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Synthesis and characterization of new triblock copolymers of isobutylene and 1,3-pentadiene

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New linear triblock copolymers consisting of a rubbery polyisobutylene (PIB) midsegment bonded both sides by glassy cyclized poly(1,3-pentadiene) (cy-PPD) blocks were synthesized by carbocationic polymerization using sequential monomer addition. First, the living polymerization of isobutylene (IB) was induced by bifunctional dicumylmethylether (DiCumOMe)/$TiCl_4$ as initiating system in *n*-hexane/CH_2Cl_2 (1/1 v/v) as solvent mixture at −60°C in the presence of DMSO as electron donor (ED). After the living PIB sequences had reached the desired number average molar weight ($\bar{M}_n$) in the range of 5000 to 25 000 g mol^{-1}, 1,3-pentadiene (PD) was added to produce the hard cy-PPD outer blocks with $\bar{M}_n$ close to 6000 g mol^{-1}. The crude copolymers were purified by CH_2Cl_2 extraction at −60°C and characterized by size exclusion chromatography (s.e.c.) and nuclear magnetic resonance (n.m.r.) spectroscopy. Copyright © 1996 Elsevier Science Ltd.

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Introduction

In the past ten years, an increasing effort has been devoted to the synthesis of new copolymers in order to develop materials exhibiting predictable and specialized properties. The synthesis of such 'tailor-made macromolecular systems' with controlled molecular weights, narrow molecular weight distributions and well-defined architectures can be achieved especially by living anionic polymerization using sequential monomer addition[1–4]. Thermoplastic elastomers (TPEs), like the linear triblock copolymers with rubbery centre block connected to glassy outer segments, are an important group among such materials and have been extensively studied[5–7]. For instance, triblocks based on styrene (St) and butadiene (BD) or isoprene (IP) are well-known commodities, e.g., Shell's poly(St-*b*-BD-*b*-St) type Kraton. Nevertheless, polydiene-containing block polymers obtained by the living anionic process present some drawbacks owing to the low stability of the central dienic sequences which must be hydrogenated to yield polymeric materials displaying higher weathering, oxidative, chemical and thermal resistance than their precursors. This explains why the direct synthesis of similar TPEs with a saturated midblock, e.g., polyisobutylene (PIB), has long been a desirable objective. The discovery of living carbocationic polymerization[8–12] followed by many investigations concerning this topic[13] led to the synthesis of a wide variety of new products, with satisfactory TPE characteristics, containing a soft PIB inner block flanked by two rigid outer segments based on St[14], St derivatives[15–20], indene[21] and methyl methacrylate[22].

In addition, there has also recently been a description of the synthesis of a new family of TPEs involving an elastomeric PIB midsegment and hard cyclopolyisoprene blocks[23]. That is the reason why, in an extension of our work on the homo- and copolymerization of 1,3-pentadiene (PD)[24–27], also known as piperylene, we have considered it convenient to investigate the possibility of using PD in the synthesis of similar linear triblocks consisting of a rubbery PIB central sequence, with well-controlled molar weight, linked to glassy cyclized polypiperylene (cy-PPD) endblocks. This research appeared of interest not only from the scientific point of view but also for practical considerations, in view of the potential applications of polymeric systems based on PD monomer readily available as a by-product of the industrial preparation of IP from C_5 petroleum sources. In the present communication, results pertaining to the carbocationic synthesis and characterization of PIB, cy-PPD and IB-PD block copolymers are reported.

Experimental

Dicumylmethylether (DiCumOMe) was synthesized as described earlier[12] and its purity was checked by ^1H n.m.r. IB (Air Liquide) was dried by passing the gas through two columns packed with $CaCl_2$ and molecular sieves (4 Å) respectively, and was then condensed under vacuum. Purification of PD (Aldrich, *trans*/*cis* ca. 55/45), *n*-hexane and CH_2Cl_2 were carried out as reported in a forthcoming paper[28]. $TiCl_4$ (Aldrich) and DMSO (Aldrich) were used as received.

