Inclusion Complex Formation between α,γ-Cyclodextrins and a Triblock Copolymer and the Cyclodextrin-Type-Dependent Microphase Structures of Their Coalesced Samples

Xintao Shuai, Francis E. Porbeni, Min Wei, Todd Bullions, and Alan E. Tonelli*

Fiber and Polymer Science Program, College of Textiles, North Carolina State University, Raleigh, North Carolina 27695-8301

Received November 30, 2001

ABSTRACT: A triblock copolymer (PCL−PPG−PCL, $M_n = 1.38 \times 10^4$) of poly(ϵ-caprolactone) (PCL) and poly(propylene glycol) (PPG) was synthesized by ring-opening polymerization of ϵ-caprolactone. Cyclodextrin (CD)-type-dependent formation of inclusion complexes (ICs) between cyclodextrins and this triblock copolymer was studied. Only PCL blocks were included as guests in the IC formed with α-cyclodextrin (α-CD), while both PCL and PPG blocks were included in the IC formed with γ-cyclodextrin (γ-CD). As a result, the copolymer coalesced from its IC crystals with α-CD showed an increased crystallinity, while to the contrary, the copolymer coalesced from its IC crystals with γ-CD exhibited a decreased crystallinity, when both were compared to the as-synthesized triblock copolymer. Fourier transform infrared (FTIR) spectra, ^{13}C CP/MAS solid-state NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and wide-angle X-ray diffraction (WAXD) measurements were employed to study the formation of ICs as well as to gauge the microphase separation in the coalesced samples.

Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides, consisting of 6, 7, or 8 glucose units, and are named α-, β-, and γ-cyclodextrin.[1] Supramolecular inclusion complexes (ICs) organized by noncovalent interactions can be formed by threading CD molecules onto polymer chains. Since the discovery[2] by Harada et al. that α-CD may form a crystalline IC with poly(ethylene glycol) in aqueous solution, many kinds of linear polymeric guests with either hydrophilic or hydrophobic natures were found to have the ability to form ICs with different types of CDs. For instance, an IC of α-CD with the biodegradable poly(ϵ-lysine) was obtained[3] recently by Yui et al., and according to literature reports, ICs of CDs and aliphatic polyesters have been studied by several groups.[4−6]

The driving force for the threading process is due to intermolecular hydrogen bonding between neighboring CDs, as well as steric compatibility and hydrophobic interactions between host and guest molecules.[7,8] Although the depth of the cavities for the three CD molecules is the same (7.9 Å), their cavity diameters are very different, with ∼4.5, 7, and 8.5−9 Å diameters for α-, β-, and γ-CD, respectively.[9] Therefore, CDs have been found to behave very differently in forming ICs with specific polymer chains. Harada et al. reported[10] that poly(propylene glycol) (PPG) of any molecular weight does not form ICs with α-CD due to the steric hindrance of the side methyl groups, while it forms ICs with both β- and γ-CD in high yield. In contrast, PCL forms ICs with all three CDs,[11] and each channel of the γ-CD−PCL IC is occupied by two parallel, side-by-side PCL chains.[11,12] On the basis of these reports, it is anticipated that architectures of ICs formed between CDs and PCL−PPG−PCL are CD-type-dependent. Consequently, coalescing the copolymer chains from different ICs might result in samples with different phase structures.

We reported very recently attempts to suppress the phase separation in immiscible polymer blends or microphase-separated block copolymer systems by first forming their common ICs with CDs and then coalescing the guest polymers from the IC crystals by washing the ICs with hot water. In this manner, we obtained two intimately mixed blends from poly(methyl methacrylate)/polycarbonate (PMMA/PC)[13] and PCL/PLLA[14] pairs. Furthermore, we obtained a block copolymer of poly(ϵ-caprolactone) and poly(L-lactide), PCL-*b*-PLLA, with very low crystallinity when coalesced from its α-CD−IC.[15]

In this paper, IC formation of PCL−PPG−PCL with α- and γ-CD and the phase separation in copolymer samples coalesced from the two different ICs were studied. Very interestingly, the copolymer sample coalesced from α-CD−copolymer IC exhibited an increase in the crystallinity of PCL blocks, while the copolymer sample coalesced from γ-CD−copolymer IC showed a decrease in the crystallinity of PCL blocks, when both were compared to the as-synthesized triblock copolymer.

