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Quasiliving Carbocationic Polymerization. VIII. Quasiliving Polymerization of Methyl Vinyl Ether and Its Blocking from Quasiliving Poly(isobutyl Vinyl Ether) Dication

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ABSTRACT

Quasiliving carbocationic polymerization of methyl vinyl ether (MVE) was achieved with the p-dicumyl chloride (p-DCC)/$AgSbF_6$ initiator system by the slow and continuous monomer-addition (quasiliving) technique. A polar solvent (CH_2Cl_2) and a low reaction temperature (-70°C) were optimum for the quasiliving MVE polymerization. Under these conditions, the number-average molecular weight ($\overline{M}_n$) of poly(MVE) increased linearly with the cumulative weight of added monomer (W_{MVE}), and linear $\overline{M}_n$ versus W_{MVE} plots passed through the origin. $\overline{M}_n$'s were inversely proportional to the initial initiator (p-DCC) concentration. Reactions in a nonpolar solvent (toluene) at -70°C or in a polar solvent (CH_2Cl_2) at -30°C resulted in deviations

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from these quasiliving characteristics. Block polymerization of MVE from quasiliving poly(isobutyl vinyl ether) dications by the quasiliving technique (p-DCC/$AgSbF_6$ initiator, CH_2Cl_2 solvent, -70°C) led to novel isobutyl vinyl ether (IBVE)-MVE block polymers in high yield (> 93 wt%) and at high blocking efficiency. The block polymers, most likely poly(MVE-b-IBVE-b-MVE), having $\overline{M}_n$ = 10,900-14,000 [$\overline{M}_n$(center block) = 6,200-9,000], were soluble in n-heptane and insoluble in water, and gave hazy homogeneous solutions when dissolved in methanol at room temperature.

INTRODUCTION

Methyl vinyl ether (MVE), the simplest homolog of alkyl vinyl ethers, can be readily polymerized cationically and the polymers exhibit unique physical properties. For instance, amorphous poly(MVE) is soluble in both cold water and common organic solvents but is insoluble in n-alkanes that are good solvents for other poly(alkyl vinyl ether)s [1]. MVE is much less reactive than the higher homologs such as isobutyl vinyl ether (IBVE) [2], suggesting that the MVE cation is relatively less stabilized by the methoxy group.

In the course of our continuing studies on the quasiliving carbocationic polymerization of vinyl ethers [3, 4], we have found [3] that IBVE, in conjunction with the p-dicumyl chloride (p-DCC)/silver hexafluoroantimonate ($AgSbF_6$) initiator, gives a typical quasiliving system in which the number-average molecular weight ($\overline{M}_n$) of poly(IBVE) increases linearly with the cumulative weight of added monomer, and leads to narrow molecular weight distributions (MWD) with $\overline{M}_w/\overline{M}_n$ = 1.4-1.7. Optimum conditions for the quasiliving IBVE polymerization (CH_2Cl_2 solvent, -70 to -90°C) have been established [3]. Our subsequent investigation [4] has shown that the quasiliving poly(IBVE) dication can initiate polymerization of α-methylstyrene (αMeSt) to yield a novel triblock polymer, poly(αMeSt-b-IBVE-b-αMeSt).

These investigations concern the quasiliving polymerization of MVE. An objective was to examine the effect of monomer structure on quasiliving carbocationic polymerization; i.e., the possibility of quasiliving polymerization of this relatively unreactive vinyl ether prone to chain transfer [5]. Another objective was to synthesize new block polymers of two vinyl ethers, e.g., IBVE-MVE block polymers, via quasiliving polymerizations of both monomers. Equation (1) outlines this block polymer synthesis:

$$\text{IBVE} \xrightarrow{\text{p-DCC/AgSbF}_6} \oplus\sim\sim(\text{PIBVE})\sim\sim\oplus \xrightarrow{\text{MVE}}$$

$$\boxed{\text{PMVE}}\sim\sim(\text{PIBVE})\sim\sim\boxed{\text{PMVE}} \qquad (1)$$

These block polymers, consisting of a lipophilic [poly(IBVE)] and a hydrophilic [poly(MVE)] component, are expected to exhibit unique solubility properties.