All experiments, i.e. polymerizations of IB or PD and block copolymerizations, were performed at −60°C under a dry nitrogen atmosphere in *n*-hexane/

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Table 1 Carbocationic polymerization conditions and characterization of triblock copolymers of isobutylene (IB) and 1,3-pentadiene (PD)[a]

					Copolymer				
		PIB[b]					Composition (PD—mol %)		
Run	[DiCumOMe] (10^{-3} mol l^{-1})	M_n (theor.)	M_n^c (expt.)	$M_w/\bar{M}_n^c$	M_n^c (expt.)	$M_w/\bar{M}_n^c$	s.e.c.	^{13}C n.m.r.	τ^d (mol %)
1	2.2	25 000	27 600	1.15	32 300	1.3	12	11	34
2	5.0	11 200	13 700	1.2	21 200	1.2	31	25	42
3	10.0	6 700	8 600	1.3	15 000	1.4	37	32	46

[a] Experimental conditions: *n*-hexane/CH_2Cl_2 (1/1 v/v); −60°C; [$TiCl_4$]/[DiCumOMe] = 25; [DMSO]/[DiCumOMe] = 3; [IB] = 1 mol l^{-1} for runs 1 and 2; [IB] = 1.2 mol l^{-1} for run 3; [PD] = 1 mol $^{-1}$; blocking time: 17 h; overall yields (wt%): 60, 90 and 98 for runs 1, 2 and 3 respectively

[b] Model rubbery PIB midblock obtained by living carbocationic polymerization

[c] Determined by s.e.c.

[d] Cyclization degree of outer cy-PPD segments measured by ^{1}H n.m.r.

CH_2CHCl_2 (1/1 v/v) solvent mixtures using the bifunctional DiCumOMe/$TiCl_4$ initiating system in the presence of DMSO as electron donor (ED). Copolymers were prepared by slowly introducing PD to the living PIB homogeneous charge, i.e. after IB was consumed in the first step, yielding desired molecular weight macrodications. The reactions were quenched with prechilled methanol. Detailed experimental conditions including concentration data are given in *Table 1*. Recovery and purification of crude products were carried out in the same manner as described previously[24]. Moreover, the copolymer samples were treated by selective solvent extraction (CH_2Cl_2 at −60°C).

Average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distributions (MWD) were determined in THF (flow rate: 1 ml min^{-1}) by use of a Waters high-pressure s.e.c. assembly (Model 510 pump, linear ultrastyragel columns, Waters 410 RI detector) coupled online with a Multi-Angle Laser Light Scattering (Wyatt Technology, Model DAWN DSP). N.m.r. spectra were recorded at 200 MHz for ^{1}H and at 50 MHz for ^{13}C in $CDCl_3$ on a Brüker AC 2008 spectrometer.

Results and discussion

Living cationic polymerization of IB: synthesis of model soft PIB midblocks. The synthesis of telechelic biliving-ended PIB by the bifunctional DiCumOMe/$TiCl_4$ initiating system has been described[29]. The present research is focused on the convenient preparation of living PIB macrodications of fixed average molecular weight able then to initiate the electrophilic polymerization of PD. After some orienting runs, this objective was reached, without perceptible side reactions, by operating in the conditions given in the Experimental section using selected ED (DMSO) to stabilize the growing carbocations and trap the proton impurities (moisture). In these conditions the polymerizations were homogeneous. The beneficial effect of proton scavengers and/or ED in mediating living cationic polymerizations has been discussed in great detail[30,31]. In the course of our investigations, three $\bar{M}_n$ values in the range of 5000 to 25 000 g mol^{-1} have been aimed to serve as model central rubbery PIB segments of triblock copolymers.

The data collected in *Table 1* clearly indicate that experimental $\bar{M}_n$ values are in good agreement with the predicted values and that the polydispersity ($\bar{M}_w/\bar{M}_n$) of the resulting PIB samples are narrow enough to support the living nature of the chain growth which has been demonstrated elsewhere[28]

Cationic polymerization of PD. In contrast to the case of IB, the cationic polymerization of PD presents no living features. Until now this research topic has been little investigated[28,32,33]. There is general agreement for considering that the cationically prepared PPDs have both low $\bar{M}_n$ values and wide MWD due to the numerous side reactions, e.g. transfers to monomer and termination processes.

