Macromolecules **1994,** *27,* 6736-6739

Immiscibility Window in Blends of Poly(hydroxy ether of Bisphenol A) with Poly(2,2-dichloroethyl methacrylate-*co*-methyl methacrylate)

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Received May 16, 1994; Revised Manuscript Received August 15, 1994[®]

ABSTRACT: The miscibility of poly(hydroxy ether of Bisphenol A) (phenoxy) with poly(2,2-dichloroethyl methacrylate-*co*-methyl methacrylate) (DCEMA-MMA) was studied by differential scanning calorimetry and Fourier-transform infrared spectroscopy. The three binary homopolymer pairs, phenoxy/poly(methyl methacrylate) (PMMA), phenoxy/poly(2,2-dichloroethyl methacrylate) (PDCEMA), and PDCEMA/PMMA, are miscible. However, phenoxy is immiscible with DCEMA-MMA when the MMA content in the copolymer is between 64 and 98 wt %, showing an immiscibility window. Infrared studies showed that phenoxy interacts more strongly with PDCEMA than with PMMA or DCEMA-MMA copolymers.

Introduction

There are numerous examples of the so-called "miscibility window" phenomenon in which a homopolymer (A) is miscible with a copolymer (BC) over a certain copolymer composition range, even though the three binary homopolymer pairs are immiscible. Such examples include blends of polymethacrylates with poly(styrene-*co*-acrylonitrile) (SAN),[1-3] poly(α-methylstyrene-*co*-acrylonitrile) (αMSAN),[4] poly(*p*-methylstyrene-*co*-acrylonitrile) (pMSAN),[5] and poly(styrene-*co*-methacrylonitrile) (SMAN).[6,7] In terms of a binary interaction model,[8-10] the interaction parameter χ_{blend} is related to three segmental interaction parameters by the equation

$$\chi_{\text{blend}} = y\chi_{\text{AC}} + (1 - y)\chi_{\text{AB}} - y(1 - y)\chi_{\text{BC}}$$

where y is the volume fraction of the C segment in the copolymer. Even though all three segmental interaction parameters are positive, a negative χ_{blend} can result over a certain range of y values if χ_{BC} is a sufficiently large positive value such that

$$(\chi_{\text{BC}})^{1/2} > (\chi_{\text{AB}})^{1/2} + (\chi_{\text{AC}})^{1/2}$$

It has been pointed out that an "immiscibility window" may exist in homopolymer A/copolymer BC blends.[9,10] In this case, the three binary homopolymer pairs are miscible, but homopolymer A is immiscible with the copolymer over a certain copolymer composition range. According to the first equation, when all the segmental interaction parameters are negative, a positive χ_{blend} can result over a certain range of y values if χ_{BC} is a sufficiently large negative value such that

$$(-\chi_{\text{BC}})^{1/2} > (-\chi_{\text{AB}})^{1/2} + (-\chi_{\text{AC}})^{1/2}$$

Shiomi et al.[11] reported that several poly(vinyl chloride-*co*-vinyl acetate) (VC-VAc) samples are immiscible with poly(*n*-butyl methacrylate-*co*-isobutyl methacrylate) (nBMA-iBMA) over a certain copolymer composition range of nBMA-iBMA, although every pair of VC-VAc copolymer/nBMA homopolymer, VC-VAc copolymer/iBMA homopolymer, and nBMA homopolymer/iBMA homopolymer is miscible. If the VC-VAc copolymer is regarded as a homopolymer, the system is then an example of the existence of an "immiscibility window" in homopolymer/copolymer blends. However, the immiscibility windows are observed only at some elevated temperatures, and the VC-VAc copolymers are completely miscible with nBMA-iBMA copolymers of various compositions at room temperature. Fernandes et al.[12] studied the miscibility of poly(methyl methacrylate) (PMMA) with poly(epichlorohydrin-*co*-ethylene oxide) and found that the three segmental interaction parameters are negative, but PMMA is miscible with the only copolymer sample (Hydrin 200) used in their study.