Thus MVE was polymerized with the p-DCC/$AgSbF_6$ bifunctional initiator system by slow and continuous monomer addition [3, 6], and optimum reaction parameters for the quasiliving polymerization of MVE were determined. Subsequent blocking experiments starting from the quasiliving poly(IBVE) dication yielded new IBVE-MVE block polymers, most likely poly(MVE-b-IBVE-b-MVE) triblocks.

EXPERIMENTAL

Materials

MVE (Matheson, purity >99.5%) was used as received in a lecture bottle. Toluene (Fisher) was washed successively with concentrated sulfuric acid, water, 10% aqueous sodium hydroxide, and water; dried over molecular sieves (3Å); and distilled at least twice over calcium hydride under dry nitrogen. Other materials (IBVE, p-DCC, $AgSbF_6$, CH_2Cl_2, and n-heptane) were used as reported [3].

Polymerization of MVE by Slow and Continuous Monomer Addition

All manipulations were carried out under dry nitrogen in a stainless steel enclosure. To a well-stirred, premixed charge of p-DCC/$AgSbF_6$ (200 cm^3; premixing 1.0 min) in a 300-cm^3 round-bottom, three-neck flask kept at -30 or -70°C [3], MVE (gas) was introduced continuously from a lecture bottle (at room temperature) through Tygon tubing and a narrow glass-tubing outlet. The monomer-addition rate, controlled by means of a regulating valve attached to the lecture bottle, was determined by condensing MVE into a 10-cm^3 graduated cylinder at -30 or -70°C. The density of MVE (0.856 g/cm^3) [2] determined at -62°C was used regardless of the reaction temperature. Subsequent procedures, including sampling and $\overline{M}_n$ determination, were the same as described for the quasiliving polymerization of IBVE [3].

Blocking MVE from Quasiliving Poly(IBVE) Dication

The preparation of the quasiliving poly(IBVE) dication by the use of the p-DCC/$AgSbF_6$ initiator system has been described [3]. At a desired time the addition of IBVE to the reactor was discontinued, an aliquot sample was withdrawn with a syringe, and ~1 min after the end of the IBVE polymerization, blocking was effected by introducing MVE continuously to the reaction mixture. During the second stage of the polymerization, samples were taken with a syringe to determine yields (gravimetry). The reaction was terminated with ~30 cm^3 prechilled methanol. Other experimental details are shown in Table 1.

After removing the silver chloride by filtration, the reaction mixture was concentrated to 30-50 cm^3 by evaporation and poured into a heterogeneous mixture of n-heptane (500 cm^3) and cold water (200 cm^3). The former is a good solvent for poly(IBVE) only; the latter for poly(MVE) only. The mixture was stirred for ~3 h at room temperature ($< 20°C$), transferred to a 1-dm^3 separatory funnel, and allowed to stand overnight for phase separation. The n-heptane and water layers were separated and the solvents were evaporated to dryness under reduced pressure. The products were recovered after drying in vacuum.

The products were characterized by ^{1}H-NMR spectroscopy and gel permeation chromatography (GPC) [3, 4]. Compositions were determined from the ratio of alkoxy ($-\overset{|}{C}HOCH_2-$ and $-\overset{|}{C}HOCH_3$; δ2.7-3.7 ppm) to aliphatic ($-C-CH_2-C-$ and $-CH(CH_3)_2$; δ0.5-2.2 ppm) protons obtained by ^{1}H-NMR (see Fig. 7). $\overline{M}_n$ was calculated from GPC traces on the basis of polystyrene calibration [3].

