍ VOHLÍDAL¹, J. SEDLÁČEK¹, M. ŽIGON²

¹Department of Physical and Macromolecular Chemistry Faculty of Science, Charles University Albertov 2030,
CZ-128 40 Prague 2 Czech Republic

²National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

Prejem rokopisa - received: 1997-10-01; sprejem za objavo - accepted for publication: 1997-10-21

During the last three years, a considerable progress has been achieved in development of catalyst systems for living polymerization of various substituted acetylenes. Nowadays, there are available single-component catalysts of this type based on stable carbene complexes and multicomponent catalysts based on MoOCl_4 and WOCl_4 , both operating in metathesis mode, as well as $\text{Rh}(\text{diene})$ complexes operating in the ZN mode. Within that time period, similar progress has been attained in polymerization of novel substituted acetylene monomers, including those bearing functional groups like $-\text{NO}_2$, $-\text{NR}_2$, $-\text{C}\equiv\text{N}$, etc. and those bearing ionic or zwitterionic pendant groups. These advancements provide an improved basis for more systematic study of functional properties of these electrically and fotonically active polymers and a better comprehension of relations between the covalent structure and functional properties of this class of polymers.

Key words: substituted acetylene polymers, living polymerization, functional polymers

V obdobju zadnjih treh let je bil dosežen znaten napredek pri razvoju katalizatorskih sistemov za živo polimerizacijo različnih substituiranih acetilenov. Danes so tako na razpolago enokomponentni katalizatorji te vrste na osnovi stabilnih karbenskih kompleksov in večkomponentni katalizatorji na osnovi MoOCl_4 in WOCl_4 , ki delujejo po metateznem načinu, ter $\text{Rh}(\text{dienski})$ kompleksi, ki delujejo po načinu Ziegler-Natta (ZN). Za isto obdobje je značilen tudi napredek na področju polimerizacije novih substituiranih acetilenskih monomerov, vključno z monomeri s funkcionalnimi skupinami, kot so npr. $-\text{NO}_2$, $-\text{NR}_2$ ali $-\text{C}\equiv\text{N}$, in z ionskimi ali zwitterionskimi stranskimi skupinami. Razvoj na tem področju zagotavlja boljšo osnovo za sistematičen študij funkcionalnih lastnosti teh električno in fotonsko aktivnih polimerov ter za boljše razumevanje povezav med kovalentno strukturo in funkcionalnimi lastnostmi te skupine polimerov.

Ključne besede: substituirani acetilenski polimeri, živa polimerizacija, funkcionalni polimeri

1 INTRODUCTION

For at least two decades, conjugated polymers attract significant interest of both academics and industry due to their potential applicability as functional materials for future electronic devices¹⁻⁸. One class of these materials are substituted acetylene polymers, SAP, that are insulators in native state and do not show metallic conductivity neither after doping. However, they exhibit other useful functional properties like photoconductivity, electroluminescence, nonlinear optical properties, etc. originating from their ability to capture, transport and mediate mutual conversions of charge and energy and from their increased higher-order optical susceptibility. Besides, they are candidates for molecular wires transporting the charge and/or energy (signals) through membranes of supramolecular systems, see, e.g. ref.⁹. Actually, carotenoid pigments like carotenes and zeaxanthines, serving as molecular wires in living systems, are oligomers of the SAP type. It can be thus said that the research on synthesis and properties of substituted acetylene polymers really meets material demands of future electronics based on the molecular and supramolecular devices.

There are a few published reviews and book chapters summarizing the state of art in the field of synthesis of substituted acetylene polymers until 1995^{2,3,5,8}. In this pa-

per a brief survey of recent developments in the field of living polymerization systems and synthesis of novel substituted acetylene polymers is presented.

2 LIVING POLYMERIZATION OF SUBSTITUTED ACETYLENES

Living polymerization systems provide: (i) the most efficient control of the polymer molecular weight, and (ii) possibility to synthesize block copolymers of substituted acetylenes that can show some new interesting properties originated from their domain interfaces.