We now report the miscibility behavior of poly(hydroxy ether of Bisphenol A) (phenoxy) with poly(2,2-dichloroethyl methacrylate-*co*-methyl methacrylate) (DCEMA-MMA). Phenoxy is miscible with PMMA, and the blends show lower critical solution temperature (LCST) behavior.[13-15] We have earlier reported that poly(2,2-dichloroethyl methacrylate) (PDCEMA) is miscible with PMMA.[16] It will be shown that phenoxy is also miscible with PDCEMA, and the blends of phenoxy with DCEMA-MMA show an immiscibility window.

Experimental Section

The monomer 2,2-dichloroethyl methacrylate (DCEMA) was prepared by esterification of methacrylic acid with 2,2-dichloroethanol as described previously.[16] Polymerization of DCEMA was carried out in a 2-butanone at reflux temperature for 20 h using 0.25% by weight of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. Monomeric methyl methacrylate (MMA) was a commerical product of Merck; it was purified by distillation at atmospheric pressure before use. A series of DCEMA-MMA copolymers of various compositions were prepared by solution polymerization in 2-butanone at reflux temperature using 0.25 wt % of AIBN as initiator. The maximum degree of conversion was controlled to about 7% to minimize composition drift. The copolymers were precipitated into excess methanol, purified, and dried as usual. The DCEMA content of the copolymers was determined by the amount of chlorine through elemental analysis. In the following discussion, the number after DCEMA-MMA denotes the weight percentage of MMA in the copolymers. The molecular weights of DCEMA-MMA copolymers were determined with a Waters 410 gel permeation chromatograph in tetrahydrofuran (THF) at 30 °C using polystyrene as standards. Phenoxy was obtained from Scientific Polymer Products Inc. The characteristics of various polymers used in this work are listed in Table 1.

All the phenoxy/PDCEMA and phenoxy/DCEMA-MMA blends in various weight ratios were prepared by solution casting

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[®] Abstract published in *Advance ACS Abstracts,* September 15, 1994.

0024-9297/94/2227-6736$04.50/0

Table 1. Characteristics of Polymers

samples	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	T_g (°C)
phenoxy	28[a]		95
PDCEMA	84	42	73
DCEMA-MMA58	52	46	101
DCEMA-MMA62	45	37	103
DCEMA-MMA64	30	17	105
DCEMA-MMA70	71	40	108
DCEMA-MMA77	52	39	110
DCEMA-MMA78	69	43	111
DCEMA-MMA81	79	46	116
DCEMA-MMA83	69	41	116
DCEMA-MMA98	110	55	120

[a] Provided by supplier.

from THF at room temperature. Solvent was allowed to evaporate slowly over a period of 1–2 days. The blends were then dried in vacuo at 90 °C for 7 days.

The glass transition temperatures (T_g) of various samples were determined with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20 °C/min. The T_g was taken as the initial onset of the change of slope in the DSC curve. To help ascertain the miscibility of the blends, samples were also subjected to an annealing process. Each sample was first heated to 125 °C and kept at the temperature for 5 min; it was then rapidly cooled to room temperature, followed by annealing at 70 °C for 21 days. The appearance of a single enthalpy recovery peak of an annealed blend is indicative of a miscible blend.[17-19] The annealing technique is particularly useful in ascertaining the miscibility of blends in which the T_g values of the component polymers are close to each other. Since the T_g values of some DCEMA-MMA copolymers are close to that of phenoxy, it is necessary to use the annealing technique to help ascertain miscibility. All the miscible blends were examined for the existence of LCST behavior by using the method described previously.[20]

Samples for Fourier-transform infrared (FTIR) investigations were prepared by casting from a 2% w/v solution in THF onto potassium bromide disks. The solvent was first allowed to evaporate slowly at room temperature. The cast films were then dried in vacuo at 90 °C for 7 days.

Infrared spectra were recorded on a Perkin-Elmer 1725X Fourier-transform infrared spectrophotometer using a SPECAC high-temperature cell equipped with an automatic heat controller. Nitrogen gas was continuously purged into the system to ensure the dryness of the sample chamber. Results from a minimum of 32 scans were signal averaged at a resolution of 2 cm^{-1}. Films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed.

