Preparation and Properties of Poly(ethylene oxide) Star Polymers

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Received 21 August 2001; accepted 29 April 2002

ABSTRACT: Poly(ethylene oxide) (PEO) star polymers were prepared by anionic polymerization of methacryloyl chloride and glyceryl trimethacrylate with *sec*-butyllithium in cyclohexane. The ensuing polymers were grafted with poly(ethylene glycol) of molecular weight 400. The final product was washed with methylene chloride and analyzed with infrared spectroscopy, differential scanning calorimetry, and thermogravimetry. Star polymers of PEO were also prepared by anionic polymerization of glycidol with *sec*-butyllithium in cyclohexane. The initiator was chosen so as to yield a polymer of 10,000 molecular weight. The resulting polymers were analyzed by nuclear magnetic resonance, infrared spectroscopy, and thermogravimetry. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 322–327, 2003

Key words: star polymers; hydrogels; biomaterials; gels; poly(ethylene oxide)

INTRODUCTION

The optical and mechanical properties of polymers depend on the conformation of the polymer chains. Star polymers are characterized by a high number of identical-size chains emerging out of a small core. The molecular architecture can significantly affect the properties of those polymeric materials. The spherical shape of these polymers and the high order of branching can lead to unique properties. These polymers are compact and have high segment density, which is unobtainable by most other types of polymers. Some of their unique properties are lower crystallinity, low diffusion coefficient, and lower melt viscosity than those of corresponding linear polymers. They are important as model materials to study the effects of branching on the rheology and morphology as they relate to the various proposed theories. Poly(ethylene oxide) (PEO) star polymers, in particular, are of interest because of their applications in enzyme immobilization, as rheology modifiers and polymer surfactants.

Synthesis of star polymers by the multifunctional core with the conjugate functional arm method involves reacting a multifunctional core containing bromine, carboxyl, amine, or hydroxyl groups with a stoichiometric amount of chains containing the conjugate group. First, chains of difunctional acrylic monomers are prepared by anionic polymerization. The anionic polymerization yields monodispersed arm lengths. To the live polymer chains, an electrophilic deactivator core with three to eight sites is added to form a three-to-eight-arm star polymer.

Star polymers have been prepared by numerous methods including arm formation with sequential polymerization of multifunctional monomers from styrene and divinylbenzene (DVB).[1] First, the living polystyrene chains are prepared by anionic polymerization. Upon the consumption of all the styrene, a plurifunctional monomer such as DVB is added. The resulting polymer is a small core with several chains that have contributed to its formation. The arm lengths can be controlled by the stoichiometric proportions of styrene and the initiator, and the arm number is regulated by the stoichiometric quantity of DVB. The "core-first" strategy is based on the multifunctional initiator scheme, in that it also requires the synthesis of a central core first. The reaction is followed by the addition of a monomer such as ethylene oxide to yield a star polymer.[1–4] The limitations of this method include variations in core sizes as dictated by agitation, which causes dispersity in the number of arms, yet this can be controlled to specify the number of arms. Another imperfection often not taken in consideration is the possible reaction of the living polymer arms with the unsaturated vinyl groups of DVB on the cores. This will result in several cores joined together to form larger cores.

Star-shaped polymers have also been synthesized using cationic polymerization as the living polymerization. This polymerization technique works better

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Contract grant sponsor: National Science Foundation.

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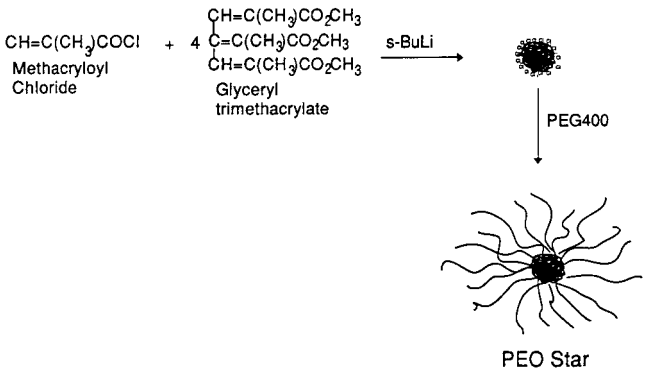

Figure 1 Production of PEO star polymers with methacrylate core.

for monomers with functional groups such as vinyl ethers.[5]