First living metathesis polymerizations of substituted acetylenes have been reported in 1987 for *o*- Me_3Si -phenylacetylene^{5,10,11} and *tert*-butylacetylene¹². Most effort has been paid to systems with phenylacetylenes bearing bulky ortho substituents and $\text{MoOCl}_4/\text{Bu}_4\text{Sn}/\text{EtOH}$ catalyst that give polymers with polydispersity $I_p < 1.10$. Analogous systems without ethanol or bulky substituents do not show living polymerization. Monomers with medium-size substituents yield only living-like systems providing I_p values about 1.2 to 1.3 and *m*- and *p*-substituted phenylacetylenes provide systems in which a termination takes place^{5,13,14}. An exception is 1-chloro-1-octyne that also provides living polymerization system¹⁵.

In 1994, Schrock et al.¹⁶ reported of the living metathesis polymerization of *o*-trimethylsilyl phenylacetylene induced by (1-adamantyl-N \equiv)[OCH(CF₃)₂]₂(2,4-lutidine)-Mo=CH-CMe₂Ph carbene complex (*I*_n = 1.05). They found that other carbene initiators with bulkier ligands do not provide living polymerization systems. Buchmeiser and Schrock have reported of the living stereoregular polymerization of three organometallic acetylenes, ethynylferrocene and ethynylruthenocene¹⁷ and 4-(ferrocenylethynyl)-4'-ethynyltolan (tolan is a trivial name for diphenylacetylene)¹⁸ induced by another Mo-carbene complex: (2,6-Me₂-C₆H₃-N \equiv)[OCH(CF₃)₂]₂Mo=CH-CMe₂Ph in THF and toluene.

Recently, Masuda et al. reported living polymerization of *o*-CF₃-phenyl-acetylene in anisole induced by WOCl₄/Bu₄Sn/*t*-BuOH catalyst (*I*_n < 1.1)¹⁹. Again, alcohol was found to be essential for the living polymerization to be achieved. Similar behaviour has been observed for the systems MoOCl₄/Et₃Al/EtOH (1:1:4), MoOCl₄/Et₃Zn/EtOH (1:1:4) and MoOCl₄/BuLi (without alcohol) for which polymer polydispersities about *I*_n = 1.02 to 1.03 are reported¹⁹.

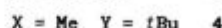
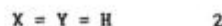
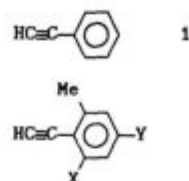
Rh^I(diene) complexes represent another class of living polymerization initiators because, unlike the previous, they operate in the Ziegler-Natta mode and induce living polymerization of sterically uncrowded acetylenes including unsubstituted phenylacetylene, PA. Kishimoto, Nyori et al. reported²⁰ of the living polymerization of PA induced by [Rh(nbd)(PPh₃)₂-(C \equiv CPh)] and the synthesis of block copolymers of PA with *p*-methoxy-PA. Living system is only obtained if a strong base like 4-(dimethylamino)pyridine, DMAP, is added into polymerization mixture. Later on, the same authors reported of the living polymerization of PA and *p*-(OCH₂CH₂CH₂O-Ph-Ph-OCH₃)-PA by bridged binuclear Rh^I complex [Rh(nbd)(OCH₃)₂]₂ in a presence of DMAP²¹. In all cases, stereoregular head-to-tail *cis*-transoid structure is reported for polymers prepared on catalysts derived from Rh(diene) complexes.

In summary, it can be said that a development of living polymerization systems has achieved considerable advances in recent years and further progress in this field seems quite promising. Besides, the catalysts forming living polymerization systems often give stereoregular polymers which is promising for a progress in analysis of microstructure of substituted acetylene polymers.

