# Cross-Linked Polymer Brushes. 1. Synthesis of Poly[$\beta$-(vinyloxy)ethyl cinnamate]-*b*-poly(isobutyl vinyl ether)

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*Received December 17, 1993; Revised Manuscript Received April 18, 1994*®

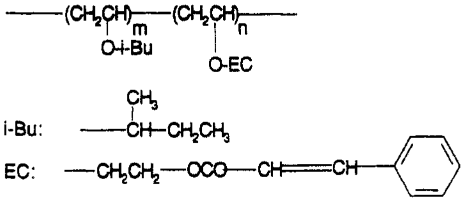
ABSTRACT: $\beta$-(Vinyloxy)ethyl cinnamate (VEC) is shown to undergo living cationic polymerization, in the presence of $EtAlCl_2$ and 1-(isobutoxy)ethyl acetate or trifluoroacetic acid and $ZnCl_2$, probably via a mechanism similar to that of isobutyl vinyl ether (IBVE) polymerization. Some kinetic data for VEC polymerization are presented. The living PVEC cations polymerized IBVE to produce poly[$\beta$-(vinyloxy)ethyl cinnamate]-*b*-poly(isobutyl vinyl ether) (PVEC-*b*-PIBVE). This diblock copolymer forms polymer brushes on glass plates and brush can be fixed by the photo-cross-linking of the PVEC block.

## 1. Introduction

A diblock copolymer, i.e. $(A)_n$-$(B)_m$, can deposit spontaneously from a block-selective solvent onto a solid substrate to form a self-assembled polymeric monolayer called a polymer brush.[1-4] Polymer brushes play an important role in the stabilization of surfactant particles[5-7] and in the modification of surface properties of solid objects.[8,9]

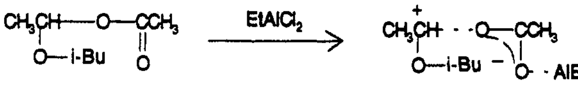
Many more applications can be speculated for polymer brushes.[10] Silica particles coated with polymer brushes can, for example, be used as reverse-phase HPLC column packing. In the HPLC application, it is important that the polymer brushes withstand solvent attack without dissolution and they, therefore, should be either chemically attached to or cross-linked on silica surfaces.

Polymer brushes studied so far have, however, been restricted to the ones that are neither chemically attached to nor cross-linked on a solid substrate. In this paper, we report the synthesis of the first diblock copolymer, i.e. poly[2-(vinyloxy)ethyl cinnamate]-*b*-poly(isobutyl vinyl ether) (PVEC-*b*-PIBVE, **1**), with a purposely incorporated cross-linkable block. This polymer, being a diblock copolymer, should form polymer brushes. After the formation of polymer brushes, the PVEC block can be cross-linked due to intermolecular photo-dimerization of the cinnamate groups.[11]

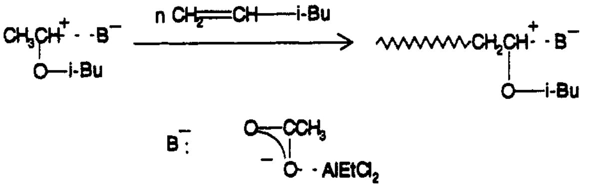


The choice of PVEC-*b*-PIBVE for demonstrating the cross-linkability of a polymer brush has been largely due to the consideration that this copolymer should be easy to synthesize, because both VEC and IBVE have been previously polymerized cationically. According to Kato and co-workers,[12,13] the polymerization of VEC using $BF_3$ etherate as the initiator yielded a linear polymer in which the double bond of the vinyloxy group in VEC had been opened for VEC incorporation while the aliphatic double bond of the cinnamate group stayed intact.

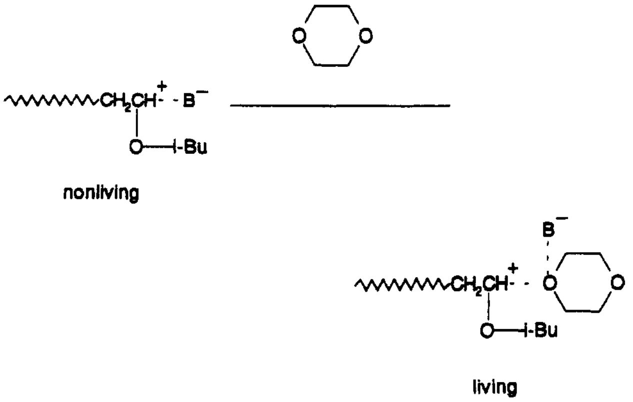
The living cationic polymerization of IBVE using various initiating systems has been reported by Higashimura and co-workers.[14-18] When 1-(isobutoxy)ethyl acetate (**2**) and $EtAlCl_2$ were used as the initiating system, **2** functioned as a protogen that reacted with $EtAlCl_2$, probably, to produce **3**. Transient species **3** then reacted with IBVE to initiate IBVE cationic polymerization.