RESULTS AND DISCUSSION

Quasiliving Polymerization of MVE in CH_2Cl_2 at -70°C

MVE was polymerized with premixed p-DCC/$AgSbF_6$ initiator systems in CH_2Cl_2 solvent at -70°C by the quasiliving technique. Polymer yields were ~100%. Figure 1 illustrates a typical set of GPC traces for poly(MVE) obtained during an experiment. The traces are shifting toward higher molecular weights and the MWD's become narrower (from $\overline{M}_w/\overline{M}_n = 2.1$ to 1.7) as the polymerization progresses.

Figure 2 shows plots of $\overline{M}_n$ against the cumulative weight of added

TABLE 1. Blocking MVE from Quasiliving PIBVE in CH_2Cl_2 at -70°C with p-DCC/$AgSbF_6$[a]

	Feed,[b] wt%		Composition,[c] wt%	$\overline{M}_n$	$\overline{M}_n$[d]	
Expt	IBVE/MVE	Fraction (wt%)	PIBVE/PMVE	(GPC)	(calcd)	$\overline{M}_w/\overline{M}_n$
A	25/75	Starting PIBVE	100/ 0	6,200	-	1.81
		n-Heptane soluble (75)	51/ 49	13,900	12,200	1.78
		n-Heptane/H_2O emulsion (22)	8/ 92	19,400	77,300	1.48
		Water soluble (3.5)	0/100	7,200	-	1.59
B	42/58	Starting PIBVE	100/ 0	8,800	-	1.73
		n-Heptane soluble (95)	51/ 49	14,000	17,200	1.58
		Water soluble (5.1)	15/ 85	7,600	60,200	1.89
C	59/41	Starting PIBVE	100/ 0	9,000	-	1.75
		n-Heptane soluble (94)	82/ 18	10,900	11,000	1.82
		Water soluble (6.5)	0/100	4,600	-	1.39

[a] $[\text{p-DCC}]_0 = 2.0$ m$\underline{M}$; $[AgSbF_6]_0 = 4.5$ m$\underline{M}$; initial volume of p-DCC/$AgSbF_6$ charge, 200 cm^3.

[b] Expt A: IBVE, 1.22 g/min, 5 min; MVE, 0.91 g/min, 20 min. Expt B: IBVE, 1.22 g/min, 10 min; MVE, 0.86 g/min, 20 min. Expt C: IBVE, 1.22 g/min, 10 min; MVE, 0.83 g/min, 10 min.

[c] Determined by ^1H-NMR.

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

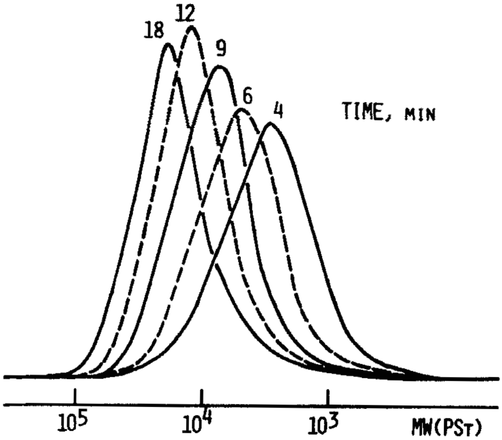

FIG. 1. MWD of poly(MVE) obtained in CH_2Cl_2 at -70°C: $[\text{p-DCC}]_0$ = 2.0 mM; $[AgSbF_6]_0$ = 4.5 mM; MVE addition rate = 0.87 g/min.