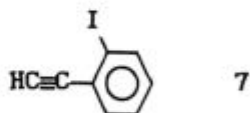
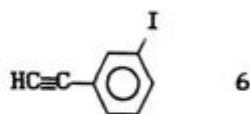
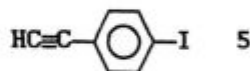
3 NEW SUBSTITUTED ACETYLENE POLYMERS

Functional properties of SAPs depend on their structure that, in the first place, is predetermined by pendant groups attached to their main chains. Great attention is, therefore, paid to design and synthesis of new polymers with more sophisticated structure that are expected to possess better functional properties. In addition, the investigation of these new polymers brings up new knowledge improving our general understanding of the rela-

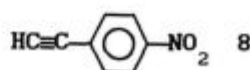
tions between the polymer structure and functional properties that is rather poor till now. Some interesting, recently prepared substituted acetylene polymers are presented in the next survey.



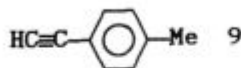
Demonstration of positive effect of bulky ortho substituents on the molecular weight, thermal stability, UV/vis absorption and other properties of PPA²². Rate of polymerization decreases from 1 to 4. Tert-butyl group improves polymer solubility: poly(3) is insoluble whereas poly(4) is soluble and provides free standing films. Copolymers of 4 with 1 and 2 were prepared. Gas permeability and dark conductivity measurements are reported.



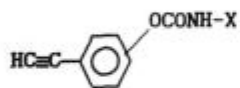
First polymerization of iodophenylacetylenes by various Mo, W and Rh based catalysts. Poly(5)s formed on MoCl₅ based catalysts are insoluble, on Rh catalyst partly soluble, and on WOCl₄ based catalyst soluble. Dioxane cosolvent increases MW of polymers prepared on WOCl₄ based catalyst. Unusual, negative effects of common cocatalysts like Ph₄Sn and Bu₄Sn have been observed. Content of *cis*-units decreases in the following order: Rh > Mo > W/dioxane > W/benzene. Poly(7) is stable in solutions exposed to air whereas poly(5) and poly(6) are not. Photoconductivity of soluble polymers prepared by WOCl₄ based catalyst is reported²³⁻²⁵.



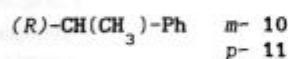
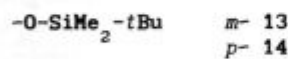
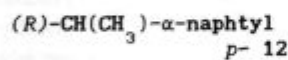
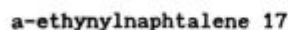
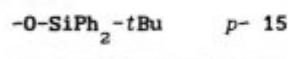
First polymerization of **8** and its copolymerization with PA by $\text{WOCl}_4/\text{Me}_4\text{Sn}$ in dioxane/benzene and $[\text{Rh}(\text{nbd})(\text{PPh}_3)_2(-\text{C}\equiv\text{CPh})]$. WOCl_4 by itself does not transform **8** to any oligomer or polymer. Homopolymers of **8** are insoluble. Photoconductivity measurements on the copolymer of **8** with PA are reported. Nitro group was found to act as a trap for photogenerated charge carriers^{25,26}.

**1****9**

Polymerizations in water, THF, Et_3N and toluene induced by various $\text{Rh}^{\text{I}}(\text{nbd})$ and $\text{Rh}^{\text{I}}(\text{cod})$ complexes: other ligands: tosyl, H_2O , Cl , piperidine, o-phenylenediamine, N-methylimidazole, bis(4-tBu)-2-pyridylmethanethiolate, tBuNH_2 , NH_3 . $[\text{Rh}(\text{cod})(\text{tosyl})(\text{H}_2\text{O})]$ complex yields all-cis polymers. Acetylenes of aliphatic type (1-octyne, 1-butyne-4-ol, 5-hexyne carboxylic acid and 2-butyne dicarboxylic acid) do not polymerize on this Rh catalyst²⁷.