**2** **3**



To render the polymerization living, esters or ethers were added to the polymerization mixture. Esters and ethers, due to their basicity, are believed to function as stabilizers for the cations via a mechanism shown below for the case of dioxane:[18]



Detailed studies revealed that in excess of $EtAlCl_2$, the molar ratio between IBVE and **2**, i.e. [IBVE]/[**2**], deter-

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® Abstract published in *Advance ACS Abstracts*, May 15, 1994.

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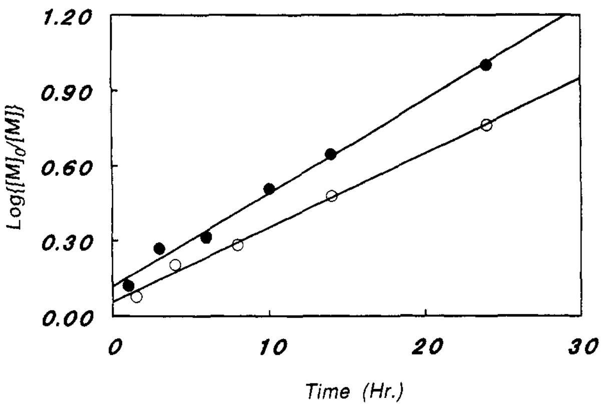

**Figure 1.** First-order kinetic curves for the polymerization of VEC in toluene in the presence of different amounts of $EtAlCl_2$: (●) $[EtAlCl_2] = 0.37$ M; (○) $[EtAlCl_2] = 0.28$ M. For both cases, $[2] = 4.7 \times 10^{-2}$ M; $[VEC] = 3.9$ M.

mined the polymer molar mass, and the rate of polymerization was largely determined by $[EtAlCl_2]$.

## 2. Results and Discussion

**Polymerization of VEC Using Living PIBVE Cations.** Monomer VEC was shown to undergo cationic polymerization but no indication was given whether the polymerization was actually living.[12,13] Since IBVE was explicitly shown to undergo living cationic polymerization, our initial strategy was to prepare the block copolymer by carrying out the living cationic polymerization of IBVE first and then using living cations of PIBVE to initiate the polymerization of VEC.

Unfortunately, this approach did not work well, because the addition of VEC to living cations of PIBVE, prepared at 0 °C in toluene by polymerizing IBVE for 4 h with $2/EtAlCl_2$, led to a polymer mixture with a bimodal molar mass distribution. The presence of a GPC peak with a significantly higher molar mass than the original PIBVE block suggested that block copolymerization did take place. The presence of a peak with a significantly lower average molar mass than the original PIBVE block suggested that VEC was impure and that protogen impurities in VEC reacted with $EtAlCl_2$ and initiated VEC homopolymerization.

**Living Cationic Polymerization of VEC.** Attempts were made to remove the trace amount of impurities in VEC. Purifying VEC via double vacuum distillation did not lead to polymers with a single peak molar mass distribution. We then attempted a different approach, i.e. polymerizing VEC first and then using living cations of PVEC to polymerize IBVE. For the new synthetic strategy to be effective, it was important to show that VEC could undergo living cationic polymerization.

The cationic polymerization of VEC and IBVE should be similar, because the functional group which is polymerized in both cases is the same. The polymerization of VEC was carried out at 0 °C in toluene at a $[EtAlCl_2]/[2]$ ratio in the range of 5–8, experimental conditions very similar to those used by Higashimura and co-workers for polymerizing IBVE.[14–18] The gradual increase in molar masses of PVEC with polymerization time and the maintenance of a low polydispersity in the molar mass distribution (<1.15) throughout a polymerization process suggested VEC polymerization was living.