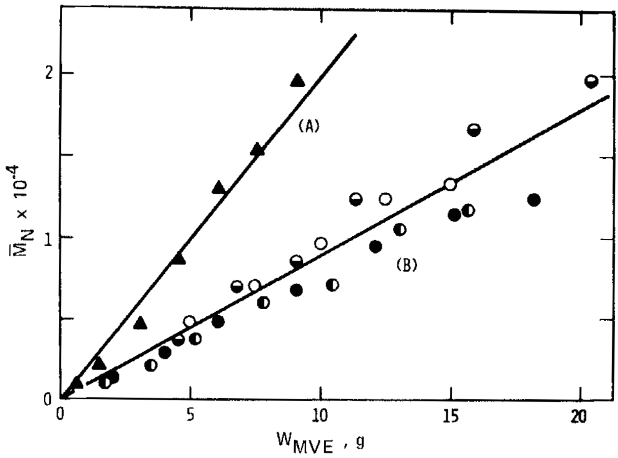

FIG. 2. $\overline{M}_n$ as functions of monomer input W_{MVE} in CH_2Cl_2 at -70°C: $[\text{p-DCC}]_0$ (mM): A, 1.0; B, 2.0. $[AgSbF_6]_0/[\text{p-DCC}]_0$ = 2.3. MVE addition rate (g/min): (▲) 0.30, (○) 0.50, (◐) 0.87, (●) 1.01, (◓) 1.13.

MVE, W_{MVE}. $\overline{M}_n$ increases linearly with increasing W_{MVE} and the lines pass through the origin. $\overline{M}_n$ is higher at a lower initial initiator concentration $[\text{p-DCC}]_0$; the slope of the plots is nearly proportional to reciprocal $[\text{p-DCC}]_0$.

These results show that quasiliving polymerization of MVE has been achieved by the use of CH_2Cl_2 solvent at -70°C. $\overline{M}_n$'s obtained at different monomer-addition rates (0.50 to 1.13 g/min) lead to a single straight line through the origin (Fig. 2), which indicates that quasiliving conditions can be maintained independent of the monomer-addition rate in that range. The same conclusion has been reached for the quasiliving polymerization of IBVE [3].

The linear $\overline{M}_n$ versus W_{MVE} plots in Fig. 2 show that the number of polymer chains produced per unit initiator, N, is constant during the polymerization. N is defined as [3]

$$N = \frac{W}{\overline{M}_n[\text{p-DCC}]_0} \tag{2}$$

where W is the cumulative weight of MVE added to a 1-dm^3 initiator charge. Although N's were constant in these experiments, their absolute values were greater than unity, the value expected for living systems (N(obs) = 2.50 and 2.79 at $[\text{p-DCC}]_0$ = 1.0 and 2.0 m$\underline{M}$, respectively). This suggests that chain transfer to monomer may have taken place during the early stages of the polymerization; this is also indicated by the relatively broad MWD curve (e.g., Fig. 1, time = 4 min).

Effects of Temperature and Solvent Polarity

Figure 3 shows $\overline{M}_n$ versus W_{MVE} plots for polymerizations in CH_2Cl_2 solvent at -30°C. At this higher temperature, although $\overline{M}_n$'s increase linearly with increasing W_{MVE}, they are much smaller than expected from the initial initiator concentration, and the $\overline{M}_n$ versus W_{MVE} plots have an intercept. The MWD's are broad ($\overline{M}_w/\overline{M}_n$ = 3-4) at the beginning of the reaction and progressively become narrower ($\overline{M}_w/\overline{M}_n \rightarrow 1.5$). Higher temperatures are evidently unfavorable for quasiliving MVE polymerization, most likely because of significant chain transfer to monomer.