Results and Discussion

All the phenoxy/PDCEMA blends were transparent and remained so on heating to 235 °C where discoloration began to develop. Figure 1 shows the T_g–composition curve of the blend system. The existence of a single T_g in each blend shows that phenoxy is miscible with PDCEMA. To further confirm the single-T_g nature of the blends, the blends were also annealed at 70 °C for 21 days. Each of the annealed blends showed only a single enthalpy recovery peak, confirming that phenoxy is indeed miscible with PDCEMA.

Figure 2 shows the FTIR spectra recorded at 30 °C of phenoxy and phenoxy/PDCEMA blends in the hydroxyl stretching region of 3100–3700 cm^{-1}. Phenoxy has a broad band at 3567 cm^{-1} which is attributed to free hydroxyl groups and a broad band centered at 3435 cm^{-1} representing a wide distribution of hydrogen-bonded hydroxyl groups. As PDCEMA is added to phenoxy, there is a gradual reduction in the intensity of the free hydroxyl band. On the other hand, the center of the hydroxyl band of phenoxy is first shifted to higher frequencies but, as the PDCEMA content in the blend increases, the center of the hydroxyl band shifts to lower frequencies. In contrast, the hydrogen-bonded hydroxyl band of phenoxy in phenoxy/PMMA blends continuously shifts to higher frequencies with increasing PMMA content.[15]

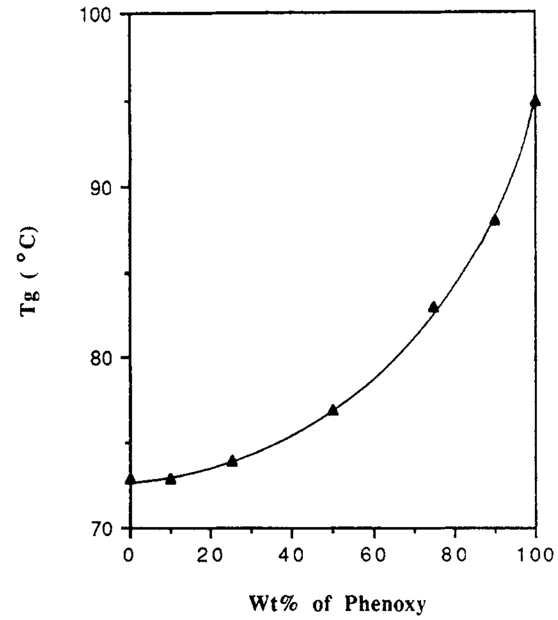

Figure 1. T_g–composition curve of phenoxy/PDCEMA blends.

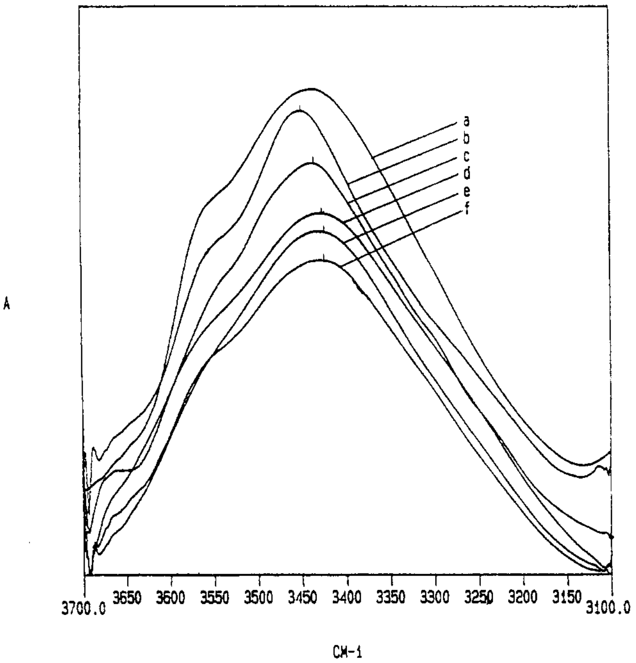

Figure 2. FTIR spectra recorded at 30 °C in the region 3100–3700 cm^{-1} for (a) 100% phenoxy and (b) 9:1, (c) 3:1, (d) 1:1, (e) 1:3, and (f) 1:9 phenoxy/PDCEMA blends.