Graft-on-graft strategy yields polymers similar to starbursts since there is branching on branches. It has the advantage of achieving high molecular weights rapidly, but the graft-on-graft polymers lose the well-defined structure of the starburst. Chains capped at their ends by a functional group, with randomly distributed grafting sites, were synthesized by anionic polymerization.[6]

PEO stars were synthesized by Merrill et al.[3] by the "core-first" strategy where living DVB cores were prepared by anionic polymerization and ethylene oxide was added to form the PEO arms. Thin films of these polymers were formed by crosslinking the PEO arms by electron-beam irradiation. The crosslinking occurred randomly between the arms, thus leaving the hydroxyl groups at the ends free. The terminal hydroxyl groups served as binding sites to bind enzymes. The high density of the hydroxyl groups at the periphery of the macromolecules enables them to bind a high concentration of the enzymes.[7] Zhou and Smid[8] also synthesized star polymers from tri- and tetraisocyanates and poly(ethylene glycol) (PEG) derivatives to form amphiphilic molecules.

PEO star polymers are inert to biological media. The PEO chains exhibit a strong tendency to crystallize when unsolvated, and crystallization rates are high; thus, recovery is easier. Finally, the ability of the PEO chains to solvate metal ions is high, especially when several chains are located in close vicinity to each other. The PEO star polymer is envisioned to act as a solubilizing agent for inorganic salts in organic media.

We have devised simple methods of synthesizing PEO star polymers. Well-defined star polymers with a large number of arms functionalized by hydroxyl groups at the tips were prepared and characterized.

EXPERIMENTAL

Synthesis of PEO star polymers

In an 100-mL three-neck flask, provided with a rubber septum, thermometer, and agitator and with a continuous purge of nitrogen provided by an ACE Burlitz device, 80 mL of cyclohexane was injected followed by 0.33 g methacryloyl chloride (MACl) and 4.15 g glyceryl trimethacrylate (GTMA). The system was maintained at 25°C using a water bath. In addition, 0.10 mL of *sec*-butyllithium (*s*-BuLi) was injected. After 12 h of reaction at 25°C, 2.5 mL of PEG with a molecular weight of 400 (PEG 400) was added rapidly to the continuously stirred mixture. The molar ratio of MACl

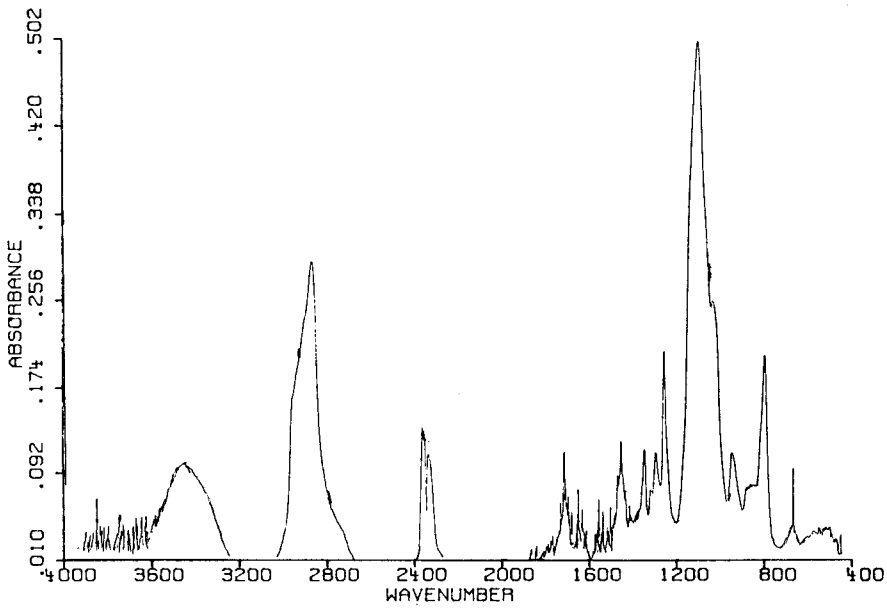

Figure 2 Infrared spectrum of PEO star polymer.