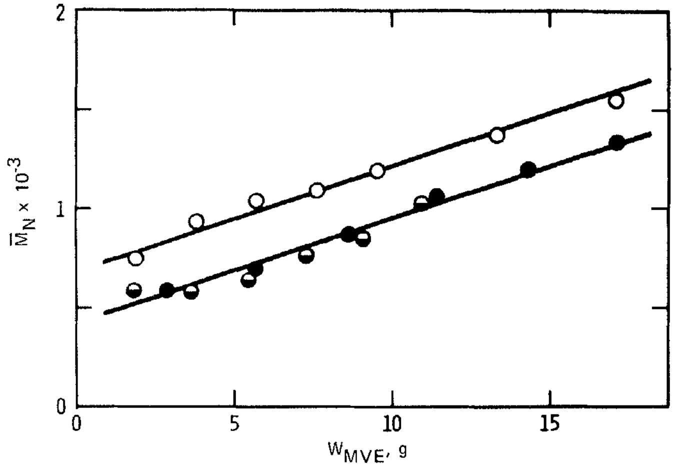

FIG. 3. $\bar{M}_n$ as functions of monomer input W_{MVE} in CH_2Cl_2 at -30° C: $[p\text{-DCC}]_0 = 2.0$ mM; $[AgSbF_6]_0 = 4.5$ mM. MVE addition rate (g/min): (◒) 0.36, (●) 0.57, (○) 0.95.

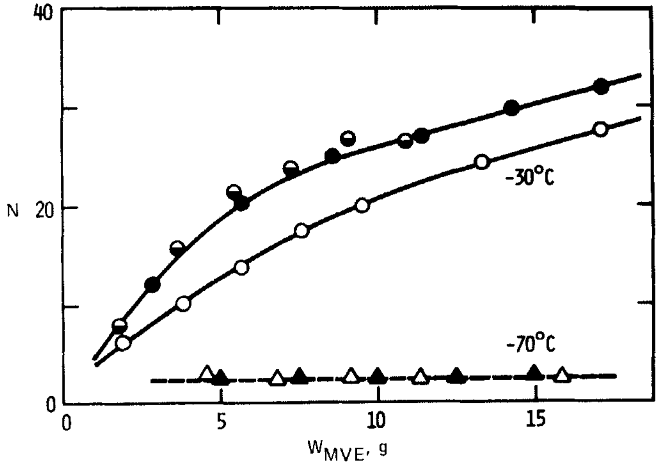

FIG. 4. Relationships between monomer input W_{MVE} and N, the number of polymer chains produced per unit p-DCC, in CH_2Cl_2 solvent. Temperature as indicated; $[p\text{-DCC}]_0 = 2.0$ mM; $[AgSbF_6]_0 = 4.5$ mM. MVE addition rate (g/min): (▲) 0.50, (△) 1.13, (◒) 0.36, (●) 0.57, (○) 0.95.

The effect of temperature on MVE polymerization can also be illustrated by plotting N against W_{MVE} (Fig. 4). The relatively large and continuously increasing N values obtained at -30°C are in sharp contrast to the constant small values (~ 2.5) for -70°C where quasiliving polymerization can be achieved.

Quasiliving polymerization of MVE was also attempted using a nonpolar solvent, toluene, at -70°C. Results are summarized in Fig. 5. Reactions in toluene led to strongly curved $\overline{M}_n$ versus W_{MVE} plots, though polymer molecular weights increased with W_{MVE}. The MWD was broad throughout the polymerization ($\overline{M}_w/\overline{M}_n$ = 2.4-3.9). In contrast to the data for polar CH_2Cl_2 solvent, N values for toluene were smaller than unity at the beginning of the reaction, increased continuously, and then exceeded unity; these observations indicate slow initiation and the presence of chain transfer to monomer.