Experimental Section

Materials. ϵ-Caprolactone (ϵ-CL) was dried over CaH_2 and distilled at reduced pressure under the protection of dry argon. Toluene (from Fisher) was dried over CaH_2 and distilled under dry argon. CDs (from Cerestar Co.), hexane, dichloromethane, and methanol (from Fisher) were used as received. All solvents were analytical grade. Hydroxyl-terminated poly(propylene glycol) (PPG, $M_n = 3500$, from Aldrich) was dried by azeotropic distillation in dry toluene.

Synthesis of PCL−PPG−PCL. The triblock copolymer was synthesized using PPG-diol and SnOct as an initiator and a catalyst, respectively. Typically, ϵ-CL, SnOct (ca. 0.1% of ϵ-CL in molar amount), and PPG-diol were weighed into a round-bottomed flask equipped with a magnetic stirring bar. The flask was sealed under argon and was immersed in an oil bath at 115 °C for 24 h. The product was purified, by twice precipitating into cold methanol from dichloromethane solu-

* To whom correspondence should be addressed. Tel +1-919-515-6588; FAX +1-919-515-6532; e-mail atonelli@tx.ncsu.edu.

10.1021/ma012085+ CCC: $22.00
Published on Web 02/13/2002

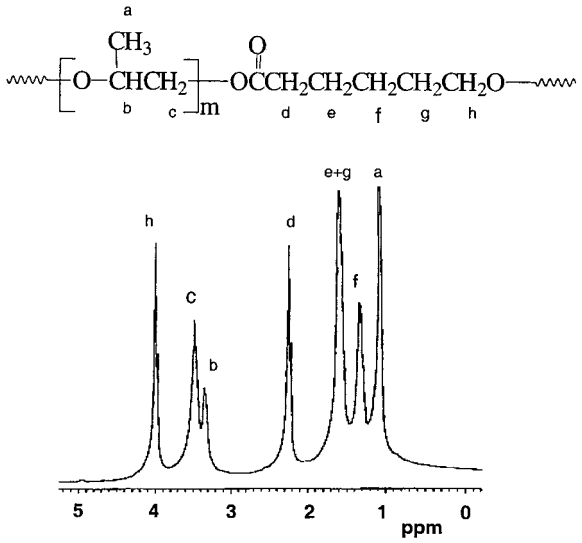

Figure 1. ^{1}H NMR spectrum of as-synthesized triblock copolymer of PCL and PPG in $CDCl_3$.

tion, and was then vacuum-dried at 40 °C. The molecular weight of the copolymer (1.38×10^4) was calculated from integrals of characteristic peaks of the PCL blocks at ~2.25 ppm (doublet, d, $-C(=O)-CH_2-$) and PPG blocks at 1.07 ppm (triplet, a, $-CH_3$) in the ^{1}H NMR spectrum, as shown in Figure 1.

Preparation of Samples. To prepare the inclusion complex, α- or γ-CD (16 g as received) was dissolved in distilled water (60 mL) and heated to 60 °C in a flask equipped with a condenser. PCL−PPG−PCL (0.8 g) was dissolved in acetone (150 mL). Then the polymer solution was added dropwise to the CD solution. After stirring for 3 h at 60 °C, the solution was allowed to cool to room temperature while continuously stirring overnight. A white powder was collected by filtration and then washed repeatedly with acetone and water to remove free polymer and uncomplexed CD, respectively. Finally, the IC was dried in a vacuum oven at 40 °C for 48 h. The coalesced copolymer sample was prepared by the same method we reported previously.[6,14]