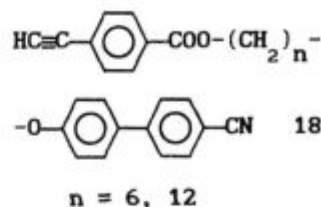


where X = :

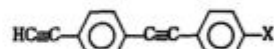
*p*- **11***p*- **14**

Homopolymerization of phenylacetylenes with bulky, optically active groups linked to phenyl ring and their copolymerization with non-chiral monomers. $[\text{Rh}(\text{nbd})\text{Cl}]_2$ in THF solvent was found to be efficient initiator yielding high cis-transoidal polymers whereas $\text{WCl}_6/\text{Ph}_4\text{Sn}$ and $\text{MoCl}_5/\text{Ph}_4\text{Sn}$ systems have provided oligomers and/or low-MW polymers only. Upfield shifts of olefinic protons' NMR signal up to 0.25 ppm are correlated to increasing co-monomer bulkiness resulting in twisting up of the main chain. Polymers of **10**, **11** and **12** as well as their copolymers with achiral acetylenes **1** and **13** to **17** show circular dichroism, CD, in 300 to 500 nm range. Stereoregularity of main chains was found to be essential for CD activity (non stereoregular polymers of

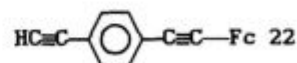
chiral monomers do not show significant CD bands). Computational study of the polymers' helical structure is presented²⁸.

**18** $n = 6, 12$

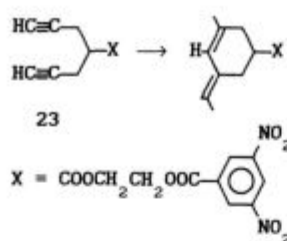
Successful transformation of both monomers **18** into cis-transoid stereoregular PPAs with pendant polar mesogenic groups by using $[\text{Rh}(\text{nbd})\text{Cl}]_2$ catalyst. $\text{WCl}_6/\text{Ph}_4\text{Sn}$ yields either cyclotrimers (in THF) or their mixture with low MW polymer (in toluene). $\text{MoCl}_5/\text{Ph}_4\text{Sn}$ catalyst has not shown activity in any solvent. DSC records as well as slow polymer dissolving prove to a formation of mesogenic structures²⁹.

**19**where X = $\text{C}\equiv\text{C}-\text{Si}^i\text{Pr}_3$ **20**

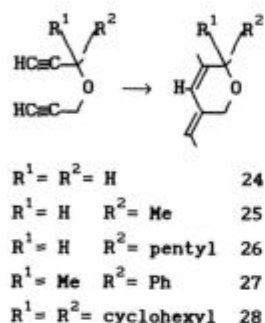
Selective polymerization of **19** and **20** by Mo, W and Rh based initiators taking place on terminal ethynyl group is reported. Polymer formed by $\text{WOCl}_6/\text{Ph}_4\text{Sn}$ catalyst in benzene involves a small amount of soluble high-MW fraction. Dioxane cosolvent suppresses this fraction formation and increases content of cis units in poly(**19**) and poly(**20**). Content of cis units increases in order: W/benzene < W/dioxane < Mo < Rh and it is well correlated even with UV spectra of polymers. Introduction of ethynylphenylene spacer increases photoconductivity and fluorescence activity of the polymer. Autoxidation kinetics of polymers is reported^{30,31}.

**1****21****22**

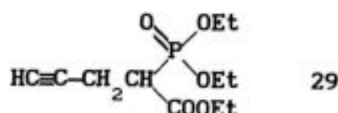
(Fc is ferrocenyl). TaCl_5 quantitatively cyclotrimerizes **21** to 1,2,4- and 1,3,5-triferrocenylbenzenes (mole ratio 3:2). Solid state structure of 1,3,5-isomer was established: up-down arrangement of Fc groups. **21** was copolymerized with **1** to a soluble statistical copolymer. **22** was selectively polymerized on terminal ethynyl group by using W and Rh based catalysts to partly soluble polymers^{32,33}.