The use of selected additives, i.e., proton scavengers and/or ED, does not seem to change these findings notably[28,33]. In addition, considerable loss of unsaturation occurs during PPD formation. Since soluble products were obtained, the consumption of the residual double bonds might be ascribed mainly to cyclization of saturated bonds. According to other studies[28,32,33], it can be assumed that the microstructure of electrophilic PPD consists of prevalent *trans*-linear unsaturations (1,4- and 1,2-units) accompanied by a minor or no detectable amount of *cis*-configurations and vinyl 3,4-enchainments. In addition there are, depending on the experimental conditions, cyclic fragments of polymer chains consisting of isolated and/or fused cyclohexane rings (ca. 2–3) containing a tetrasubstituted double bond[28,32].

Three polymerization runs of PD, performed using an identical procedure to that in the case of standard PIB centre blocks (*Table 1*), gave similar partially-cyclized PPD samples. Their characteristics were as follows: $\bar{M}_n$ values ranging from 5000 to 7000 g mol^{-1}; polydispersity indexes close to 3; PD-linear units linked fully in the *trans*-configuration with a ratio of 1,4-structure/1,2-structure ca. 65/35; degree of cyclization (τ) varying between 35 and 50 mol% with increasing $TiCl_4$ and DiCumOMe concentrations; cyclized sequences consisting mainly of mono- and bi-cyclohexane condensed rings.

Synthesis and characterization of triblock copolymers poly-(PD-b-IB-b-PD). Resulting from the first experiments described in the two preceding subsections, a series of three triblock samples with various well-defined molar weight PIB midsegments were synthesized. *Table 1* and *Figures 1* and *2* summarize reaction