The living feature was further verified by the fact that the rate of VEC polymerization can be approximately described by first-order kinetics (Figure 1), i.e. the log $[M]_0/[M]$ versus $t$ plots are approximately linear, where $[M]_0$ and $[M]$ represent VEC concentrations at time 0 and $t$, respectively.[19] Moreover, approximately linear relationships were observed between $\bar{M}_n$ of PVEC and VEC percentage conversion $p\%$ for two polymerizations as illustrated in Figure 2.[19]

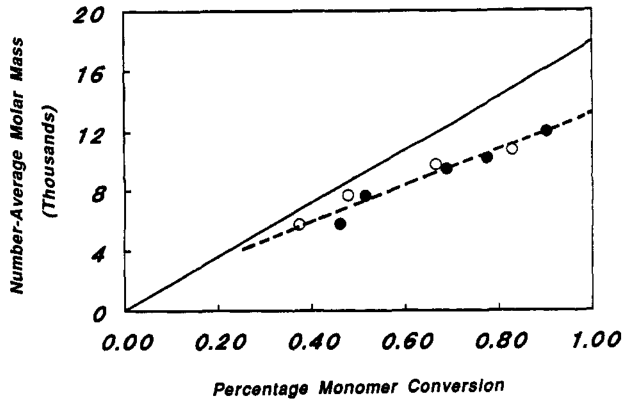

**Figure 2.** $\bar{M}_n$ vs conversion plot for the polymerization of VEC in toluene at 0 °C in the presence of different amounts of $EtAlCl_2$: (●) $[EtAlCl_2] = 0.37$ M; (○) $[EtAlCl_2] = 0.28$ M. For both cases, $[2] = 4.7 \times 10^{-2}$ M; $[VEC] = 3.9$ M. (—) represents the calculated $\bar{M}_n$ vs $p\%$ plot.

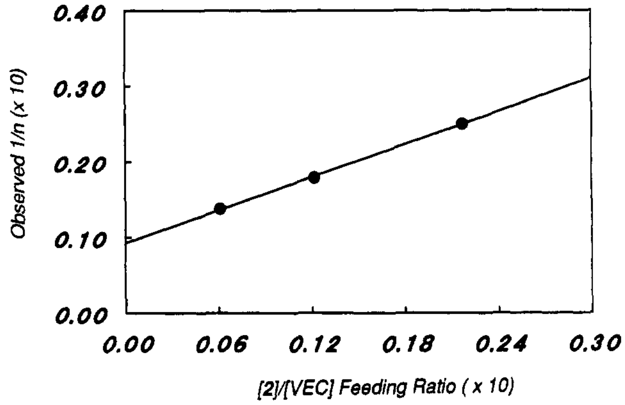

**Figure 3.** Plot of $1/n$, where $n$ is the number of repeat units in PVEC as determined by GPC, versus $[2]/[VEC]$ feeding ratios. The straight line has a non-zero intercept of 0.00926 or $n = 108$.

In Figure 2, the experimental $\bar{M}_n$ versus $p\%$ plot is compared with that calculated theoretically. The experimental $\bar{M}_n$, determined by GPC using polystyrene as the calibration standards, were found to be smaller than those calculated. The discrepancy can be partially due to the erroneous use of polystyrene standards for GPC calibration but is largely accounted for by the fact that VEC contains protogen impurities that can react with $EtAlCl_2$ to initiate the polymerization of VEC as will be elaborated later.

As $[EtAlCl_2]$ increases, the slope of the straight line in Figure 1 or the rate constant for VEC polymerization $k_P$ increases, which is in agreement with the trend observed for IBVE polymerization.[18] Despite its effect on VEC polymerization rate, Figure 2 clearly shows that $[EtAlCl_2]$ had no effect on the molar mass of the final polymer.

In the presence of excess amount of $EtAlCl_2$, the molar mass of PVEC was found to depend only on the ratio $[VEC]/[2]$. This is clearly demonstrated by the linear relation between $1/n$ and $[2]/[VEC]$ as illustrated in Figure 3, where $n$ is the number of repeat units of VEC as determined by GPC.