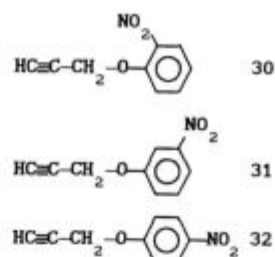
The first reported polymerization of acetylene bearing nitro group. Cyclopolymerization of dipropargylic monomer induced by $\text{MoCl}_5/\text{Ph}_4\text{Sn}$ and PdCl_2 catalysts. The former yields only partly soluble (solubility depends on the solvent used in polymerization), whereas the latter completely soluble poly(23). W-based catalysts were found as inactive. Polymer shows UV/vis absorption up to ca 650 nm³⁴.



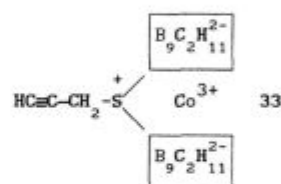
Cyclopolymerization of series of dipropargyl ethers. MoCl_5 based catalysts (EtAlCl_2 and Bu_4Sn cocatalysts) were found to be most active providing high yields of medium-MW polymers. WCl_6 based catalysts are almost inefficient and PdCl_2 gives only 25% yield of poly(27). Poly(24) is insoluble. Solubility of poly(25) and poly(26) depends on the monomer concentration in polymerization mixture (above $[\text{M}] = 0.5 \text{ mol/L}$, the formed polymers are insoluble). On the contrary, poly(27) and poly(28) are well soluble. Bulky α -substituents are suggested to support intramolecular cyclization and suppress intermolecular crosslinking, thus ensuring good polymer solubility. UV/vis absorption up to 600 nm and dark conductivity in both native and iodine doped state are reported³⁵.



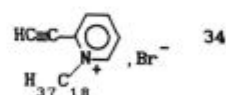
By itself MoCl_5 and WCl_6 do not induce polymerization of 29 but together with EtAlCl_2 or Ph_4Sn cocatalysts provide good yields of low-to-medium-MW yellow polymers ($\langle M \rangle_w$ below 10000). PdCl_2 gives only lower yield of brown poly(29). UV/vis absorption up to 500 nm is reported³⁶.



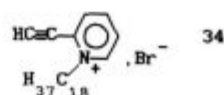
$\text{MoOCl}_4/\text{Me}_4\text{Sn}$ and $\text{MoCl}_5/\text{EtAlCl}_2$ polymerize 30 to insoluble polymer, 31 to insoluble polymer and methanol-soluble fraction, and 32 to soluble, high-MW polymer ($\langle M \rangle_w$ value up to 480 000) and methanol soluble fraction. Methanol soluble fractions formed on MoOCl_4 consist of oligomers only (MW below 1000), whereas in those formed on MoCl_5 involve polymers of $\langle M \rangle_w$ value up to 35000. The former catalyst is more active than the latter one. $\text{WOCl}_4/\text{Me}_4\text{Sn}$ system in dioxane/benzene (highly active in polymerization of nitroPA, 8) shows low activity at room temperature (only methanol soluble polymer is reported) but no activity at 60°C³⁷.

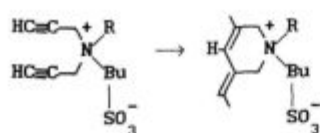


First preparation of polyacetylene with deltahedral sandwich carborane pendant groups is reported. $\text{WOCl}_4/\text{Ph}_4\text{Sn}$ catalyst induces polymerization of 33 to a polymer partly soluble in DMSO. Strong intermolecular interactions of zwitterionic carborane groups (dipole moment $17.7 \times 10^{-30} \text{ Cm}$) are perhaps responsible for low solubility. The same catalyst copolymerizes 33 with 1 to a soluble statistical copolymer³⁸.