Measurements. The FTIR spectral studies were carried out with a Nicolet 510P FTIR spectrometer using a resolution of 2 cm^{-1}. All powder samples were pressed into KBr pellets for the FTIR measurements. Solution ^{1}H NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer in DMSO-d_6 at room temperature. Solid-state ^{13}C NMR data were collected using a Bruker DSX wide-bore system (75 MHz for ^{13}C) with MAS speeds of 4−5 kHz and a CP contact time of 1 ms. DSC measurements were performed at a heating rate of 10 °C/min on a Perkin-Elmer differential scanning calorimeter (DSC-7) calibrated with indium. The thermal decomposition behaviors of samples were measured with a Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA) at a heating rate of 20 °C/min. X-ray diffraction analysis of powder samples was conducted with a Siemens type-F X-ray diffractometer (30 kV, 20 mA) using Ni-filtered Cu Kα radiation.

Results and Discussion

The WAXD patterns of α-CD−copolymer IC and γ-CD−copolymer IC are shown in Figure 2 and Figure 3. The WAXD pattern of pure PCL−PPG−PCL shows diffraction peaks at 22° and 23.8°, which are from crystalline PCL blocks.[15] The diffraction patterns of the two ICs are very different from those of the copolymer and α- or γ-CD and obviously are not simple superpositions of the IC components. No diffraction peaks corresponding to the crystalline phase of PCL blocks were detected in the two ICs. For the α-CD−copolymer IC, two prominent peaks were observed at 20° and 22.6°

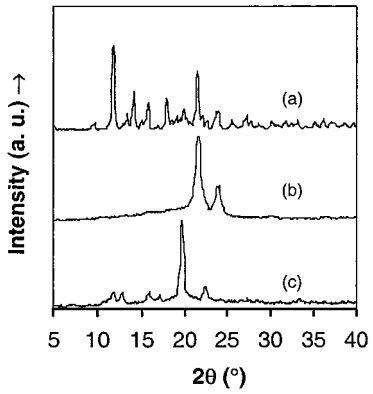

Figure 2. X-ray diffraction patterns of α-CD (a), as-synthesized PCL−PPG−PCL (b), and α-CD−copolymer IC (c).

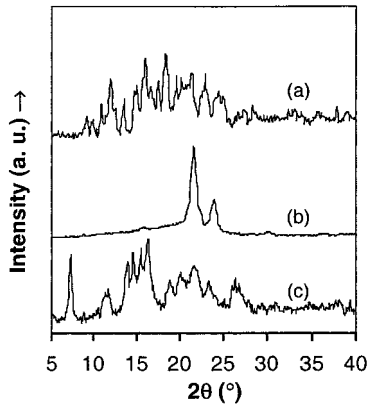

Figure 3. X-ray diffraction patterns of γ-CD (a), as-synthesized PCL−PPG−PCL (b), and γ-CD−copolymer IC (c).

(2θ), which are well-known to be characteristic of α-CD-based IC crystals adopting a channel structure.[3,10,14] For the γ-CD−copolymer IC, a new strong diffraction peak was observed at 7.6°, which is well-known to be characteristic of γ-CD-based IC crystals adopting a channel structure.[10,11,16] The 7.6° peak characteristic of channel structure γ-ICs is not present in the diffraction pattern of pure γ-CD, because it adopts a cage structure.[10,11]

These results indicate that copolymer and α-CD, as well as γ-CD, have formed ICs with a channel structure in which at least the PCL blocks of the copolymer chains are fully included inside the α- or γ-CD channels. Each or pairs of PCL blocks are isolated from others by the surrounding α- or γ-CD molecules; therefore, PCL blocks may not aggregate to form a crystalline phase other than the new generated IC crystals. Since the atactic PPG block is completely amorphous and therefore does not show any diffraction peaks, it is not clear whether the PPG blocks have also been included on the basis of the WAXD measurements. The formation of the two ICs was studied further by FTIR, solid-state CP/MAS ^{13}C NMR, DSC, and TGA measurements.