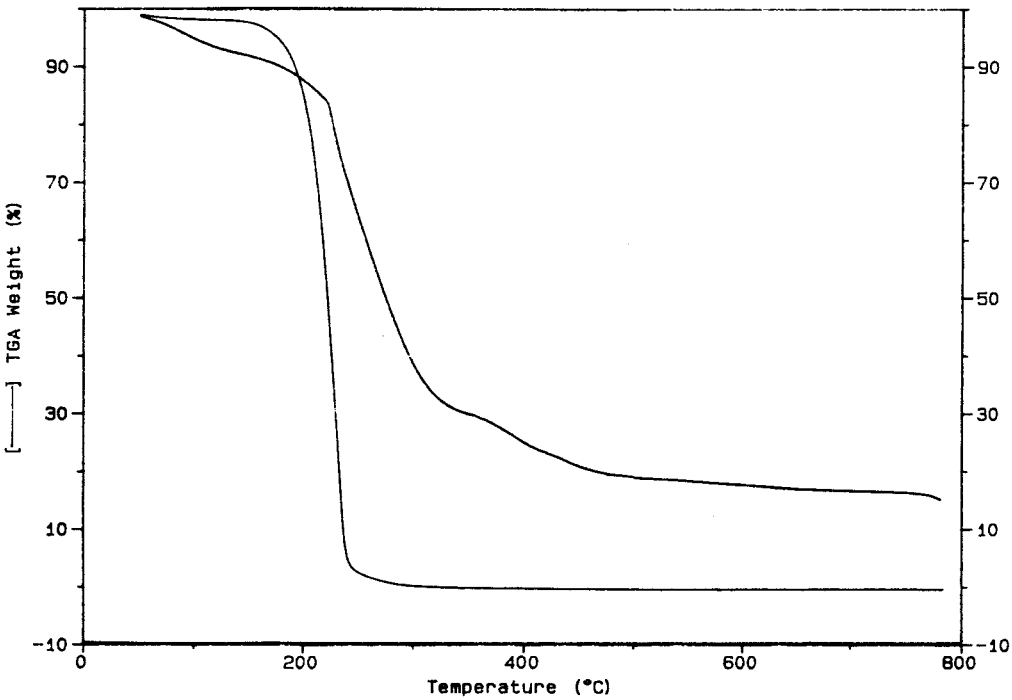

Figure 3 Thermogram of PEO star polymers on thermogravimetric analyzer.

to PEG 400 was 2:1. After an additional 2 h, the nitrogen was turned off and the mixture was recovered.

Star polymer recovery and purification were done by first evaporativing the cyclohexane using a vacuum oven (40°C/10 mmHg). The ensuing polymer was added to dry methylene chloride and the PEO star polymer was precipitated while the excess PEG was dissolved in methylene chloride. The solvent was removed with a pipette while the solids remained at the bottom of the flask. Precipitation and decanting were repeated to obtain the star product in pure form. Finally, the resulting polymer was left in a vacuum oven at 50°C/10 mmHg for 8 h to obtain the final pure PEO star product.

A second type of PEO star polymer was produced in the following way: In a 250-mL three-neck flask equipped with an agitator, thermometer, rubber septum, and a dry nitrogen purge, 180 mL of anhydrous ethyl ether was injected, followed by 5.5 mL of *s*-BuLi. After 1 h, 4.25 mL of GTMA was injected. About 12 min later, 0.75 mL of MACl was injected dropwise. The ensuing polymer was injected into four vials containing purified PEG of molecular weights 400, 1000, 2000, and 3400, respectively.

In a third method, PEO polymer arms were formed by taking an 100-mL three-neck flask equipped with a septum agitator, thermometer, and nitrogen purge and adding 80 mL cyclohexane followed by 4 mL glycidol and 0.10 mL *s*-BuLi. This amount of BuLi was the theoretically necessary quantity for the production of a polymer with a final molecular weight of 10,000. Polymerization took place at 25°C in a water bath for 18 h. The resultant product was a two-layer mixture, the top consisting of cyclohexane, and the bottom, of the polymer. The polymer was very viscous. The cyclohexane was decanted off and the polymer was placed in a vacuum at 100°C/10 mmHg to remove the remaining cyclohexane.

For the production of a pentaerythritol core star polymer, a 250-mL three-neck flask was equipped with an agitator, rubber septum, and nitrogen purge. The rubber septum was momentarily removed and 0.175 μg of pentaerythritol was added with 125 mL of cyclohexane. Ten minutes later, 4.2 mL of *s*-BuLi and 0.34 mL of glycidol were added. A sample of 0.68 mL of glycidol was injected 12 h later. After 1.5 h, 8.3 mL of *s*-BuLi and, another 3 h later, 1.36 mL of glycidol were added. The remaining active ends of the polymer were terminated by 35 mL of anhydrous ethanol addition.