Figure 3 shows the FTIR spectra of phenoxy/PDCEMA blends recorded at 150 °C which is above the T_g's of various blends. As compared to the spectra at 30 °C, the free hydroxyl band is more intense, showing that thermal agitation disrupts some of the self-association in phenoxy. An increase in the PDCEMA content leads to a reduction in the intensity of the free hydroxyl band and a shift to a lower frequency of the hydrogen-bonded hydroxyl band. Since frequency shift can be taken as a measure of the average strength of intermolecular interaction,[21] the present results show that the interaction between the hydroxyl groups in phenoxy and PDCEMA is stronger than that of the self-association of hydroxyl groups of phenoxy and it is also stronger than that between phenoxy and PMMA.

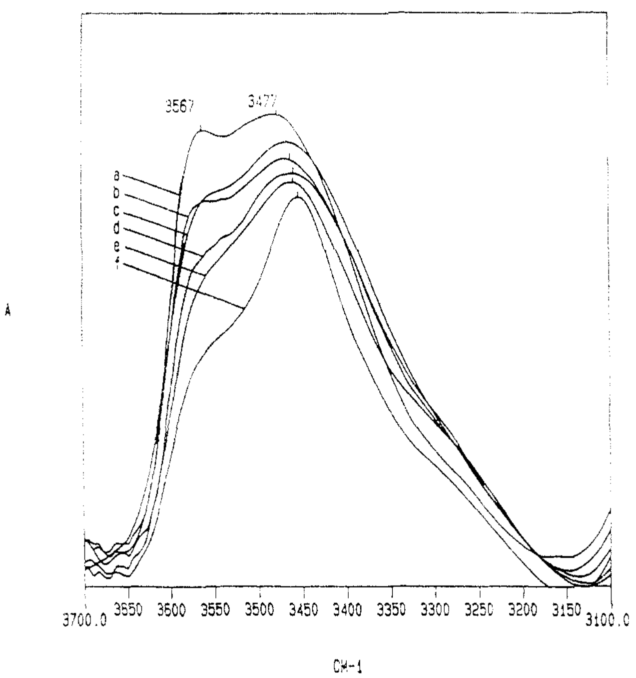

Figure 3. FTIR spectra recorded at 150 °C in the region 3100–3700 cm^{-1} for (a) 100% phenoxy and (b) 9:1, (c) 3:1, (d) 1:1, (e) 1:3, and (f) 1:9 phenoxy/PDCEMA blends.

All the blends of phenoxy and DCEMA-MMA58 and DCEMA-MMA62 were transparent and remained so on heating to about 235 °C where discoloration began to develop. Each of the annealed blends showed a single enthalpy recovery peak which moved progressively to a higher temperature with increasing DCEMA-MMA content. The results show that phenoxy is miscible with these two copolymer samples.

In contrast, all the blends of phenoxy with DCEMA-MMA copolymers having MMA contents between 64 and 98 wt % were cloudy, suggesting the heterogeneous nature of the blends. Each of the annealed blends showed two enthalpy recovery peaks, indicating that phenoxy is immiscible with these copolymer samples. The present study shows that while phenoxy is miscible with PMMA and PDCEMA, it is immiscible with DCEMA-MMA copolymer when the MMA contents are in the range 64–98 wt %, showing an immiscibility window. The cloudiness of the cast blends at room temperature indicates that the immiscibility window exists at room temperature.

Figure 4 shows the FTIR spectra recorded at 30 °C in the hydroxyl stretching region of various phenoxy/DCEMA-MMA (1:1) blends. One notable point is that the center of the broad hydrogen-bonded hydroxyl band of phenoxy shifts to higher frequencies upon mixing with various copolymers. This observation shows that the self-association of phenoxy is stronger than the interactions between phenoxy and the copolymers. This is in contrast with that observed in the phenoxy/PDCEMA blends in which the interpolymer interaction is stronger than the self-association of phenoxy.

