Polymer Bulletin 39, 589–596 (1997)

Polymer Bulletin

Synthesis and bulk properties of poly(tetrahydrofuran)-poly(2-methyl-2-oxazoline) ABA triblock copolymers

Peter Van Caeter[1], **Eric J. Goethals**[1], **Valeria Gancheva**[2], **Roumania Velichkova**[2]

[1] Department of Organic Chemistry, Polymer Division, University of Ghent,
Krijgslaan 281 (S4-bis), B-9000 Ghent, Belgium
[2] Institute for Polymers, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria

Received: 20 March 1997/Revised version: 5 September 1997/Accepted: 8 September 1997

Summary

A series of linear triblock-copolymers of the ABA type in which the central B-block is poly(tetrahydrofuran) (polyTHF) and the A-segments are poly(2-methyl-2-oxazoline) (polyMeOX) were synthesized by a one-pot sequential monomer addition copolymerization, utilizing the living nature of the cationic ring-opening polymerization of both monomers.

Films of the copolymers, casted from chloroform solutions, exhibit excellent mechanical properties in comparison with the homopolymers with comparable molecular weights, which was ascribed to the phase separation occurring between the two copolymer segments. Materials, in which the polyTHF B-segment have a molecular weight 13000 g/mol or higher and each polyMeOX A-block a molecular weight 1500 g/mol, kept elastomeric properties up to 130°C notwithstanding the fact that this temperature is considerably higher than the melting point of polyTHF and the glass transition temperature of polyMeOX. It was found that these triblock-copolymer materials show a shape memory effect. These observations are attributed to the high degree of phase separation between the two blocks and the strong polar interactions between the polyMeOX segments.

Introduction

ABA-type of block-copolymers are a well known class of compounds which give rise to materials with interesting physical properties (1). If the A-blocks are polymer chains with a high glass transition temperature, Tg, or a high melting point and the B-block is a soft, amorphous, low Tg polymer, the block-copolymers are thermoplastic materials, the mechanical properties of which can be varied over a wide range by variation of the relative lengths of the two blocks.

A well known method for the synthesis of block-copolymers is the sequential monomer addition in living polymerization systems. In cationic ring-opening polymerization, two well documented living polymerizations are those of tetrahydrofuran (THF) (2) and 2-

alkyl-*2*-oxazolines (3). The active species for the polymerization of THF are oxonium ions which are strong alkylating agents and, therefore, efficient initiators for the polymerization of oxazolines resulting in the formation of block-copolymers. This principle has already been used by Kobayashi et al. for the synthesis of relatively low molecular weight poly(THF-*b*-MeOX) AB block-copolymers (4) (MeOX stands for *2*-methyl-*2*-oxazoline). Due to the hydrophilic character of polyMeOX and the hydrophobic character of polyTHF, these block-copolymers showed interesting properties as non-ionic emulsifying agents.

In the present paper we wish to report on the synthesis of ABA block-copolymers in which A is a polyMeOX block and B a relatively high molecular weight polyTHF block and on the mechanical properties of the resulting materials.

Experimental part

Materials

Tetrahydrofuran (THF) was purified by distillation followed by drying over sodium wire under reflux in the presence of a trace of benzophenone until a persistant blue color was obtained. The monomer was distilled just before use, b.p. 66°C. *2*-Methyl-*2*-oxazoline (MeOX) was purified by refluxing over potassium hydroxide for 2 hours, followed by distillation over calcium hydride under dry nitrogen. The monomer was distilled just before use, b.p. 109°C. Trifluoromethanesulfonic anhydride (triflic anhydride), b.p. 82°C, and morpholine, b.p. 128°C, were distilled under dry nitrogen. Acetonitrile was purified by distillation over calcium hydride and distilled just before use, b.p.81°C.

Procedures

Synthesis of poly(MeOX-THF-MeOX) block-copolymer - Prior to the reaction, the polymerization flask was kept in an oven (100°C) for 12 hours and dried under vacuum during 3-5 hours. A typical run was as follows. To 200 ml of freshly distilled THF, 0.416 ml (2.5 mmol) of triflic anhydride was added under stirring. After 50 min, 4 ml of dry MeOX was added. Unreacted THF was removed by distillation under vacuum and replaced by 200 ml of dry acetonitrile. To this mixture, 30 ml of MeOX (0.35 mol) was added and the polymerization was continued at 70°C for 2 hours. The reaction was terminated by adding 8 ml of morpholine. The solution was stirred for another 20 mins at 70°C and was then poured into a cold aqueous 0,1 N potassium hydroxide solution. The precipitate was filtered off, washed with distilled water and dried under vacuum, leaving 26 g of the ABA block-copolymer.