**Preliminary Kinetic Studies of VEC Polymerization.** Two more features should be noted about Figure 1. First, the rate of VEC polymerization is ~10 times slower than that of IBVE as reported by Higashimura and co-workers.[18] The main reason may be due to the different

**Table 1. Characterization of a PVEC-*b*-PIBVE Sample**

| the PVEC block | | | PVEC-*b*-PIBVE | | |
|---|---|---|---|---|---|
| $\bar{M}_n$ calcd ($\times10^{-4}$) | $\bar{M}_n$ GPC ($\times 10^{-4}$) | $\bar{M}_w/\bar{M}_n$ GPC | $\bar{M}_n$ calcd ($\times10^{-4}$) | $\bar{M}_n$, LS* ($\times10^{-4}$) | $\bar{M}_w/\bar{M}_n$ LS* |
| 1.24 | 0.77 | 1.11 | 2.4 | 1.34 | 1.07 |

* LS stands for light scattering.

reactivity between VEC and IBVE. Another factor might be that VEC, with an ester group, can complex with PVEC cations and thus slow down the polymerization of VEC. This is in accordance with the observed effect of esters on the rate of IBVE polymerization using $EtAlCl_2$ and **2** as the initiator.[14] The complexation of VEC ester or PVEC pedant ester groups with PVEC cations has been further substantiated by the observed polymerization of VEC with $EtAlCl_2$ and **2** in the absence of dioxane to produce living PVEC with a polydispersity ~1.3. The PVEC cations initiated further polymerization of IBVE to yield PVEC-*b*-PIBVE with a polydispersity ~1.4. Studies of Higashimura and co-workers of IBVE polymerization by $EtAlCl_2$ and **2** have revealed that the presence of esters and ethers were essential to render it living. Without added esters, PIBVE produced had polydispersities ~2.6.

Then, the straight lines of Figure 1 are found to have non-zero log $[M_0]/[M]$ values even at $t = 0$. This is due to experimental errors associated with VEC concentration assessment. VEC concentrations at different polymerization times were obtained from its GC peak areas relative to those of an internal standard, i.e. dodecane, added to a polymerization mixture. Before GC analysis, each sample was washed with aqueous ammonia and methanol mixture and then with dilute aqueous HCl. This base and acid treatment is necessary, because without it, VEC exists as some kind of complex with $EtAlCl_2$ or with some other component in the polymerization mixture and cannot be detected by GC. The treatment freed VEC but also partially decomposed VEC even in the absence of $EtAlCl_2$ and **2** as was verified by the appearance of a new GC peak after washing a pure VEC sample in toluene with the ammonia and HCl solutions. The washing could also have introduced an error in [VEC]/[dodecane] ratio even in the absence of VEC decomposition due to the possibly different partition coefficients of the two components in water and toluene (the solvent used for polymerization). To minimize the error introduced due to VEC decomposition and due to the possibly different partition coefficients of VEC and dodecane in water and toluene, we took a sample at $t = 0$ and this sample was subjected to the same base and acid treatment as applied to samples taken for polymerization kinetic studies. The sample was then analyzed by GC to obtain a peak area ratio of VEC to dodecane, i.e. $A_V^0/A_d^0$. Later VEC percentage conversions were calculated using

$$p\% = 1 - \frac{A_V/A_d}{A_V^0/A_d^0} \tag{2}$$

**Polymerization of IBVE by Living Cations of PVEC.** Living cations of PVEC successfully polymerized IBVE to produce PVEC-*b*-PIBVE with single and narrow GPC peaks. Results of a block copolymerization are illustrated in Table 1. The polydispersity of the PVEC-*b*-PIBVE sample was low. The $\bar{M}_n$ value determined using light scattering is significantly lower than that calculated using the monomers to **2** feeding ratio. The lower $\bar{M}_n$ determined has without ambiguity confirmed the presence of protogen impurities in VEC which reacted with $EtAlCl_2$ to polymerize VEC.

**Table 2. Comparison between the Molar Masses of PVEC Prepared Using Different Initiating Systems and the Theoretical Values**

| initiating system | calcd $\bar{M}_n$ (g/mol) | GPC $\bar{M}_n$ (g/mol) | GPC $\bar{M}_w$ (g/mol) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|
| $EtAlCl_2$ + **2** | $1.79 \times 10^4$ | $1.21 \times 10^4$ | $1.40 \times 10^4$ | 1.16 |
| | $3.57 \times 10^4$ | $1.57 \times 10^4$ | $1.78 \times 10^4$ | 1.13 |
| $CF_3COOH + ZnCl_2$ | $1.09 \times 10^4$ | $1.16 \times 10^4$ | $1.39 \times 10^4$ | 1.20 |
| | $2.18 \times 10^4$ | $2.06 \times 10^4$ | $2.40 \times 10^4$ | 1.17 |