It may appear surprising that the incorporation of only 2 wt % of DCEMA segment into PMMA leads to immiscibility with phenoxy. Phenoxy is miscible with PMMA but not with other poly(alkyl methacrylate)s such as poly(ethyl methacrylate) and poly(*n*-propyl methacrylate).[22,23] As mentioned earlier, the interaction between PMMA and phenoxy is weaker than the self-association of phenoxy. It is then reasonable that a slight modification in the structure of PMMA could significantly affect its miscibility with phenoxy.

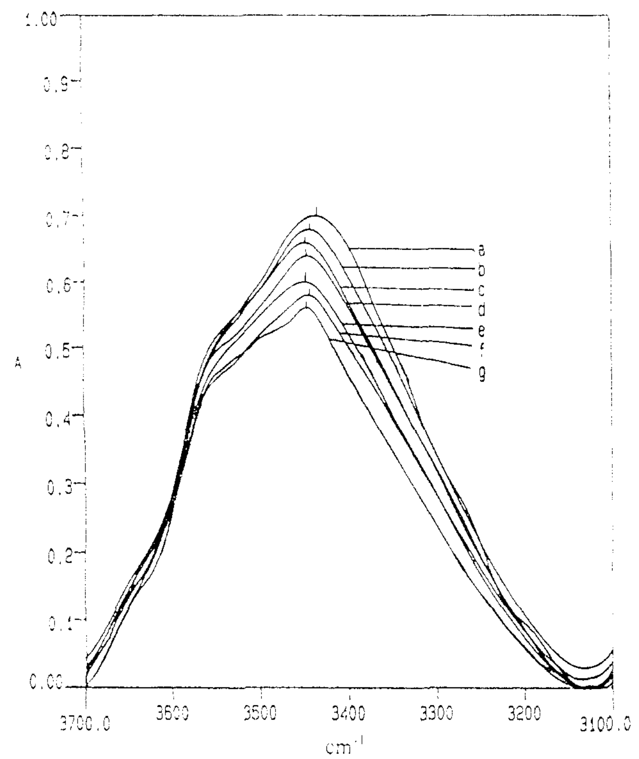

Figure 4. FTIR spectra recorded at 30 °C in the region 3100–3700 cm^{-1} for phenoxy/DCEMA-MMA (1:1) blends: (a) 100% phenoxy; (b) DCEMA-MMA58; (c) DCEMA-MMA62; (d) DCEMA-MMA64; (e) DCEMA-MMA77; (f) DCEMA-MMA83; (g) DCEMA-MMA98.

In terms of the binary interaction model, the interaction parameter χ_{blend} of the phenoxy/DCEMA-MMA blend system is given by the equation

$$\chi_{\text{blend}} = y\chi_{\text{phenoxy/MMA}} + (1-y)\chi_{\text{phenoxy/DCEMA}} - y(1-y)\chi_{\text{DCEMA/MMA}}$$

where y is the volume fraction of MMA in the copolymer. The criterion for miscibility is that

$$\chi_{\text{blend}} < \chi_{\text{crit}}$$

where $\chi_{\text{crit}} = 0.5(N_1^{-1/2} + N_2^{-1/2})^2$, with N_1 and N_2 being the degrees of polymerization in terms of a certain reference volume. At the miscibility/immiscibility boundary, χ_{blend} equals χ_{crit} which is zero for polymers with high molecular weights. Thus the two y values at the phase boundaries and a knowledge of any one of the segmental interaction parameters would enable the evaluation of the remaining two segmental interaction parameters. Unfortunately, all the segmental interaction parameters are unknown. The evaluation of $\chi_{\text{DCEMA/MMA}}$ from the phase behavior of DCEMA-MMA copolymers with PMMA or PDCEMA is not feasible. χ_{blend} for the PMMA/DCEMA-MMA and PDCEMA/DCEMA-MMA systems are expressed by $(1-y)^2\chi_{\text{DCEMA/MMA}}$ and $y^2\chi_{\text{DCEMA/MMA}}$, respectively. Since $\chi_{\text{DCEMA/MMA}}$ is smaller than χ_{crit} in view of the miscibility of PMMA/PDCEMA blends, there will be no miscibility/immiscibility boundaries for the two blend systems. For the mixing of two DCEMA-MMA copolymers of different compositions, χ_{blend} is given by $(x-y)^2\chi_{\text{DCEMA/MMA}}$ where x and y are the volume fractions of MMA in the two copolymers. Similarly, there will be no miscibility/immiscibility boundaries to enable the evaluation of $\chi_{\text{DCEMA/MMA}}$. Nonetheless, the variation of χ_{blend} as a function of y for the phenoxy/DCEMA-MMA blend system is shown schematically in Figure 5 in which $\chi_{\text{phenoxy/MMA}}$

