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Quasiliving Carbocationic Polymerization. VII. Block Polymerization of α-Methylstyrene from Quasiliving Poly(isobutyl Vinyl Ether) Dication

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ABSTRACT

Poly(α-methylstyrene-b-isobutyl vinyl ether-b-α-methylstyrene) triblock polymers have been prepared by blocking α-methylstyrene (αMeSt) from biheaded quasiliving poly(isobutyl vinyl ether) (PIBVE) cations generated with the bifunctional p-dicumyl chloride/$AgSbF_6$ initiating system in methylene chloride solvent at -90°C. The products were fractionated with 2-propanol, a good solvent for PIBVE and a nonsolvent for PαMeSt. The 2-propanol-insoluble fractions had much higher molecular weights ($\overline{M}_n$ = 30,500-69,100) than the starting PIBVE ($\overline{M}_n$ = 6,600-10,600) and contained 13-29 wt% IBVE together with 87-71 wt% αMeSt units. The 2-propanol-soluble fractions ($\overline{M}_n$ = 7,300-11,600) contained ~90 wt% IBVE and ~10 wt% αMeSt units.

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INTRODUCTION

The quasiliving cationic polymerization of IBVE with the p-dicumyl chloride (p-DCC)/silver hexafluoroantimonate ($AgSbF_6$) initiating system has been described [1]. Experiments carried out under a variety of conditions have shown that quasiliving IBVE polymerization is optimum in CH_2Cl_2 solvent in the range from -70 to -90°C. The number-average molecular weights ($\overline{M}_n$) of PIBVE obtained under these conditions increased linearly with the cumulative weight of added monomer, the $\overline{M}_n$ versus monomer input plots pass through the origin, and the polymers exhibit the expected narrow molecular weight distributions (MWD) with $\overline{M}_w/\overline{M}_n = 1.4\text{-}1.7$.

This communication concerns an extension of this quasiliving system to the synthesis of new IBVE-αMeSt block polymers that consist of rubbery (PIBVE) and glassy (PαMeSt) segments. The synthesis involves blocking αMeSt from quasiliving PIBVE cations generated by the bifunctional initiating system p-DCC/$AgSbF_6$ in CH_2Cl_2 solvent at -90°C. The technique of slow and continuous monomer addition [1, 2] was employed to achieve quasiliving polymerization of IBVE and subsequent blocking of αMeSt. Product analyses indicate the formation of IBVE-αMeSt block polymers and, in view of the bifunctional initiator employed, the main product is a poly(αMeSt-b-IBVE-b-αMeSt) triblock copolymer.

EXPERIMENTAL

αMeSt (Aldrich), washed free from an inhibitor, was freshly distilled twice over calcium hydride under reduced pressure. 2-Propanol (Fisher, reagent) was used as received. Other materials were purified and used as described [1, 3].

Quasiliving polymerization of IBVE was achieved in CH_2Cl_2 at -90°C by introducing the monomer (25 vol% solution) slowly and continuously to a premixed p-DCC/$AgSbF_6$ charge (200 cm^3) under dry nitrogen [1]. At a given time monomer introduction into the reactor was stopped and a sample was withdrawn with a syringe through a serum cap. The reactor was stoppered and stirring was continued at -90°C. Then the monomer-supply system was rinsed with an αMeSt solution ($\sim$5 min from the end of the IBVE polymerization), and αMeSt (25 vol% solution) was slowly added to the reaction mixture in the same manner as IBVE. At desired times samples were withdrawn with a syringe to determine yields gravimetrically. The second stage of the polymerization was quenched with prechilled methanol (30 cm^3). Other experimental details are given in Table 1.