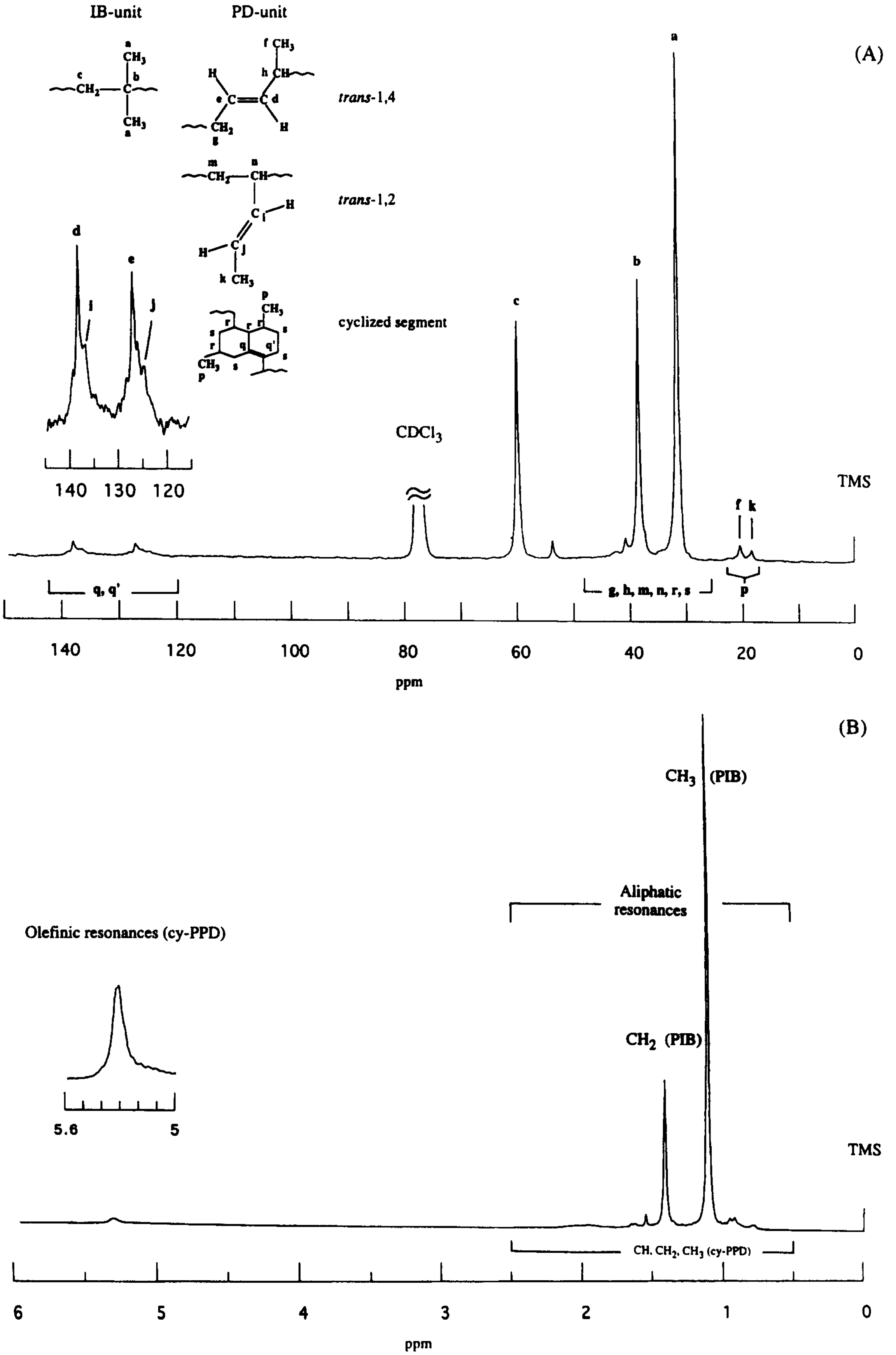

Figure 1 N.m.r. spectra of cationically prepared triblock copolymer of isobutylene (IB) and 1,3-pentadiene (PD) in $CDCl_3$ at room temperature (run 3 in *Table 1*). (A) ^{13}C spectrum at 50 MHz; (B) ^{1}H spectrum at 200 MHz

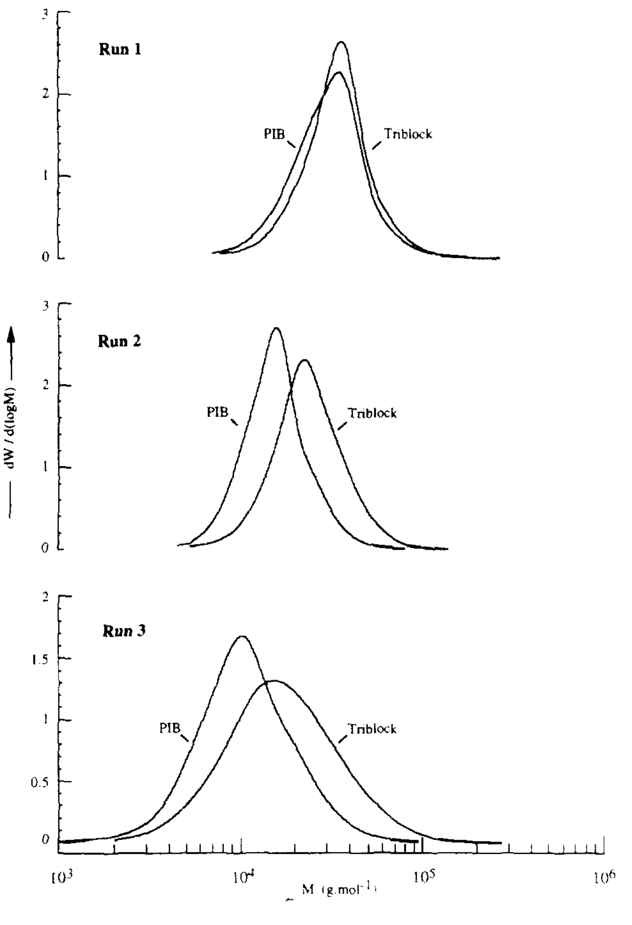

Figure 2 Molecular weight distributions of standard polyisobutylene (PIB) centre blocks and corresponding triblock copolymers obtained under the conditions detailed in *Table 1*