Method of analysis

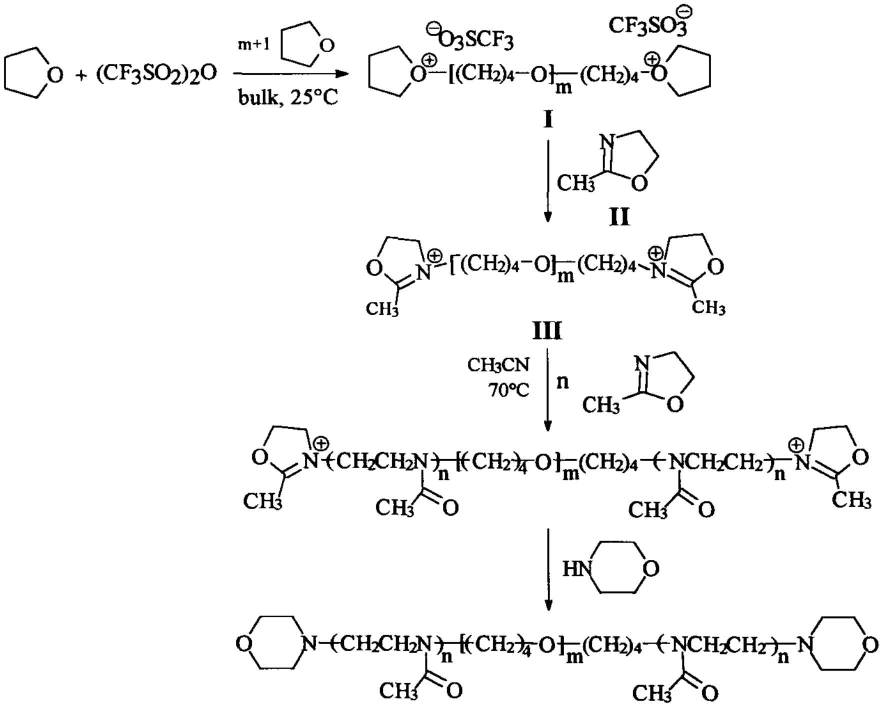
All copolymers are characterized by ^{1}H-NMR and by gel permeation chromatography (GPC). ^{1}H-NMR spectra were recorded on Bruker 500 MHz spectrometer in $CDCl_3$. Molecular weights and molecular weight distributions of the polymers were measured with GPC using an RI detector under the following conditions : PL-Gel 10μ MIX Å with THF eluent (using polyTHF standards) or Waters μStyragel HT 10^3 Å (10μ) + 10^4 Å (10μ) with *1*-methyl-*2*-pyrrolidinone as eluent (using polystyrene standards) at 80°C.

Values of tanδ were measured by a Polymer Laboratories dynamic mechanical thermal analysis (DMTA) type PL-MKII at a heating rate of 2°C/min at a frequency of 1Hz. Differential scanning calorimetry (DSC) analyses were performed on a DSC-7 Perkin-Elmer apparatus. Values of G' an G'' were measured by a Physica rheometer, type OS300, at a heating rate of 2°C/min at a frequency of 1Hz. Tensile strength tests on polymer films were performed on a HT Hounsfield apparatus at tension and compression with crosshead speed 10 mm/min. The starting distance between the clams was 50mm.

Results and discussion

Synthesis of poly(MeOX-b-THF-b-MeOX) (IV)

It is known that bifunctionally living polyTHF (I) can be obtained by polymerization of THF with trifluoromethanesulfonic anhydride ("triflic anhydride") (5). The kinetics of this polymerization and the control of the molecular weight of the polymers has been reported elsewhere (6). End-capping of the living polymers with MeOX (II) results in the corresponding α,ω-bis(2-methyloxazolinium)-terminated polyTHF's (III). These polymers are then used to initiate the polymerization of MeOX. Since this second polymerization occurs in polar solvents, the excess THF, remaining after the first polymerization, was removed by distillation and replaced by acetonitrile. The polymerization of MeOX was carried out at 70°C. The complete reaction scheme is as follows :