Characterization of the star polymers

Solubilities of the polymers were determined in various solvents. Infrared spectroscopy was performed using an FTIR spectrometer (Nicolet 800, Madison, WI). The PEO star polymer was solubilized in *N,N*-dimethylformamide (DMF). The polymer solution was placed onto polished KBr plates and pressed in a vacuum oven at 23.4 mmHg and 100°C. A fine coating of the PEO star polymer was also obtained by suspension of the polymer in methylene chloride followed by evaporation. A small amount of the PEO star was placed in an NMR spectroscopy tube and the NMR

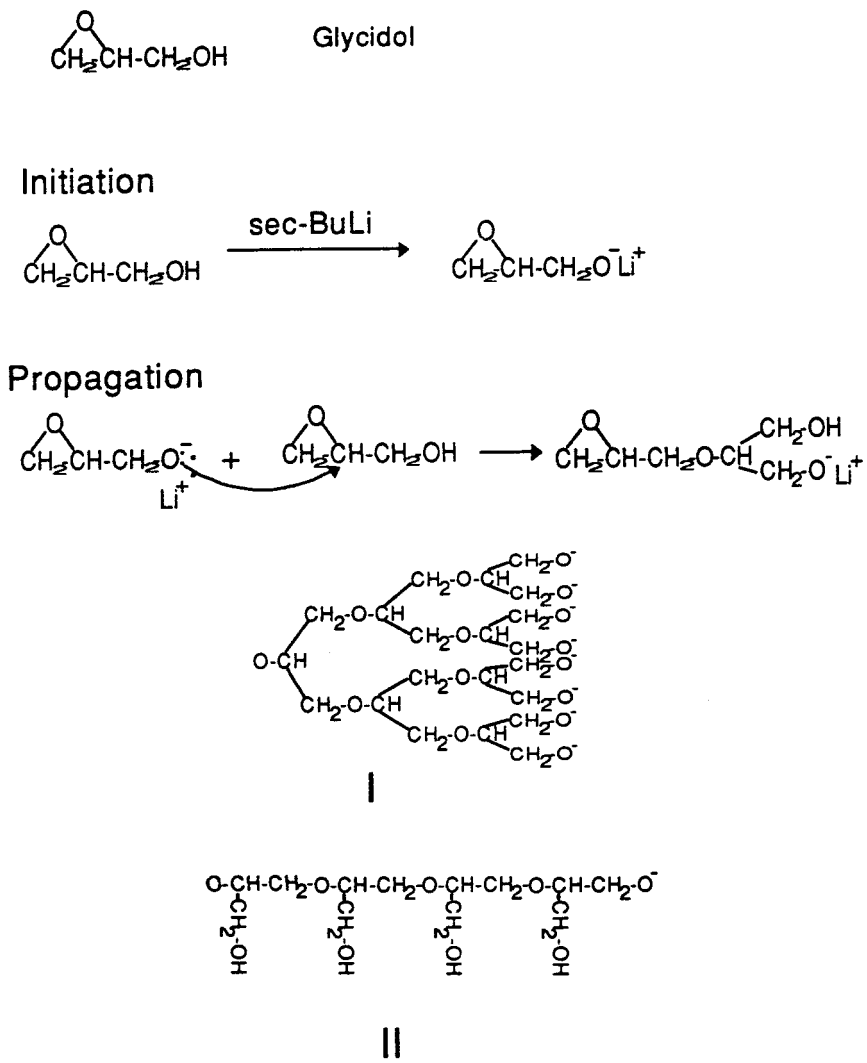

Figure 4 Production of PEO star polymers.

spectrum was recorded on a Gemini-200 spectrometer in $CDCl_3$ as a solvent with tetramethylsilane as an internal standard.

Differential scanning calorimetry (DSC 2910, TA Instruments, Wilmington, DE) was performed at a scanning speed of 10°C/min. The PEO star was heated from room temperature to 300°C. The thermal stability of the polymers and of known molecular weight PEG was tested in a high-resolution thermogravimetric analyzer (Model 2950 TGA, TA Instruments, Wilmington, DE). The scanning speed was set to 10°C/min and the samples were heated from 50 to 800°C.