The solid-state CP/MAS ^{13}C NMR spectra of γ-CD and γ-CD-copolymer IC are shown in Figure 4. The spectrum of γ-CD in the uncomplexed state shows strong splitting for all C_{1-6} resonances, indicating that γ-CD molecules are in a rigid, less symmetric cyclic conformation. On the contrary, for the two ICs prepared in this paper, all ^{13}C resonances of δ-CD showed reduced splitting. This indicates that δ-CD in the ICs has adopted a more symmetric cyclic conformation. Comparable results were obtained for the α-CD−copolymer IC. Similar observa-

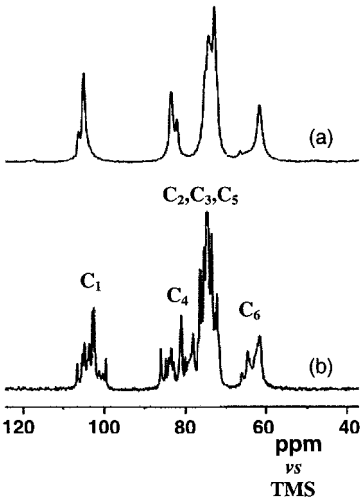

Figure 4. ^{13}C CP/MAS NMR spectra of γ-CD−copolymer IC (a) and γ-CD (b).

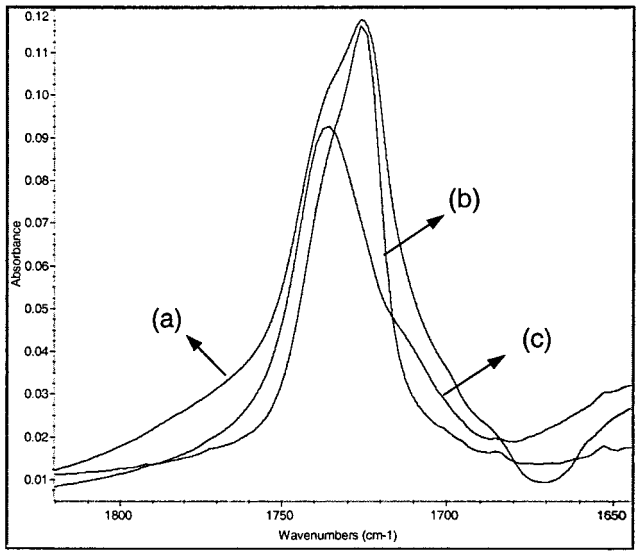

Figure 5. FTIR spectra of as-synthesized PCL−PPG−PCL (a), the sample coalesced from the α-CD−copolymer IC (b), and α-CD−copolymer IC (c).

tions, which are believed to support the formation of ICs between CDs and polymers, have been observed in the solid-state CP/MAS ^{13}C NMR spectra of ICs of various polymers formed with different CDs.[3,10,16]

We have reported that the expansion of the carbonyl regions of FTIR spectra of PCL−CD−ICs gives us very useful information concerning their formation and the phase structures of their coalesced and as-synthesized samples.[15] The PCL carbonyl absorption band (s, $\nu_{C=O}$) of PCL−PPG−PCL is well resolved into a peak at ∼1726 cm^{-1} and a prominent shoulder at ∼1736 cm^{-1}, corresponding to the carbonyl absorption of the crystalline PCL phase and that of the amorphous PCL regions, respectively, according to previous research on semicrystalline PCL.[17] As shown in Figure 5 and Figure 6, the C═O absorption of crystalline PCL regions completely disappears, and only the C═O absorption of noncrystalline PCL blocks is detected in the spectrum of the ICs. This result indicates that, consistent with the WAXD measurement results, no crystalline PCL phase exists in the two ICs, and all PCL blocks have been involved in the inclusion process.