Quaternization of 2-vinylpyridine with 1-bromo-octadecane is accompanied by a spontaneous polymerization of formed 34. Poly(34) was also prepared by quaternization of thermally prepared poly(2-vinylpyridine). Multilayers thin films of poly(34) were prepared by LB technique and their properties were investigated. Electrical conductivity of native and iodine doped polymer and oxygen and nitrogen permeation of membranes deposited on Nafion as substrate are reported. The multilayer membranes have shown excellent long term stability^{39,40}.





R = Et	35
R = Bu	36
R = hexyl	37
R = octyl	38

Synthesis of amorphous, conjugated polybetaines by cyclopolymerization of **35** to **38** induced by MoCl_5 , WCl_6 and PdCl_2 catalysts. Negative effect of cocatalysts (EtAlCl_2 and Bu_4Sn) has been observed for the first two catalysts (viz. also polymerization of iodophenylacetylene **5**). Solubility of polymers in various solvents, UV/vis absorption up to 600 nm, dark conductivity in native and iodine doped state are reported⁴¹.

ACKNOWLEDGEMENT

Financial supports from Grant Agency of Charles University (contract No. 189/97/B-CH) and EU Commission (PECO, supplementary contract ERBCIPDCT 940617) are greatly acknowledged.

4 REFERENCES

- J. C. W. Chien, *Polyacetylene - Chemistry, Physics and Material Science*. Academic Press, New York, 1984
- T. Masuda, T. Higashimura, *Adv. Polym. Sci.*, **81** (1987) 121
- J. L. Brédas, R. Silbey (Eds), *Conjugated Polymers*. Kluwer Academic Publishers, Dordrecht, 1991
- G. H. Kiess (Ed.), *Conjugated Conducting Polymers*. Springer Verlag, Berlin, 1992
- H. Shirakawa, T. Masuda, K. Takeda, in: *The Chemistry of Triple-Bonded Functional Groups, Supplement C2* (Patai S. Ed.), Wiley, New York, 1994, p. 945
- S. Nešpůrek, V. Cimrová, J. Pflieger, I. Kmínek, *Polym. Adv. Technol.*, **7** (1996) 459
- R. Giesa, *J. Macromol. Sci. Macromol. Chem. Phys.*, **C36** (1996) 4, 631
- K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, London, 1997
- A. C. Benniston, V. C. Goule, A. Harriman, J.-M. Lehn, B. Marczinke, *J. Chem. Phys.*, **98** (1994) 7798
- T. Masuda, T. Yoshimura, J. Fujimori, T. Higashimura, *J. Chem. Soc. Chem. Commun.*, (1987) 1805
- T. Yoshimura, T. Masuda, T. Higashimura, *Macromolecules*, **21** (1988) 1899
- J. Kunzler, V. Percec, *Polym. Bull.*, **18** (1987) 303 and *ibid.* **29** (1992) 335
- T. Mizumoto, T. Masuda, T. Higashimura, *Macromol. Chem. Phys.*, **196** (1995) 1769
- H. Seki, T. Masuda, T. Higashimura, *J. Polym. Sci. Polym. Chem. Ed.*, **33** (1995) 117
- K. Akiyoshi, T. Masuda, T. Higashimura, *Makromol. Chem.*, **193** (1992) 755
- H. H. Fox, M. O. Wolf, R. O'Dell, B. L. Lin, R. R. Schrock, M. S. Wrighton, *J. Am. Chem. Soc.*, **116** (1994) 2827
- M. Buchmeiser, R. R. Schrock, *Macromolecules*, **28** (1995) 6642