conditions and results. The predicted microstructure of the polymeric materials was similar to that of the IP-based homologous materials obtained by Kaszas *et al.*[23]. The main structural elements incorporated in the chains were identified by n.m.r. spectroscopy[28] as IB units and PD units including *trans*-1,4, *trans*-1,2 and cyclized segments (*Figures 1* and *2*).

It must be pointed out that crude copolymers were mainly contaminated by cy-PPD homopolymer (ca. 5–25 wt%), as evidenced by s.e.c. measurements and due to adventitious protic initiations, e.g. residual moisture introduced with the diene into the charge as well as protons liberated during the blocking process. The solubility characteristics of PIB and PPD are similar and, in order to eliminate fully PPD contamination, selective solvent extraction has been carried out with chilled CH_2Cl_2 at $-60°C$ (a good solvent for cy-PPD, poor for PIB).

Each copolymerization run was made with a companion experiment (IB homopolymerization) realized under the same conditions. Therefore, on the basis of these standard PIB samples, it was possible to evaluate $\bar{M}_n$ of the rubbery PIB centre blocks present in the corresponding copolymers. Data reported in *Table 1* indicate that the resulting average molar weights of triblocks agree well, within experimental error, with the expected values calculated from $\bar{M}_n$ of model PIB and $\bar{M}_n$ of cy-PPD endblocks (ca. 6000 g mol^{-1}). On the other hand it seems that the copolymer compositions may be directly deduced from $\bar{M}_n$ values determined by s.e.c. Nevertheless, more accurate results are provided by means of ^{13}C n.m.r. spectroscopy by comparing the peak area of methylene carbon resonance of IB units (peak at 60 ppm in *Figure 1A*) with the total area of the spectrum. The two series of values thus obtained (*Table 1*) are fairly close and the observed divergences may be considered to be included in the margin of error of the two analytical methods.

Comparison between MWD of PIB samples and corresponding extracted copolymers clearly shows (*Figure 2*) a significant shift in the traces toward higher molecular weights for the copolymers relative to the precursor PIB midsegments according to the formation of block copolymers. The great difference of $\bar{M}_n$ values between PPD fractions and triblocks for runs 1 and 2 allows one to check the whole extraction of PPD homopolymer by the absence of low molar weight polymers. It is difficult to avoid fully the formation of PIB and/or diblock copolymer, and they cannot be separated from the triblock. In addition, it is impossible to count them. However, both the polydispersities (*Table 1*) and the MWD traces (*Figure 2*) of copolymers are as narrow as those of the model PIB: these findings are in good agreement with the mainly triblock nature of such copolymers.

The extent of cyclization (τ in *Table 1*) of cy-PPD outer fragments was quantified by ^1H n.m.r. spectroscopy (*Figure 1B*) from the values of the overall area of aliphatic peaks (0.5–2.5 ppm), weighed by PD fraction containing copolymer, and the area of olefinic resonances, at 5–5.5 ppm, due to the linear PD unsaturations[28].

Conclusions

Living carbocationic polymerization of IB and the subsequent synthesis of poly(PD-*b*-IB-*b*-PD) block copolymers have been successfully carried out by the sequential monomer addition technique. The resulting products exhibit both composition and microstructure in good agreement with the expected results. However, the characteristics of the cy-PPD endblocks, i.e., $\bar{M}_n$ values close to 6000 g mol^{-1} and cyclization levels in the range of 35–50 mol%, are too low for these polymeric materials to be endowed with satisfying TPE properties. This implies other investigations (now being performed in our laboratory) to control both the extent of cyclization and the lengths of the cy-PPD sequences.