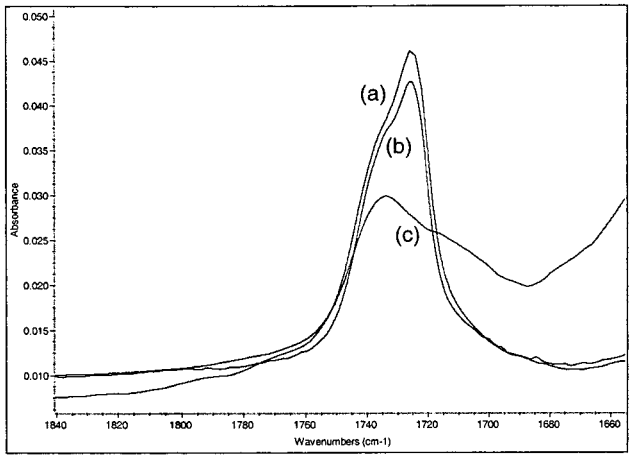

Figure 6. FTIR spectra of as-synthesized PCL−PPG−PCL (a), the sample coalesced from γ-CD−copolymer IC (b), and γ-CD−copolymer IC (c).

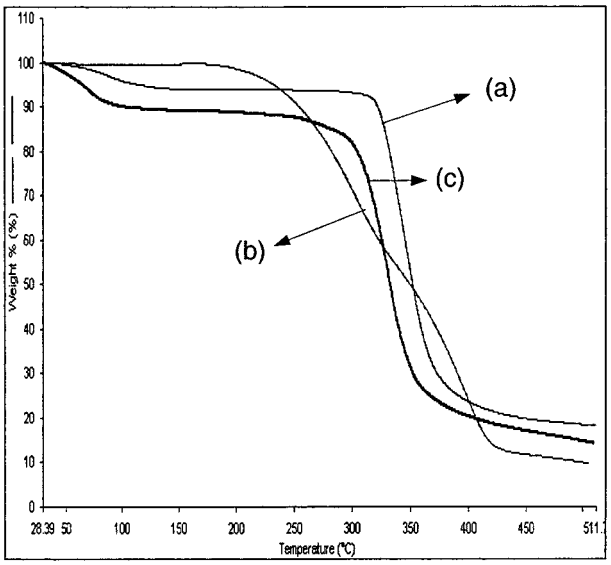

Figure 7. TGA scans of γ-CD (a), as-synthesized PCL−PPG−PCL (b), and γ-CD−copolymer IC (c).

TGA scans are shown in Figure 7 and Figure 8. As-synthesized copolymer shows two distinct decomposition transitions corresponding to the decompositions of PCL and PPG blocks. On the contrary, the γ-CD−copolymer IC exhibits, as shown in Figure 7, a single thermal decomposition transition, indicating that no or negligible amounts of free γ-CD exist, and both PCL and PPG blocks of each copolymer chain were fully included. In contrast, the α-CD−copolymer IC exhibits two thermal decomposition transitions; i.e., a clear decomposition transition of PPG blocks was detected, as shown in Figure 8. Therefore, PPG blocks are not included in the α-CD−copolymer IC channels, though the PCL blocks have been included. These results are consistent with the previous reports that α-CD does not form IC with PPG.[10]

In the DSC measurements of as-synthesized PCL−PPG−PCL, a strong melting peak for the PCL blocks was observed. Although the atactic PPG is completely amorphous, the glass transition of the PPG blocks is too weak to be detected, because the PPG block is too short (DP = 60). No fusion peak was observed for the two ICs in the heating run, which indicates again that PCL blocks have been included in both CD−ICs.