RESULTS AND DISCUSSION

PEO star polymers

PEO star polymers were synthesized by forming cores of MACl and GTMA via anionic polymerization with *s*-BuLi in cyclohexane. After core formation, PEG of molecular weight 400 (PEG 400) was grafted. The PEG 400 donated a proton to the carbanion, thus terminating the carbanion, attaching itself to the cores to become the arms of the star polymer. The strategy of the synthesis of the new polymer is shown in Figure 1. The star polymers were purified by taking advantage of the high solubility of the PEG 400 and the low solubility of the star polymer in methylene chloride.

The PEO star polymer prepared by the first technique did not dissolve in water, acetone, DMF, chloroform, absolute ethanol, or methylene chloride. However, these star polymers partially dissolved in PEG 400, when excess PEG was added to the core. In principle, the PEO star polymers dissolve when larger PEG chains are grafted and the core character disappears. This behavior was observed in the PEO stars produced by Lutz and Rempp,[1] where the DVB core character was lost when arms of molecular weight 2000 were produced. The PEO star polymer prepared by the second method with 3400 molecular

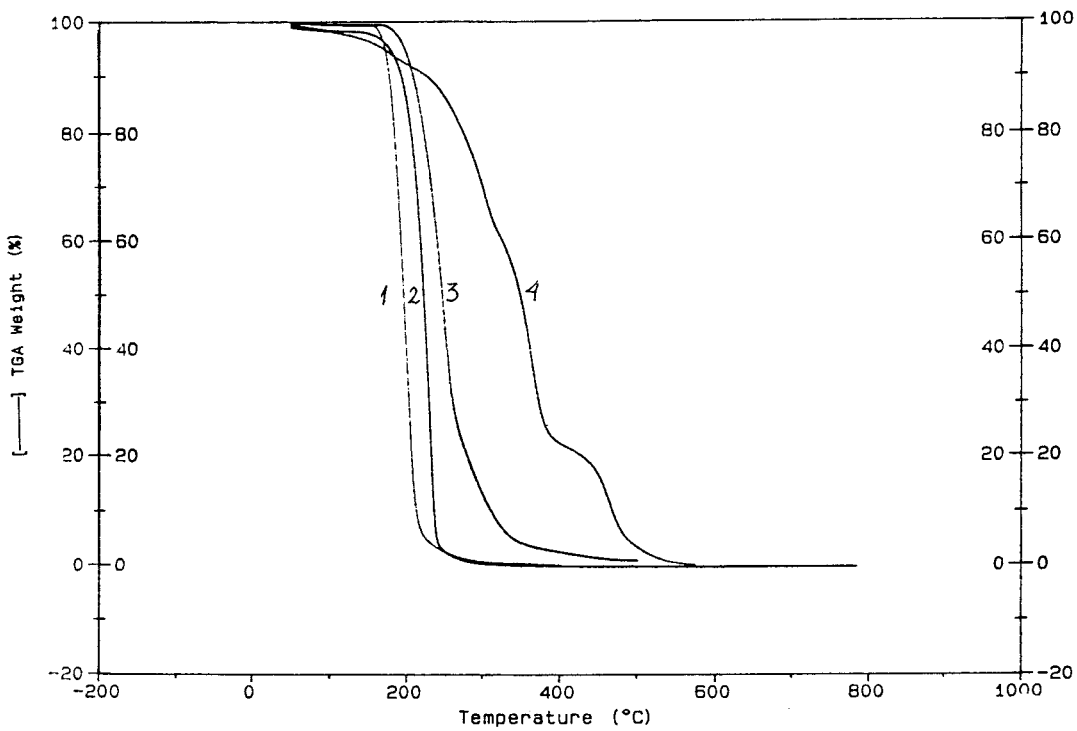

Figure 5 Thermogram of PEO star polymers of number-average molecular weights of (curve 1) 400, (curve 2) 10,000, (curve 3) 14,000, and (curve 4) 19,000.

weight PEG arms dissolved in water and methylene chloride. However, a star polymer with 400 molecular weight PEG arms did not completely dissolve in water.