TABLE 1. Blocking αMeSt from Quasiliving PIBVE in CH_2Cl_2 at -90°C with p-DCC/$AgSbF_6$ Initiator

Expt	$[p\text{-DCC}]_0$[a] (mM)	Feed,[b] wt% IBVE/αMeSt	Fraction (wt%)	Composition,[c] wt% IBVE/αMeSt	$\overline{M}_n$ (GPC)	$\overline{M}_n$[d] (calcd)	$\overline{M}_w/\overline{M}_n$
A	0.50	14/86	Starting PIBVE	100/ 0	10,600	-	1.73
			2-PrOH soluble (13)	89/11	11,600	11,900	1.71
			2-PrOH insoluble (87)	13/87	69,100	83,500	2.20
B	2.0	30/70	Starting PIBVE	100/ 0	6,600	-	1.40
			2-PrOH soluble (22)	90/10	7,300	7,400	1.36
			2-PrOH insoluble (78)	21/79	35,700	32,300	2.41
C	2.0	36/64	Starting PIBVE	100/ 0	7,100	-	1.36
			2-PrOH soluble (27)	90/10	7,700	8,000	1.42
			2-PrOH insoluble (73)	29/71	30,500	24,900	2.32
D	0.50	36/64[e]	Starting PIBVE	100/ 0	22,800	-	1.43
			2-PrOH soluble (100)	62/38	35,300	36,700	1.89

[a] $[AgSbF_6]_0/[p\text{-DCC}]_0 = 2.3$; initial volume of p-DCC/$AgSbF_6$ charge, 200 cm^3.

[b] Expt A: IBVE, 0.76 g/min, 2 min; αMeSt, 0.91 g/min, 10 min. Expt B: IBVE, 0.37 g/min, 10 min; αMeSt, 0.44 g/min, 20 min. Expt C: IBVE, 0.37 g/min, 10 min; αMeSt, 0.44 g/min, 15 min. Expt D: IBVE, 0.76 g/min, 5 min; αMeSt, 0.45 g/min, 15 min.

[c] Determined by ^{1}H-NMR.

[d] $\overline{M}_n$ (calcd) = ($\overline{M}_n$ of starting PIBVE)/(wt fraction of IBVE).

[e] αMeSt conversion was not quantitative.

After filtering off the silver chloride, the reaction mixture was washed twice with distilled water to remove inorganic residues, concentrated to ~30 cm^3 by evaporation, and poured into excess 2-propanol (700 cm^3). A white precipitate formed. The mixture was stirred overnight at room temperature and separated by filtration into 2-propanol-soluble and -insoluble fractions. The insoluble part was rinsed 5 times with 2-propanol (75 cm^3 each); the filtrate and the washings were combined and evaporated to dryness under reduced pressure. Both the insoluble and soluble fractions were finally dried in vacuo for 2-3 d to give, respectively, a white powder and a sticky transparent semisolid.

The products were analyzed by gel permeation chromatography (GPC) and ^{1}H-NMR spectroscopy [1, 3]. $\overline{M}_n$'s were calculated from GPC traces using polystyrene calibration. For both PIBVE and IBVE-αMeSt block polymers, these $\overline{M}_n$ values were in good agreement with the corresponding absolute values determined by GPC/low-angle laser light-scattering technique [1], i.e., for an IBVE-αMeSt block polymer (2-propanol-insoluble fraction, experiment A, Table 1): $\overline{M}_n$(absolute) = 65,000; $\overline{M}_n$(polystyrene calibration) = 69,100. The composition of the products was determined by ^{1}H-NMR (aromatic ring protons (δ6.9 ppm) for PαMeSt, $-CHOCH_2$-peak (δ2.8-3.6 ppm) for PIBVE; see Fig. 2).

Homopolymers, PIBVE and PαMeSt, for film-casting experiments were prepared in the same way as above under conditions similar to those in Experiment C in Table 1: $[\text{p-DCC}]_0$ = 2.0 $\underline{M}$, $[AgSbF_6]_0$ = 4.5 m$\underline{M}$; IBVE, 0.38 g/min, 10 min, or αMeSt, 0.45 g/min, 15 min. According to GPC analysis: PIBVE, $\overline{M}_n \cong 7{,}300$, $\overline{M}_w/\overline{M}_n = 1.35$; P$\alpha$MeSt, $\overline{M}_n \cong 24{,}500$, $\overline{M}_w/\overline{M}_n = 3.01$.

RESULTS AND DISCUSSION

αMeSt was block-polymerized from biheaded quasiliving PIBVE cations using CH_2Cl_2 solvent at -90°C. The αMeSt feed was added slowly and continuously to a well-stirred solution of the PIBVE cations. Polymer yields at any reaction time were in good agreement with the cumulative weight of added monomers, indicating consistently quantitative αMeSt conversion.