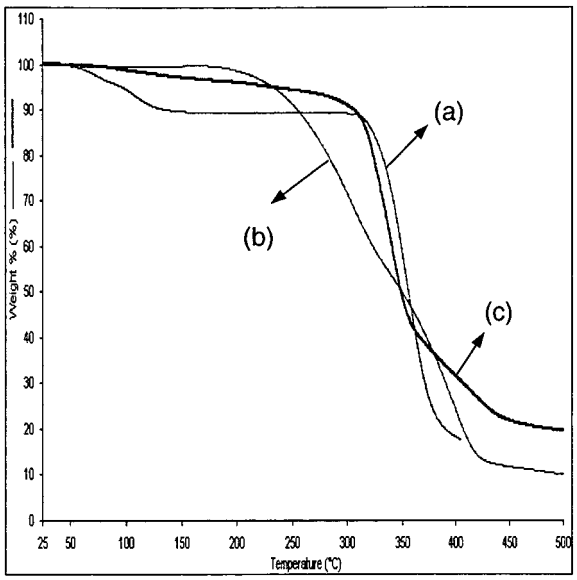

Figure 8. TGA scans of α-CD (a), as-synthesized PCL−PPG−PCL (b), and α-CD−copolymer IC (c).

Table 1. Thermal Properties and Crystallinity of Various PCL−PPG−PCL Triblock Copolymer Samples As Revealed by DSC

identity	T_{m-PCL} (°C)	ΔH_{PCL} (J/g_{sample})	χ_{c-PCL}[a] (%)
as-synthesized copolymer	57.3	58.62	56.5
sample coalesced from α-CD−copolymer IC	63.8	76.84	74.1
sample coalesced from γ-CD−copolymer IC	63.0	51.33	49.5

[a] PCL fraction in the copolymer is 74.6% (in wt %) according to the ^{1}H NMR results, and see ref 15 for χ_c calculation.

From the results discussed above, we concluded that, in the γ-CD−copolymer IC, both PCL and PPG blocks have been included, while in the α-CD−copolymer IC only PCL blocks have been included.

We reported very recently attempts to suppress the phase separation in block copolymers by first forming their inclusion complexes with CDs as the host and then coalescing the guest copolymers from their CD−IC crystals, by washing the ICs with hot water. In this manner, we obtained a coalesced sample of PCL-*b*-PLLA with very low crystallinity; i.e., a decrease in crystallinity of ca. 50% and up to 79% for PCL and poly(L-lactide) (PLLA) blocks, respectively, was detected in DSC measurements of the coalesced sample.[15] In the present work, the crystallinities (χ_c) of PCL blocks in the samples coalesced from γ-CD−copolymer IC and from α-CD−copolymer IC were investigated. DSC results shown in Table 1, however, indicate opposite changes in the PCL crystallinity for the two coalesced samples, compared to the as-synthesized PCL−PPG−PCL. The crystallinity of PCL blocks in the sample coalesced from γ-CD−copolymer IC decreased, while the crystallinity of PCL blocks in the sample coalesced from α-CD−copolymer IC showed an obvious increase. Melting temperatures of the PCL blocks (T_m) in both coalesced samples increased slightly, which are consistent with the results discovered in the coalesced sample from α-CD/PCL-*b*-PLLA IC.

The expansion of the carbonyl region of the FTIR spectra, as shown in Figure 5, also shows evidence that the crystallinity of PCL blocks in the sample coalesced from α-CD−copolymer IC is higher than that of PCL blocks in the as-synthesized copolymer sample. The $\nu_{C=O}$ band of PCL becomes sharper, and the noncrystalline $\nu_{C=O}$ shoulder at 1736 cm^{-1} becomes weaker. In contrast, the $\nu_{C=O}$ band of PCL blocks in the sample coalesced from γ-CD−copolymer IC does not show obvious changes compared to that of PCL blocks in the as-synthesized copolymer, probably because the decrease of PCL crystallinity in the coalesced sample, as revealed by DSC measurement, was too small for detection by FTIR.