ABA-block copolymer, IV

The block-copolymers were analyzed by gel permeation chromatography (GPC) and by ^{1}H-NMR-spectroscopy. The molecular weight of the central polyTHF block was determined by withdrawing a sample of the reaction mixture just prior to the endcapping reaction with MeOX. The thus isolated polyTHF was terminated with methanol and analyzed by GPC to determine its molecular weight. The polymerization of the MeOX was terminated by addition of morpholine so that the end-groups of the final block-copolymer could be analyzed by NMR. This NMR analysis allows to determine the number of end-groups relative to the polyMeOX and the ratio of the MeOX to THF structural units. Since the molecular weight of the central polyTHF block is known, the molecular weight of the polyMeOX blocks can be calculated. As an example, Fig.1 shows the NMR spectrum of a polymer with a central polyTHF block of molecular weight 9000 g/mol and two polyMeOX blocks of molecular weight 1500 g/mol.

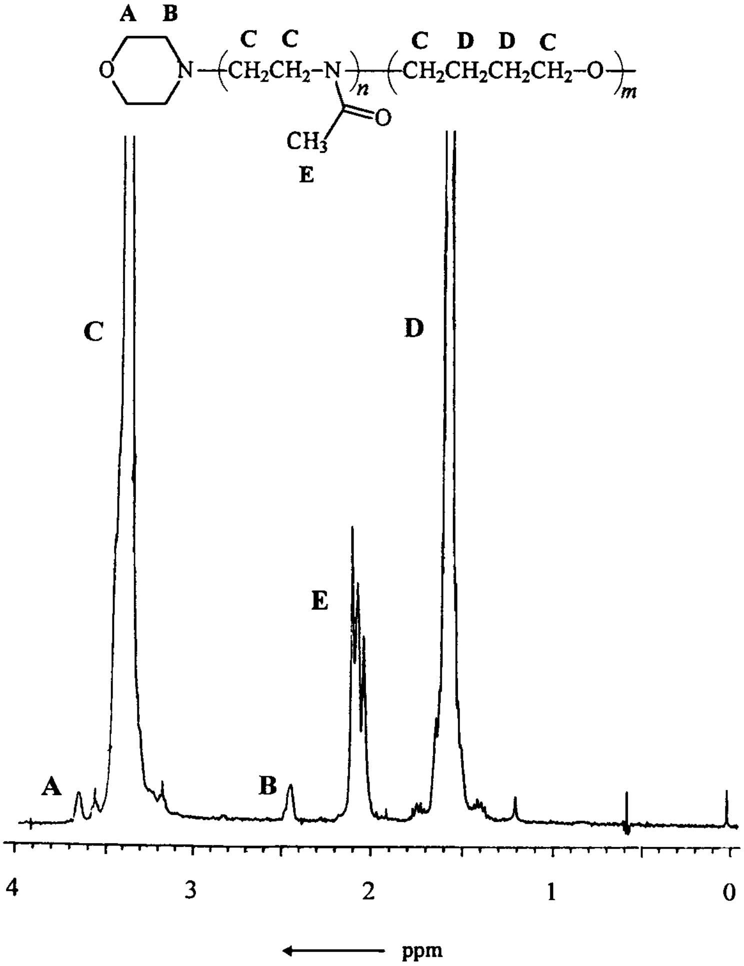


Fig.1. 500 MHz ^{1}H-NMR spectrum (in $CDCl_3$) of block-copolymer BC3 (see Table 1).

Table 1. Characterization of poly(MeOX-*b*-THF-*b*-MeOX) copolymers

Entry	$\overline{M}_{n,\,B\text{-}block}$ [a]	Dispersity[a]	$\overline{M}_{n,\,triblock}$ [b] poly(MeOX-THF-MeOX)	Dispersity[c]
BC1	4100	1.2	1500-4100-1500	1.3
BC2	5900	1.2	1500-5900-1500	1.3
BC3	8900	1.2	1500-8900-1500	1.3
BC4	11000	1.1	1500-11000-1500	1.3
BC5	13200	1.2	1500-13200-1500	1.3
BC6	16100	1.1	1500-16100-1500	1.3
BC7	18800	1.1	1500-18800-1500	1.3

[a] In g/mol; measured by GPC analysis. Column: PL-Gel 10μ MIX Å; eluent: THF, calibrated on polyTHF standards.