Figure 1 shows typical GPC traces of the products, and the corresponding $\overline{M}_n$'s are listed in Table 1. The molecular weight of the 2-propanol-insoluble fraction obtained in Experiment C was much higher ($\overline{M}_n$ = 30,500) than that of the starting PIBVE ($\overline{M}_n$ = 7,100). The MWD trace was relatively broad ($\overline{M}_w/\overline{M}_n$ = 2.32) and apparently

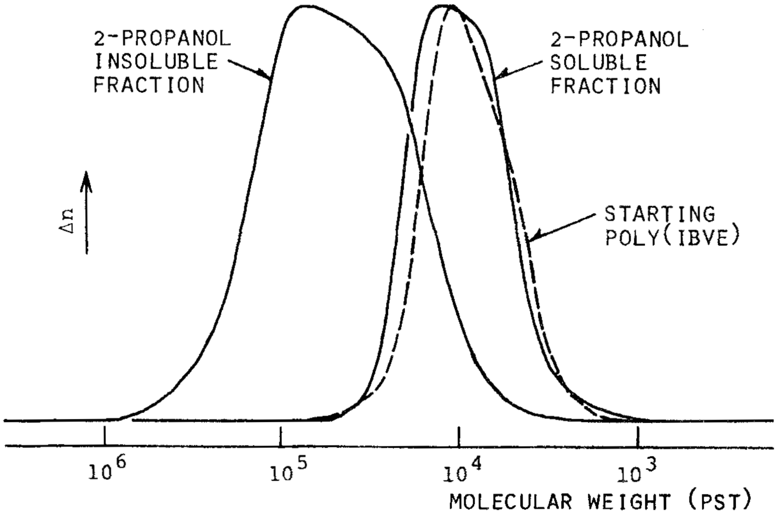

FIG. 1. MWD of the 2-propanol-soluble and -insoluble fractions and the starting PIBVE obtained in Experiment C, Table 1.

bimodal but did not show significant tailing toward the lower molecular weights. The 2-propanol-soluble part exhibited a narrow MWD and an $\overline{M}_n$ (7700) that was clearly, though slightly, higher than that of the starting PIBVE. Similar results were obtained in Experiments A-C summarized in Table 1. The 2-propanol-insoluble fractions ranged from 73 to 87 wt% of the total products and increased with increasing αMeSt feed.

The composition of the products was analyzed by ^{1}H-NMR spectroscopy (Fig. 2 and Table 1). The 2-propanol-insoluble fractions (e.g., Fig. 2a) exhibited signals due to αMeSt and IBVE units (αMeSt, $\delta \sim 0.1$ and 6.9 ppm; IBVE, $\delta \sim 0.9$ and 2.8-3.6 ppm), i.e., the spectra indicated the presence of PIBVE and PαMeSt segments. As 2-propanol is a good solvent for PIBVE and is a nonsolvent for PαMeSt, the 2-propanol-insoluble fraction cannot contain the former homopolymer. Thus the existence of IBVE units in the 2-propanol-insoluble fractions is strong evidence for the presence of IBVE-αMeSt block polymers in these fractions. These block polymers are insoluble in 2-propanol because of their high αMeSt contents (71-87 wt%).

Although PαMeSt should be absent in the 2-propanol-soluble fractions, these fractions showed a resonance characteristic of αMeSt units (aromatic ring protons, $\delta \sim 6.9$ ppm) together with signals characteristic of IBVE units (e.g., Fig. 2b). Evidently the 2-propanol-soluble fractions also contain IBVE-αMeSt block polymers. These block polymers most likely carry short PαMeSt segments pulled into 2-propanol by the attached PIBVE segments.