**Impurities in VEC.** The presence of protogen impurities in VEC was further supported by the data of Figure 3. When plotting $1/n$, where $n$ is the number of repeat units of VEC in PVEC, versus [**2**]/[VEC], a straight line was obtained, yielding an $n$ value of 108 at [**2**]/[VEC] = 0. This $n = 108$ value is too large to be discounted as an error from GPC molar mass measurement and suggests that VEC will polymerize even in the absence of **2** with the help of protogen impurities (may include water) in VEC. That VEC would polymerize without **2** has been verified experimentally and we produced a polymer with $\bar{M}_n = 1.5 \times 10^4$ g/mol with $EtAlCl_2$ alone as the initiator.

The protogen impurities in VEC did not seem to interfere with VEC polymerization if $CF_3COOH$ and $ZnCl_2$ were used as the initiating system. When used by Higashimura and co-workers, this initiating system increased the rate of IBVE polymerization significantly relative to the case when **2** and $EtAlCl_2$ were used as the initiator.[16] The molar mass of PIBVE only depended on [IBVE]/[$CF_3COOH$]. In our case, the use of the $CF_3COOH$ and $ZnCl_2$ initiating system increased PVEC molar masses, and the GPC $\bar{M}_n$ agreed well with those calculated from [VEC]/[$CF_3COOH$] ratios as illustrated in Table 2. The excellent molar mass agreement in this case may be attributed to the impeded reaction between protogen impurities in VEC with $ZnCl_2$ because $ZnCl_2$ is a weaker Lewis acid than $EtAlCl_2$.

**Cross-Linked Brushes from PIBVE-*b*-PVEC.**[20] A PVEC-*b*-PIBVE sample with ~200 units of VEC and ~58 units of IBVE at the concentration of ~20 g/L has been found to deposit out from a hexanes/ethyl acetate (v/v = 1/3) solvent mixture on a bear glass plate to form a polymer brush with the PVEC block as the anchoring layer.[20] Irradiating the polymer brush with light from a 1000-W mercury lamp passing through a 260-nm cut-off filter for 1 min rendered it insoluble even after 15-min soak in chloroform, a good solvent for both blocks, as was indicated by the unchanged high water contact angle of the coated surface. Whereas soaking a control, a sample prepared in exactly the same fashion but not irradiated, in chloroform for 15 min led to considerable polymer loss and a change in the water contact angle from 78° to 47°.

## 3. Experimental Section

**Materials.** Toluene (BDH, ACS grade) was washed four times with 98% sulfuric acid, twice with 10% aqueous $Na_2CO_3$ solution, and then four times with distilled water. Washed toluene was dried over calcium chloride and phosphorus pentoxide. After filtration, calcium hydride was added and the solvent was refluxed under argon, followed by distillation over $CaH_2$ before use. 1,4-Dioxane, acetic acid, and IBVE (Aldrich, 99%) were purified following literature procedures.[14-18] $EtAlCl_2$ (Aldrich, 1.0 M in *n*-hexane), *trans*-cinnamic acid (Aldrich, 97%), and $\beta$-chloroethyl vinyl ether (Aldrich, 99%) were all used as received. Literature methods were adopted for the synthesis of **2**[14-18] and VEC.[13]

**Instruments and Methods.** GPC measurement was carried out in ethyl acetate on a Varian Model 5000 HPLC instrument using Styragel HR 4 (Waters) and Zorbax PSM 60-S (Chromatography Specialties) columns in series. Both UV and RI detectors are used for sample detection. The instrument was calibrated using polystyrene standards purchased from Polysciences. For VEC concentration assessment at different polymerization times, a Hewlett-Packard 5890 GC was used. The stationary phase for the megabore capillary column was OV-101.

**Polymerization Procedures.** Three-necked round-bottom flasks for polymerization were evacuated under high vacuum, flamed, and filled with argon. Into the flasks was injected the right amounts of toluene, monomer, and compound 2 under a positive argon pressure. The mixture was chilled to 0 °C with icy water. The addition of EtAlCl$_2$ at this point using a syringe through a Teflon-tape-wrapped rubber septum started the polymerization.