[b] In g/mol; determined by integral ratio of the peaks in the 500MHz ^{1}H-NMR spectra.

[c] Measured by GPC-RI analysis. Colomn: Waters μ Styragel HT 10^3Å (10μ) + 10^4Å (10μ); eluent: *1*-methyl-*2*-pyrrolidinone (80°C), calibrated on polystyrene standards.

The composition of the block-copolymers was varied by changing the molecular weight of the central block from 4000 to 19000 g/mol and keeping the molecular weight of the external blocks constant at a value of 1500 g/mol. Table 1 gives the composition and characteristics of a few representative examples.

Properties of the ABA block-copolymers

PolyTHF is a semi-crystalline polymer with a melting point ranging from 20°C to 40°C for molecular weights from 2000 to 20000 g/mol (7). The Tg of polyTHF is -65°C.

PolyMeOX is an amorphous polymer with a Tg of appr. 80°C (8). The block-copolymers described above were all solids at room temperature. According to DSC measurements, all compositions showed a crystalline melting point close to the one corresponding to the pure polyTHF. Dynamic mechanical thermal analysis (DMTA) of the materials, recorded up to 30°C, showed a maximum for the tanδ value at the Tg of the polyTHF segment. This result gives an indication to the presence of micro-phase separation in these materials. This incompatibility was expected on the bases of the large difference in solubility parameters, δ, of the two polymers (9): the δ-value of polyTHF is 17.3 $(MPa)^{1/2}$ (10), that of polyMeOX is 25 $(MPa)^{1/2}$ (11).

The polymers with a central polyTHF block with a molecular weight 13000 g/mol or higher were surprisingly strong materials at room temperature. This is evidenced in Fig. 2 in which a number of stress-strain curves of different block-copolymers of varying composition are shown. The high elasticity moduli at small deformations indicate stress-induced crystallization of the polyTHF segments. These materials still show pronounced elastomeric properties above the melting point of the polyTHF segments. Above this temperature, the materials did not melt nor turn into viscous liquids as is the case with pure polyTHF's of the same molecular weights. This is in agreement with the fact that the outer blocks of these ABA copolymers have a Tg of 90°C (measured with a rheometer as the maximum in the tanδ versus temperature curve) and therefore form glassy domains which act as physical cross-links.

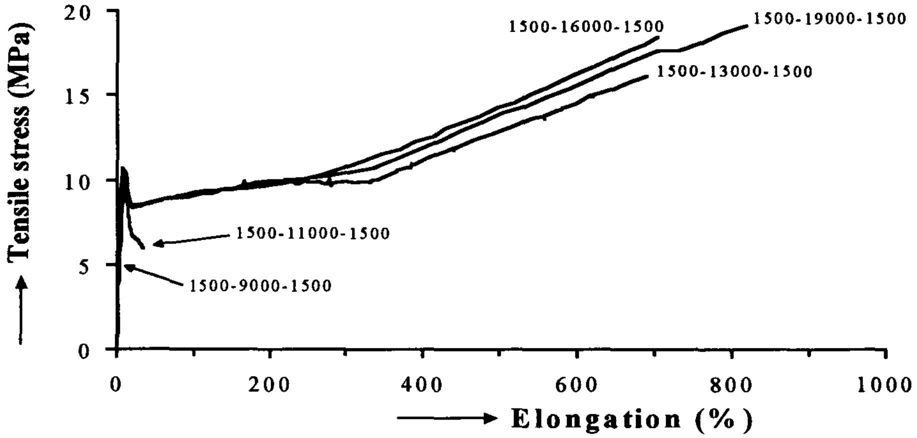
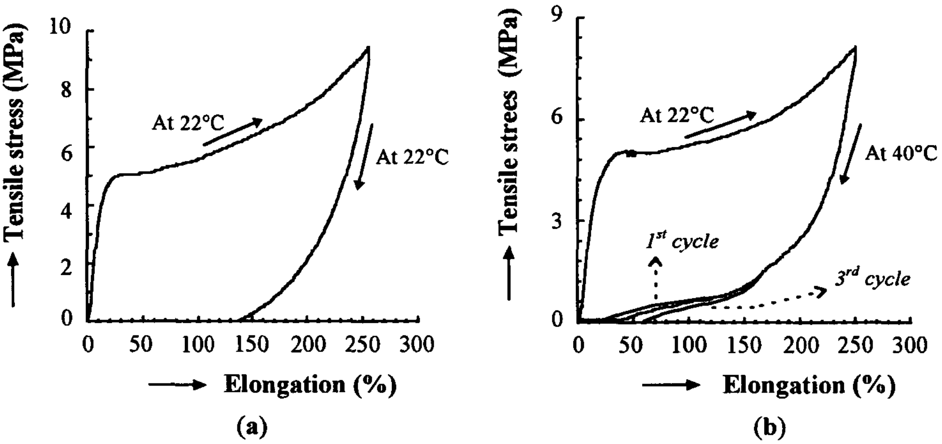