- M. Buchmeiser, R. R. Schrock, *Macromolecules*, **30** (1997) 2274
- T. Masuda, *Proceedings of ISOM 12 Symposium on Metathesis and Related Chemistry*, Flagler College, St. Augustine, Florida, July 13-18, 1997, p. 25, papers in preparation
- Y. Kishimoto, P. Eckerle, T. Miyatake, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.*, **116** (1994) 12131
- Y. Kishimoto, T. Miyatake, T. Ikariya, R. Noyori, *Macromolecules*, **29** (1996) 5054
- T. Yoshida, Y. Abe, T. Masuda, T. Higashimura, *J. Polym. Sci. Polym. Chem.*, **34** (1996) 2229
- J. Vohlídal, J. Sedláček, M. Pacovská, O. Lavastre, P. H. Dixneuf, H. Balcar, J. Pflieger, *Polymer*, **38** (1997) 3359
- J. Pflieger, S. Nešpůrek, J. Vohlídal, *Adv. Mat. Opt. Electronics*, **6** (1996) 325
- J. Vohlídal, J. Sedláček, M. Pacovská, N. Patev, H. Balcar, S. Cabioch, O. Lavastre, P. H. Dixneuf, *Proceedings of ISOM 12 Symposium on Metathesis and Related Chemistry*, Flagler College, St. Augustine, Florida, July 13-18, 1997, p. 97; papers in preparation
- J. Sedláček, J. Vohlídal, S. Cabioch, O. Lavastre, P. H. Dixneuf, H. Balcar, M. Štícha, J. Pflieger, V. Blechta, *Macromol. Chem. Phys.* **199** (1998) 155
- B. Z. Tang, W. H. Poon, S. M. Leung, W. H. Leung, H. Peng, *Macromolecules*, **30** (1997) 2209
- E. Yashima, S. Huang, T. Mitsushima, Y. Okamoto, *Macromolecules*, **28** (1995) 4184
- B. Z. Tang, X. Kong, X. Wan, X.-D. Feng, *Macromolecules*, **30** (1997) 5620
- J. Vohlídal, J. Sedláček, N. Patev, M. Pacovská, S. Cabioch, O. Lavastre, P. H. Dixneuf, H. Balcar, J. Pflieger, V. Blechta, P. Matějka, *Macromolecules* (submitted)
- J. Sedláček, M. Pacovská, T. Etrych, M. Dlouhý, N. Patev, S. Cabioch, O. Lavastre, H. Balcar, M. Žigon, J. Vohlídal, *Polym. Mater. Sci. Eng.*, **77** (1997) 52
- P. Štěpnička, I. Císařová, J. Sedláček, J. Vohlídal, M. Poláček, *Collect. Czech. Chem. Commun.*, **62** (1997) 1577
- J. Sedláček, J. Vohlídal, N. Patev, M. Pacovská, S. Cabioch, O. Lavastre, H. Balcar, P. Matějka, V. Blechta, *Macromol. Chem. Phys.*, (submitted)
- J.-H. Lee, J.-W. Park, J.-M. Oh, S.-K. Choi, *Macromolecules*, **28** (1995) 377
- H.-J. Lee, Y.-S. Gal, W.-C. Lee, J.-M. Oh, S.-H. Jin, S.-K. Choi, *Macromolecules*, **28** (1995) 1208
- Y.-S. Gal, B. Jung, W.-C. Lee, H.-J. Lee, S.-K. Choi, *Macromolecules*, **28** (1995) 2086
- H. Balcar, T. Kalisz, J. Sedláček, V. Blechta, P. Matějka, *Polymer*, in print
- J. Vohlídal, J. Plešek, J. Sedláček, I. Císařová, P. Matějka, S. Heřmánek, *Collect. Czech. Chem. Commun.*, **61** (1996) 877
- P. Zhou, A. Blumstein, *Polymer*, **37** (1996) 1477
- P. Zhou, L. Samuelson, K. S. Alva, C.-C. Chen, R. B. Blumstein, *Macromolecules*, **30** (1997) 1577
- D.-C. Choi, S.-H. Kim, J.-H. Lee, H.-N. Cho, S.-K. Choi, *Macromolecules*, **30** (1997) 176