For kinetic studies, samples were taken using syringes at different polymerization times. For preparing a block copolymer, VEC was normally allowed to polymerize at 0 °C for 24 h, IBVE was added, and polymerization was continued for another 24 h at the same temperature. Polymerizations were terminated by adding 60:1/methanol:ammonia mixture to the polymerization flask. Polymerization mixtures with methanol/ammonia were then washed twice with 3.6% hydrochloric acid and twice with water. The organic layer was dried with CaCl$_2$ and concentrated. The polymer was purified by precipitation from methanol. Yields are typically in the range 80–90%. The structure of block copolymers PVEC-*b*-PIBVE have been confirmed by H$^1$ NMR analysis. Its NMR spectrum is just a combination of those of homopolymers PIBVE[14–18] and PVEC.[12,13]

**Kinetic Studies.** For kinetic studies, a small amount of dodecane (Aldrich, 99%, and treated with freshly-cleft sodium metal) was added to the polymerization mixture. The decrease in the area of the GC peak of VEC relative to that of dodecane is used to calculate VEC conversion at different polymerization times using eq 2.

## 4. Summary

We have introduced the concept of polymer brush fixation via the cross-linking of the anchoring block of a diblock copolymer. A diblock copolymer, i.e. PVEC-*b*-PIBVE, with double bonds in the PVEC block for the subsequent photo-cross-linking after brush formation has been synthesized for demonstrating this idea.

The polymerization of VEC using living PIBVE cations led to polymers with bimodal distributions. The reason is due to the insufficient purity of VEC samples used. The synthesis of PVEC-*b*-PIBVE was successful by polymerizing VEC first. Preliminary studies suggest that the cationic polymerization of VEC is similar to that of IBVE. The polymerization of VEC was living when 2 and EtAlCl$_2$ were used as the initiating system and so was that of IBVE initiated using PVEC cations.

**Acknowledgment.** The authors thank the Natural Sciences and Engineering Research Council of Canada and VX Optronics Corp. for financially sponsoring this research. X. Xu is grateful to the China National Petroleum Corp. for partial financial support of her stay in Canada. Wyatt Technology Corp. is acknowledged for getting the molecular weight of a PVEC-*b*-PIBVE sample done using their GPC system attached with a mini-Dawn light-scattering detector. We are also indebted to Miss Krystyna Skupinska for her help with the precipitation of certain polymers and Mr. Greg Butlin and Carl K. Smith for their contributions in the very early stage of this project.

## References and Notes

(1) Milner, S. T. *Science* **1991**, *251*, 905.
(2) Tuzar, Z.; Kratochvil, P. *Surf. Colloid Sci.* **1992**, *15*, 1.
(3) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1991**, *100*, 31.
(4) de Gennes, P. G. *Adv. Colloid Interf. Sci.* **1987**, *27*, 189.
(5) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1983.
(6) Jakubauskas, H. L. *J. Coat. Techn.* **1986**, *58*, 71.
(7) Vicent, B. In *Polymer Adsorption and Dispersion Stability*, ACS Symposium Series 240, American Chemical Society: Washington, DC, 1984.
(8) Lee, J. H.; Kopecek, J.; Andrade, J. D. *J. Biomed. Mater. Res.* **1989**, *23*, 351.
(9) Ruckenstein, E.; Chung, D. B. U.S. Pat. 4,929,510, 1990.
(10) Liu, G. U.S. patent filed.
(11) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985; Chapter 12.
(12) Watanabe, S.; Kato, M. *J. Polym. Sci.* **1984**, *22*, 2801.
(13) Kato, M.; Ichijo, T.; Ishii, K. *J. Polym. Sci.* **1971**, *9*, 2109.
(14) Aoshima, S.; Higashimura, T. *Macromolecules*, **1989**, *22*, 1009.
(15) (a) Miyomoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265. (b) *Ibid.* 2228. (c) Higashimura, T.; Miyamoto, M.; Sawamoto, M. *Macromolecules* **1985**, *18*, 611.
(16) Sawamoto, M.; Kojima, K.; Higashimura, T. *Macromolecules* **1989**, *22*, 1552.
(17) Kojima, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 2658.
(18) Kishimoto, Y.; Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 3877.
(19) Young, R. J.; Lovell, P. A. *Introduction to Polymers*, 2nd ed.; Chapman & Hall: London, 1991.
(20) Liu, G.; Xu, X.; Skupinska, K.; Yao, H. *J. Appl. Polym. Sci.*, in press.