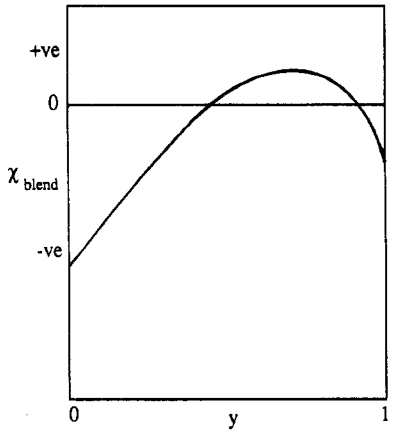

Figure 5. Variation of χ_{blend} as a function of copolymer composition.

is taken to be a small negative quantity. In addition, $\chi_{\text{phenoxy/DCEMA}}$ is taken to be smaller (more negative) than $\chi_{\text{phenoxy/MMA}}$ since FTIR studies have shown that phenoxy interacts more strongly than PDCEMA than with PMMA. Under those conditions, a y value slightly smaller than unity could give rise to a positive χ_{blend} and an immiscibility window could be observed for copolymers with rather high MMA contents.

In summary, the present study shows the existence of an immiscibility window in blends of phenoxy with DCEMA-MMA copolymers. To our knowledge, this is the first example of a homopolymer/copolymer system showing an immiscibility window at room temperature.

Acknowledgment. We thank the National University of Singapore for its financial support of this research.

References and Notes

(1) Suess, M.; Kressler, J.; Kammer, H. W. *Polymer* **1987**, *28*, 957.
(2) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.
(3) Cowie, J. M. G.; Lath, D. *Makromol. Chem. Macromol. Symp.* **1988**, *16*, 103.
(4) Cowie, J. M. G.; Elexpuru, E. M. *Eur. Polym. J.* **1992**, *28*, 623.
(5) Goh, S. H.; Siow, K. S.; Lee, S. Y. *Eur. Polym. J.* **1991**, *27*, 921.
(6) Goh, S. H.; Lee, S. Y.; Siow, K. S.; Chen, J. *Polymer* **1993**, *34*, 2898.
(7) Cowie, J. M. G.; Watson, L. M.; McEwen, I. J. *Polym. Bull.* **1993**, *31*, 729.
(8) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(9) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(10) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(11) Shiomi, T.; Suzuki, M.; Tohyama, M.; Imai, K. *Macromolecules* **1989**, *22*, 3578.
(12) Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1986**, *32*, 5481.
(13) Chiou, J. S.; Paul, D. R. *J. Appl. Polym. Sci.* **1991**, *42*, 279.
(14) Erro, R.; Gaztelumendi, M.; Nazabal, J. *New Polym. Mater.* **1992**, *3*, 87.
(15) Soh, Y. S. *J. Appl. Polym. Sci.* **1992**, *45*, 1831.
(16) Low, S. M.; Goh, S. H.; Lee, S. Y. *Macromolecules* **1994**, *27*, 3764.
(17) Bosma, M.; ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(18) Grooten, R.; ten Brinke, G. *Macromolecules* **1989**, *22*, 1761.
(19) Jorda, R.; Wilkes, G. L. *Polym. Bull.* **1988**, *20*, 479.
(20) Goh, S. H.; Lee, S. Y.; Siow, K. S.; Neo, M. K. *Polymer* **1990**, *31*, 1065.
(21) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228.
(22) Coleman, M. M.; Yang, X.; Painter, P. C.; Graf, J. F. *Macromolecules* **1992**, *25*, 4414.
(23) Goh, S. H.; Lee, S. Y.; Siow, K. S.; Hong, J. *Polym. Bull.* **1993**, *30*, 691.