Considering the structural differences between the two IC samples, the opposing changes in the PCL crystallinity of the two coalesced samples are not unexpected. Since only PCL blocks are included in the α-CD-copolymer IC, the neighboring IC channels should be filled only with extended PCL blocks. Therefore, PCL blocks will aggregate easily when the CD molecules are washed way. Although PPG may affect the crystallization of PCL blocks in the as-synthesized copolymer, the aggregation of neighboring PCL blocks should not be affected by the uncomplexed PPG blocks in the process of copolymer coalescence. Therefore, the observed increased crystallinity of PCL blocks in this coalesced sample is reasonable. In contrast, PCL and PPG blocks should have the opportunity to be included in neighboring channels of the γ-CD−copolymer IC, since both PCL and PPG blocks have been included. This means that the aggregation of some PCL blocks might be hindered by PPG blocks in the process of copolymer coalescence, as occurred with PCL-*b*-PLLA.[15] Therefore, a decrease in PCL crystallinity for this coalesced sample also seems reasonable.

Conclusions

Triblock copolymer, PCL−PPG−PCL, was synthesized by coordinated ring-opening polymerization of ϵ-caprolactone with PPG-diol as the initiator. In the IC of PCL−PPG−PCL and α-CD, only PCL blocks were included. In contrast, both PCL and PPG blocks were included in the IC of PCL−PPG−PCL and γ-CD. Consequently, coalescence of the copolymer chains from these two CD−ICs yielded samples showing opposite changes in the PCL block crystallinity. The crystallinity of the sample coalesced from α-CD−copolymer IC is obviously higher than that of the as-synthesized copolymer. On the contrary, the crystallinity of the sample coalesced from γ-CD−copolymer IC is lower than that of the as-synthesized copolymer.

Acknowledgment. We are grateful to the National Textile Center (U.S. Department of Commerce) for supporting this research. X.S. is grateful to ERC and the Technical Research Center of Physics and Chemistry of the Chinese Academy of Sciences for allowing him to visit with Prof. A. E. Tonelli. We also thank Prof. Jeffrey L. White for the use of his solid-state NMR spectrometer.

References and Notes

(1) Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 803.
(2) Harada, A.; Kamachi, M. *Macromolecules* **1990**, *23*, 2821.
(3) Huh, K. M.; Ooya, T.; Sasaki, S.; Yui, N. *Macromolecules* **2001**, *34*, 2402.

(4) Weickenmeir, M.; Wenz, G. *Macromol. Rapid Commun.* **1997**, *18*, 1109.
(5) Harada, A.; Nishiyama, T.; Kawaguchi, Y.; Okada, M.; Kamachi, M. *Macromolecules* **1997**, *30*, 7115.
(6) (a) Rusa, C.; Luca, C.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 1318. (b) Huang, L.; Allen, E.; Tonelli, A. E. *Polymer* **1998**, *39*, 4857.
(7) Fujita, H.; Ooya, T.; Yui, N. *Macromolecules* **1999**, *32*, 2534.
(8) Ceccato, M.; Lo Nostro, P.; Baglioni, P. *Langmuir* **1997**, *13*, 2436.
(9) Harada, A.; Li, J.; Kamachi, M. *Nature (London)* **1994**, *370*, 126.
(10) Harada, A.; Suzuki, S.; Okada, M.; Kamachi, M. *Macromolecules* **1996**, *29*, 5611.
(11) Kawaguchi, Y.; Nishiyama, T.; Okada, M.; Kamachi, M.; Harada, A. *Macromolecules* **2000**, *33*, 4472.
(12) Lu, J.; Mirau, P. A.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 3276.
(13) Wei, M.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 4061.
(14) Rusa, C. C.; Tonelli, A. E. *Macromolecules* **2000**, *33*, 5321.
(15) Shuai, X.; Porbeni, F. E.; Wei, M.; Shin, I. D.; Tonelli, A. E. *Macromolecules* **2001**, *34*, 7355.
(16) Porbeni, F. E.; Edeki, E. M.; Shin, I. D.; Tonelli, A. E. *Polymer* **2001**, *42*, 6907.
(17) He, Y.; Inoue, Y. *Polym. Int.* **2000**, *49*, 623.

MA012085+