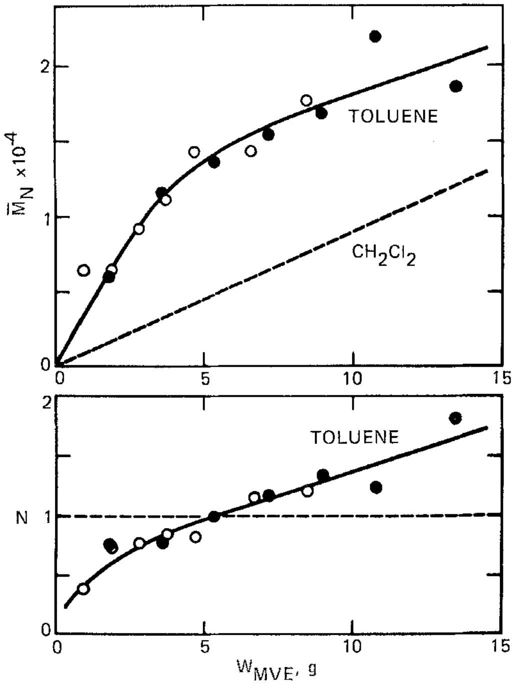

FIG. 5. $\overline{M}_n$ and N as functions of monomer input W_{MVE} in toluene at -70°C: $[p\text{-DCC}]_0$ = 2.0 mM; $[AgSbF_6]_0$ = 4.5 mM. MVE addition rate (g/min): (○) 0.47, (●) 0.90.

Thus polar media (CH_2Cl_2) and low reaction temperatures (-70°C) are required to achieve the quasiliving polymerization of MVE. The use of nonpolar solvents or higher temperatures is detrimental for quasiliving conditions. These trends are similar to those observed for quasiliving IBVE polymerization (see Table 1, Ref. 3a).

Block Polymerization of MVE from Quasiliving Poly(IBVE) Dication

Since conditions for the quasiliving polymerizations of MVE and IBVE are similar (CH_2Cl_2, -70°C), efforts were made to block MVE from quasiliving poly(IBVE) dications. Experimentally, IBVE was polymerized with the p-DCC/$AgSbF_6$ initiator system using CH_2Cl_2 solvent at -70°C by the slow and continuous monomer-addition technique to form the quasiliving poly(IBVE) dication, and subsequently the latter was used to initiate the block copolymerization of MVE by the same technique. Polymer yields during blocking were always close to the sum of weights of IBVE and MVE feeds, indicating consistently quantitative conversions of both monomers. The products were fractionated into n-heptane-soluble and water-soluble fractions. Table 1 summarizes the results of blocking experiments at different IBVE/MVE feed ratios.

The n-heptane-soluble fractions were very viscous, sticky, gummy materials, completely different from either poly(IBVE) or poly(MVE). Molecular weights were considerably higher than those of the starting poly(IBVE) (Table 1). Figure 6 illustrates a typical set of GPC traces; a shift of the MWD curve toward higher molecular weights upon blocking is clearly visible.

The ^{1}H-NMR spectra of the n-heptane-soluble fractions (e.g., Fig. 7A) exhibited a sharp resonance at δ3.3 ppm ($-OCH_3$), characteristic of poly(MVE) units, and a doublet at δ 0.9 ppm [$-\overset{|}{C}(CH_3)_2$], characteristic of poly(IBVE) units. As n-heptane is a good solvent for poly(IBVE) but a nonsolvent for poly(MVE), the n-heptane-soluble fractions cannot contain homopoly(MVE), i.e., these fractions contain IBVE-MVE block polymers.

The poly(MVE) content in the n-heptane-soluble fractions increases with increasing amounts of MVE in the feed. The $\overline{M}_n$'s are close to theoretical values calculated by assuming that these fractions consist entirely of IBVE-MVE block polymers (Table 1). Evidently the n-heptane-soluble fractions are predominantly if not entirely IBVE-MVE block polymers, and in view of the dicationic nature of the starting poly(IBVE) the products are most likely triblocks, poly(MVE-b-IBVE-b-MVE).

The solubility characteristics of the n-heptane-soluble products have been investigated. When dissolved (~1 g/150 cm^3) in methanol,

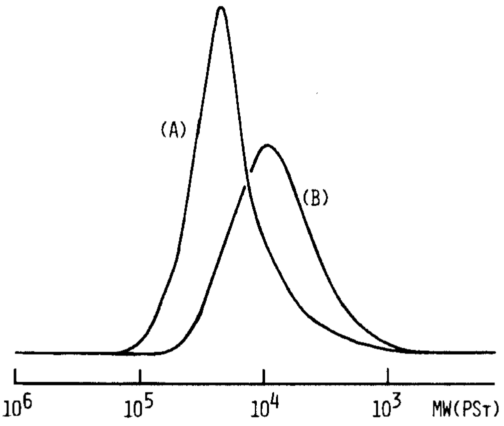

FIG. 6. MWD of the n-heptane-soluble fraction (A) and the starting poly(IBVE) (B) obtained in Experiment A, Table 1.