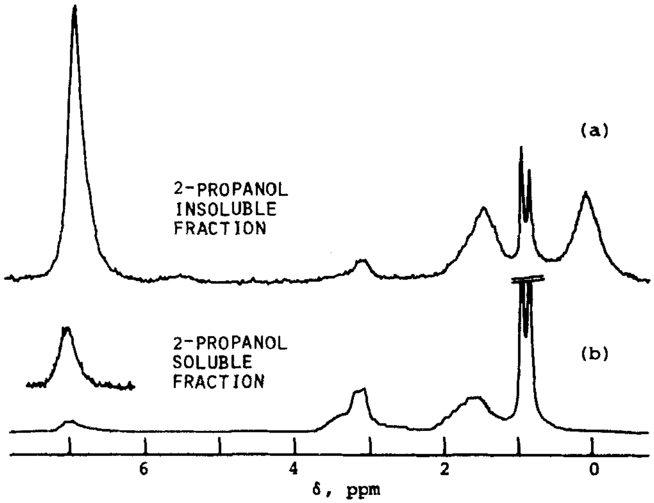

FIG. 2. ^{1}H-NMR spectra of the 2-propanol-soluble and -insoluble fractions obtained in Experiment A, Table 1.

In Experiment D (Table 1), where the molecular weight of the starting PIBVE was set deliberately higher than those in the other runs, the product was completely 2-propanol soluble. A hazy homogeneous solution was obtained on pouring the reaction mixture into the alcohol. The isolated product was a white sticky gum completely different in appearance from PIBVE. The ^{1}H-NMR spectrum of this material showed a resonance characteristic of ring protons in αMeSt units (34 wt%) and its $\overline{M}_n$ was higher than that of the starting PIBVE (35,300 versus 22,800). Evidently IBVE-αMeSt block polymers soluble in 2-propanol were produced in Experiment D.

Assuming that each fraction consists entirely of IBVE-αMeSt block polymers, the $\overline{M}_n$'s can be calculated by the following equation:

$$\overline{M}_n(\text{calcd}) = \frac{\overline{M}_n \text{ of the starting PIBVE}}{\text{weight fraction of IBVE}}$$

Table 1 compares calculated $\overline{M}_n$'s with experimental values [$\overline{M}_n$(GPC)] determined by GPC. The good agreement between $\overline{M}_n$(calcd) and $\overline{M}_n$(GPC) for the 2-propanol-soluble fractions indicates that they are composed mostly of block polymers. The absence of homoPIBVE in these products provides further support for the quasiliving nature of the first-stage IBVE polymerization [1]. In view of the dicationic structure expected for the starting quasiliving PIBVE [1], the block polymers formed in these experiments are most likely triblocks, i.e., poly(αMeSt-b-IBVE-b-αMeSt).

A discrepancy exists between $\overline{M}_n$(calcd) and $\overline{M}_n$(GPC) for the 2-propanol-insoluble fractions. This discrepancy, coupled with the presence of short αMeSt blocks in the 2-propanol-soluble fractions, suggests that the 2-propanol-insoluble fractions contain, in addition to IBVE-αMeSt block polymers, αMeSt homopolymers as well. The latter PαMeSt is presumably formed via chain transfer to monomer. Chain transfer during blocking of αMeSt may occur since our conditions (pure CH_2Cl_2 solvent) may not be optimum for quasiliving polymerization of αMeSt [2]. Since it was difficult to separate PαMeSt from IBVE-αMeSt block polymers rich in PαMeSt, blocking efficiencies could not be determined accurately.

The conclusion that IBVE-αMeSt block copolymers can be readily prepared by adding αMeSt to quasiliving PIBVE cations derived from the above considerations has been further corroborated by visual observations and comparisons of dilute and concentrated solutions of our products and those of physical blends of PαMeSt and PIBVE, and film-casting experiments. Thus dilute and concentrated (20 wt%) solutions of 2-propanol-insoluble products in THF (a common solvent) at room temperature remained perfectly homogeneous and did not show the slightest tendency of separation into layers even after storage for several weeks in test tubes. In contrast, physical mixtures of PαMeSt and PIBVE of similar $\overline{M}_n$'s as in the blocks were consistently opaque in THF. Thin films cast on aluminum surfaces of the 2-propanol-insoluble fractions were homogeneous, nonsticky, brittle solids; the film obtained in Experiment A (Table 1) was transparent whereas those in Experiments B and C were slightly hazy. In contrast, films cast under the same conditions using blends of the homopolymers gave heterogeneous, white, very sticky brittle solids, clearly reflecting the properties of the two homopolymer components.

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