Fig. 2. Stress-strain curves at 22°C of a series of poly(MeOX-THF-MeOX) block-copolymers. The numbers represent the molar masses of the blocks, in g/mol.

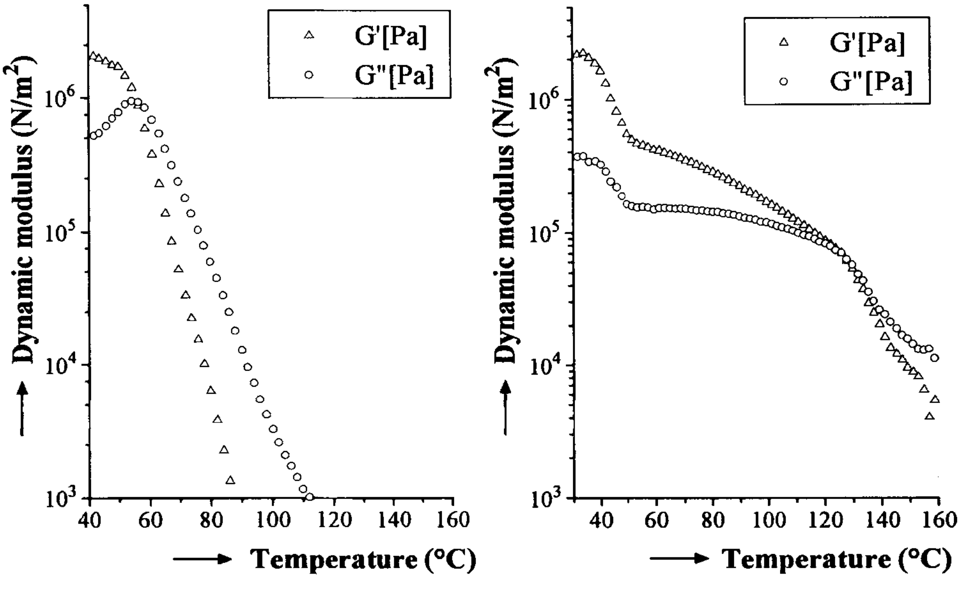


(a) (b)

Fig. 3. Cyclic tensile behaviour of a poly($MeOX_{1500}$-THF_{19000}-$MeOX_{1500}$) block-copolymer: (a) loading and unloading at 22 °C, and (b) loading at 22 °C and unloading at 40 °C.

That some kind of physical network is present, is further evidenced by the observation that these materials show a pronounced shape memory effect if the molecular weight of the central polyTHF block exceeds approximately 11000 g/mol. If a sample is elongated for 250% at 22°C, the deformation is predominantly permanent due to the crystallization of the polyTHF segments. If the deformed sample is heated at 40°C, i.e. above the melting point of the polyTHF segments, it returns almost completely to its original shape. This is shown in Fig. 3.