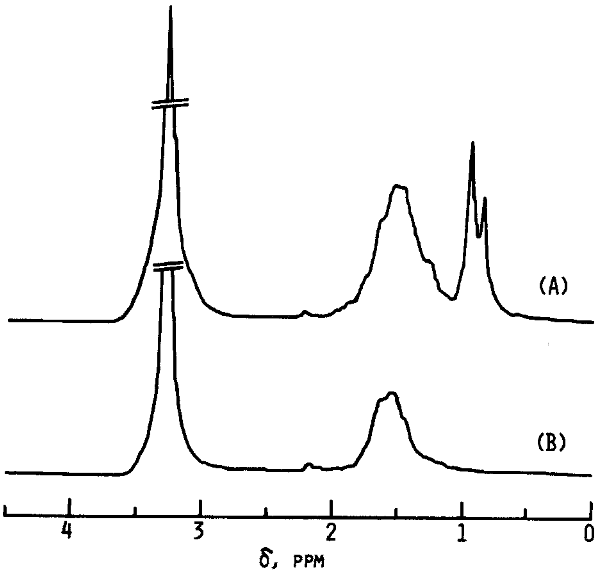

FIG. 7. ^{1}H-NMR spectra of the n-heptane-soluble (A) and the water-soluble (B) fractions obtained in Experiment A, Table 1.

a good solvent for poly(MVE) and a nonsolvent for poly(IBVE), these products gave hazy but homogeneous solutions free from solid or oily precipitates (a small amount of fine white powder appeared after a week of storage in the product obtained in Experiment C, Table 1). These observations also suggest IBVE-MVE block polymer formation; apparently the methanol-soluble poly(MVE) segments attached to the ends of the poly(IBVE) center block render the entire block polymer miscible with methanol. The n-heptane-soluble products gave transparent viscous solutions in CH_2Cl_2, CCl_4, tetrahydrofuran, and toluene at relatively high solid levels ($\sim$25 wt%) at room temperature.

The water-soluble fractions obtained in Experiments A and C were homopoly(MVE). Figure 7(B) shows a representative ^{1}H-NMR spectrum. At a higher MVE feed ratio (Experiment B), the water-soluble fraction contained a small amount of poly(IBVE), and at the highest MVE feed ratio (Experiment A), fractionation by n-heptane and water resulted in an emulsion. After evaporation of the solvents, this emulsion gave a very viscous material containing a small amount of poly(IBVE) (Table 1). Evidently IBVE-MVE block polymers rich in poly(MVE) are highly hydrophilic.

While the presence of homopoly(MVE) indicates chain transfer to this monomer, the amounts of the water-soluble fractions are small (less than 6.5 wt%), i.e., the blocking efficiency of MVE must be very high. Efficient blocking is consistent with the quasiliving character of MVE polymerization under our reaction conditions, as discussed in the preceding sections.

CONCLUSIONS

Quasiliving carbocationic polymerization of MVE was achieved by the use of the difunctional p-DCC/$AgSbF_6$ initiator system and slow and continuous monomer-addition. The use of a polar medium (CH_2Cl_2) and a low temperature (-70°C) was mandatory for quasiliving MVE polymerization. A nonpolar solvent (toluene) or a higher temperature (-30°C) resulted in deviations from the quasiliving conditions, probably due to chain transfer to monomer. Blocking MVE from quasiliving poly(IBVE) dications under the above optimum conditions led to novel IBVE-MVE block polymers in high yield and at high blocking efficiency.

ACKNOWLEDGMENTS

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