An infrared spectrum of the PEO polymer cast onto a KBr plate with methylene chloride as the solvent is shown in Figure 2. Here, the carbonyl peaks at 1717 cm^{-1} and the C—O—C stretching bands between 1000 and 1200 cm^{-1} confirm the structure of the polymer as one containing a methacrylate core and PEO arms. The absence of the C═C peak at 1600 cm^{-1} further suggests that all the MACl and GTMA reacted. Of course, if there was a moisture leak in the system, the chloride would have been replaced by a hydroxyl group to form an acid. The absence of the large characteristic acid peak validates that MACl was pure and that the moisture-removal procedure was successful.

The purified samples of the star polymers were analyzed by DSC. The degradation behavior was checked by TGA. A purified sample of the star polymer was analyzed from 50 to 800°C as shown in Figure 3. The figure compares the degradation of the star polymer with the degradation curve of PEG 400. PEG 400 completely degraded between 220 and 240°C. The star polymer began to lose weight from the start but maintained 15% of the original weight even after 800°C. The degradation of the PEG arms occurred at a higher temperature between 250 and 325°C, indicating higher thermal stability. The initial weight loss from 50 and 200°C may be due to trapped water or solvent in the polymer matrix.

PEO stars prepared by the third method, that is, by polymerization of glycidol with *s*-BuLi in cyclohexane, led to polymers obtained as viscous white liquids. The order of addition of glycidol and *s*-BuLi dictated the structure of the macromolecule. If *s*-BuLi was added to glycidol in solution, the product obtained was primarily linear (Case II, Fig. 4) since the attacking anion propagated before the second hydrocyl group had a chance to hydrolyze. When glycidol was added slowlyto *s*-BuLi in solution, the hydrocyl groups at the ends were already available. Thus, all epoxide ring openings resulted in two active ends. Thus, a symmetrical structure could be obtained (Case I, Fig. 4).

NMR spectroscopic studies were performed on the polymer in deuterated chloroform. The spectrum shows two types of protons: CH at 3.8δ and CH_2 at 3.6δ. The peaks were integrated and the relative ratio was calculated as 1:4. Thus, there is one CH for every two CH_2. Similarly, from the analysis of pentaerythritol-cored PEO star polymers, we detected CH at 3.8δ and CH_2 at 3.6δ. The ratio of CH to CH_2 was 7.9 to 33.3. The ratio is greater since the CH_2 from the pentaerythritol appears in the NMR spectrum.

The IR spectrum of the glycidol polymer showed the characteristic stretch of PEO between 1300 and 1500 cm^{-1} and the C—O—C stretch at 1000–1200 cm^{-1}, which confirmed that the polymer is PEO. At 1600 cm^{-1}, there was a peak indicating a C═C bond.

The degradation curve of the starburst PEO and three PEO samples of molecular weights of 400, 14,000, and 18,500 were obtained using TGA (Fig. 5).

The TGA curves shift to the right with increasing molecular weight. The starburst PEO TGA curve has a smaller slope, indicating a lower degradation rate than that of all the linear PEOs, even though its theoretical molecular weight is 10,000. The initial weight loss may be due to trapped water or solvent.

CONCLUSIONS

We showed that PEO star polymers can be produced by three relatively simple methods of polymerization. Their spectroscopic analysis showed a rather simple star structure.

This work was supported, in part, by a grant from the National Science Foundation.

References

1. Lutz, P.; Rempp, P. Makromol Chem 1988, 189, 1051.
2. Martin, M. K.; Ward, T. C.; McGrath, J. E. In Anionic Polymerization: Kinetics, Mechanisms, and Synthesis; ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981; pp 126–132.
3. Merrill, E. W.; Wright, K. A.; Sagar, A.; Pekala, R. W.; Dennison, K. A.; Tay, S.-W.; Sung, C.; Chaikof, E.; Rempp, P.; Lutz, P.; Callow, A. D.; Connolly, R.; Ramberg, K.; Verdon, S. Paper presented at the Fourth International Conference on Polymers in Medicine, Riva del Garda, Italy, Sept. 1990.
4. Cha, X.; Yin, R.; Zhang, X.; Shen, J. Macromolecules 1991, 24, 4985.
5. Kanaoka, S.; Sawamoto, M.; Higashimura, T. Macromolecules 1991, 24, 5741.
6. Gauthier, M.; Moller, M. Macromolecules 1991, 24, 4548.
7. Gnanou, Y.; Lutz, P.; Rempp P. Makromol Chem 1988, 189, 2885.
8. Zhou, G.; Smid, J. Polym Prepr 1991, 32–33, 613.