Analysis of the block-copolymer materials with a rheometer, shown in Fig. 4b, indicates a decrease of the storage modulus G' at 35°C, corresponding to the melting of the crystalline polyTHF fraction, but the loss modulus G'' shows an analogous decrease so that the ratio G''/G' remains constant, i.e. the material does not become a liquid beyond the melting point. The cross-over point of the G' and the G'' curve, which corresponds to the transition of the rubber-like state to the liquid-like state, occurs, for this sample, at 125°C, indicating that a kind of physical cross-linking continues to exist up to this temperature. This is surprising considering the fact that in polyMeOX homopolymers the cross-over point of the G' and the G'' curve occurs at around 60°C (see Fig. 4a). This shift in cross-over point can be explained by the formation of polar polyMeOX domains dispersed in a matrix of polyTHF chains and acting as physical cross-linking sites, as shown schematically in Fig. 5. The polyMeOX blocks are anchored in their domains due to strong dipole-dipole bonding. Indeed, the dipolar resonance form of an amide contributes to the structure for about 40%. In the event of phase separation, interfacial tension favors a reduction in surface area. When a sample is heated under stress, the polyMeOX domains will be disrupted, the physical network loses its strength and eventually the block-copolymer can flow (see Fig. 4b). At this transition, the interfacial tension of the system increases due to the increase in the interfacial surface area. In a polyMeOX homopolymer this phenomenon is non-existant, because it consists of only one phase. This resistance to increase the surface tension leads to a considerable increase of the cross-over point in the G' and the G'' curve: 60°C for a polyMeOX homopolymer (Fig. 4a), versus 125°C for the ABA block-copolymer (Fig. 4b).



(a) (b)

Fig. 4. Evaluation of G' and G" as a function of temperature for (a) poly($MeOX_{1600}$) and (b) a poly($MeOX_{1500}$-THF_{18800}-$MeOX_{1500}$) triblock-copolymer. (Frequency: 1Hz).

These properties show that physical cross-linking caused by phase-separated A-blocks in ABA block-copolymers, does not necessarely require a solid or glassy state of the A-domains. As expected, however, these materials show a marked stress-relaxation behavior above 40°C.

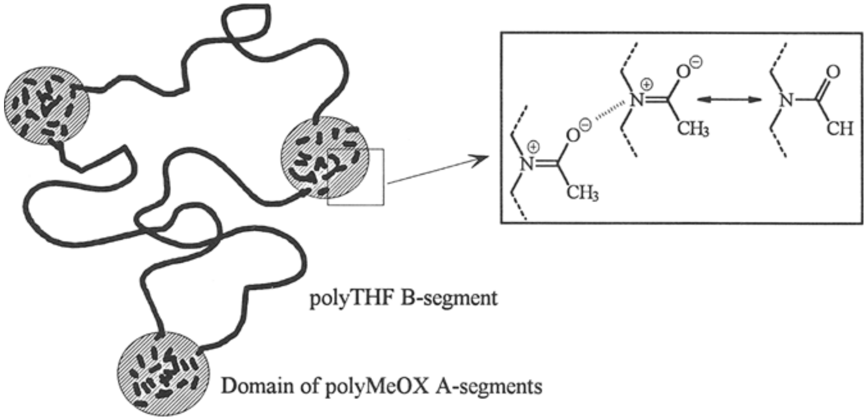


Fig. 5. Proposed model to explain the shape memory effect in the poly($MeOX_{1500}$-THF_{19000}-$MeOX_{1500}$) block-copolymer.

Acknowledgement

PVC thanks the IWT (Vlaams Instituut voor de Bevordering van het Wetenschappelijk-Technologisch Onderzoek in de Industrie) for a scholarship. The Belgian Programme on inter-university attraction poles initiated by the Belgian State, Prime Minister's Office, Science Policy Programming is acknowledged for financial support.

References

1. Riess G, Hurtrez G, Bahudur P (1985) Encyclopedia of Polymer Science and Engineering (Kroschwitz JI, Ed.), Wiley Interscience, New York, Volume 2, p. 324
2. Penczek S, Kubisa P, Matyjaszewski K (1980) Adv Polym Sci 37:1
3. Kobayashi S (1990) Prog Polym Sci 15:751
4. Kobayashi S,Uyama H, Ihara E, Saegusa T (1990) Macromolecules, 23:1586,
5. Smith S, Schultz WJ, Newmark RA (1977) J Macromol Sci A-7:1399
6. D'Haese F, Goethals EJ (1988) Br Polym J 20:103
7. Pruckmayer G, Dreyfuss P, Dreyfuss MP (1996) Encyclopedia of Chemical Technology (Kroschwitz JI, Howy-Grant M, Eds), Wiley Interscience, New York, Volume 19, p. 743
8. Bassari TG, Levy A, Litt M (1967) J Polym Sci B-5:871
9. Donatelli AA, Sperling LH, Thomas DA (1976) Macromolecules 9:671
10. Polymer Handbook, 3rd edition (Brandrup J, and Immergut EH, Eds.), J. Wiley & Sons, New York (1989) chapter VI and VII
11. Van Caeter P, Goethals EJ, unpublished results