References

1 Szwarc, M. 'Carbanions, Living Polymers and Electron Transfer Processes', Interscience, New York, 1968
2 Morton, M. 'Anionic Polymerization: Principles and Practice', Academic Press, New York, 1983
3 Rempp, P., Franta, E. and Hertz, J. E. *Adv. Polym. Sci.* 1988, **86**, 145
4 Müller, A. H. E. in 'Comprehensive Polymer Science' (Eds. G. Allen and J. C. Bevington), Pergamon, Oxford, 1988, Vol. 3, p. 387
5 Allport, D. C. and Janes, W. H. 'Block Copolymers', Applied Science, London, 1973
6 Kraus, G. and Rollman, W. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1133
7 Noshay, A. and McGrath, J. E. 'Block Copolymers', Academic Press, New York, 1977
8 Miyamoto, M., Sawamoto, M. and Higashimura, T. *Macromolecules* 1984, **17**, 265
9 Higashimura, T. and Sawamoto, M. *Adv. Polym. Sci.* 1984, **62**, 49

10 Faust, R. and Kennedy, J. P. *J. Polym. Bull.* 1986, **15**, 317

11 Faust, R. and Kennedy, J. P. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 1847

12 Mishra, M. K. and Kennedy, J. P. *J. Macromol. Sci.-Chem.* 1987, **A24**, 933

13 Kennedy, J. P. and Ivan, B. 'Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice', Hanser Publishers, Munich, 1991

14 Kaszas, G., Puskas, J. E., Kennedy, J. P. and Hager, W. G. *J. Polym. Sci., Polym. Chem. Edn.* 1991, **29**, 427

15 Kennedy, J. P. and Kurian, J. *J. Polym. Sci., Polym. Chem. Edn.* 1990, **28**, 3725

16 Kennedy, J. P., Meguriya, N. and Keszler, B. *Macromolecules* 1991, **24**, 6572

17 Tsunogae, Y. and Kennedy, J. P. *Polym. Bull.* 1992, **27**, 631

18 Tsunogae, Y. and Kennedy, J. P. *J. Polym. Sci., Polym. Chem. Edn.* 1994, **32**, 403

19 Fodor, Z. and Faust, R. *J. Macromol. Sci.—Pure Appl. Chem.* 1995, **A32**, 575

20 Oh, J.-M., Kang, S.-J., Kwon, O.-S. and Choi, S.-K. *Macromolecules* 1995, **28**, 3015

21 Kennedy, J. P., Keszler, B., Tsunogae, Y. and Midha, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, **32**, 310

22 Kennedy, J. P. and Price, J. L. *Mater. Sci. Eng.* 1991, **64**, 40

23 Kaszas, G., Puskas, J. and Kennedy, J. P. *J. Appl. Polym. Sci.* 1990, **39**, 119

24 Petit, A. and Néel, J. *J. Polym. Sci., Polym. Chem. Edn.* 1986, **24**, 883

25 Petit, A., Cung, M. T. and Néel, J. *J. Polym. Sci., Polym. Chem. Edn.* 1988, **26**, 1093

26 Petit, A., Cung, M. T. and Néel, J. *J. Chim. Phys.* 1988, **85**, 319

27 Petit, A. *Eur. Polym. J.* 1993, **29**, 1419

28 Vautrin-Ul, C., Pla, F. and Petit, A. (to be published)

29 Kaszas, G., Puskas, J. and Kennedy, J. P. *Polym. Bull.* 1987, **18**, 123

30 Kennedy, J. P. and Atsuschi Hayashi *J. Macromol. Sci.—Chem.* 1991, **A28**, 197

31 Pratap, G., Wang, J. and Heller, J. P. *J. Appl. Polym. Sci.* 1992, **46**, 1117

32 Denisova, T. T., Livshits, I. A. and Gershtein, Y. R. *Polym. Sci. USSR* 1974, 1017

33 Peng, Y. X., Nguyen, H. A., Macedo, A. and Cheradame, H. *Eur. Polym. J.* 1994, **30**, 69