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Quasiliving Carbocationic Polymerization. VI. Quasiliving Polymerization of lsobutyl Vinyl Ether

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Quasiliving Carbocationic Polymerization. VI. Quasiliving Polymerization of Isobutyl Vinyl Ether

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ABSTRACT

Quasiliving carbocationic polymerization of isobutyl vinyl ether (IBVE) was achieved with the p-dicumyl chloride (p-DCC)/ $AgSbF_6$ initiating system in methylene chloride solvent at -70 and -90°C. The monomer was introduced as a steady, continuous stream to a premixed, well-stirred initiator solution (quasiliving technique). The number-average molecular weights ($\overline{M}_n$) of poly(IBVE) increased linearly with the cumulative weight of added monomer (W_{IBVE}), and linear $\overline{M}_n$ versus W_{IBVE} plots passing through the origin were obtained. $\overline{M}_n$'s were inversely proportional to the initial initiator concentration ($[\text{p-DCC}]_0$) and were in agreement with theoretical values ($W_{IBVE}/[\text{p-DCC}]_0$) expected for quasiliving systems. The number of polymer chains produced per unit initiator (p-DCC) was close to unity and remained unchanged during the early stages of the reactions. The poly(IBVE) exhibited narrow molecular weight distributions with $\overline{M}_w/\overline{M}_n$ ranging from 1.4 to 1.7. Polymerizations using methylene

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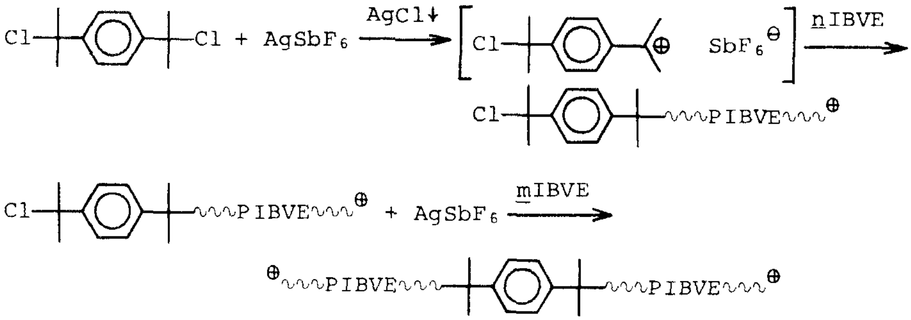
chloride solvent at higher temperatures (-30 and -50°C) also yielded linear ascending $\overline{M}_n$ versus W_{IBVE} plots; however, they showed intercepts. Using a nonpolar solvent (n-heptane), $\overline{M}_n$ did not increase with W_{IBVE} (-50°C) or $\overline{M}_n$ versus W_{IBVE} plots were strongly curved (-70°C), indicating slow initiation and the absence of quasiliving conditions. Evidently optimum conditions for quasiliving IBVE polymerization prevail only in polar media at lower temperatures.

INTRODUCTION

Recently it has been demonstrated that α-methylstyrene and other hydrocarbon olefins can be polymerized under so-called quasiliving conditions where the number-average molecular weight ($\overline{M}_n$) of polymers increases linearly with the weight of the added monomer [1]. Also the molecular weight distribution (MWD) of the products was shown to be decisively narrower ($\overline{M}_w/\overline{M}_n$ = 1.4-1.7) than that expected to arise under conventional conditions ($\overline{M}_w/\overline{M}_n \approx 2.0$). The theory of quasiliving polymerizations together with ways of achieving quasiliving conditions have been discussed in the first part of this series [2].

This study concerns the quasiliving cationic polymerization of isobutyl vinyl ether (IBVE) with the bifunctional p-dicumyl chloride [3] (p-DCC)/silver hexafluoroantimonate ($AgSbF_6$) initiating system. This bifunctional initiating system was selected because our intention was to generate two-headed growing species which in turn was expected to lead to triblock copolymers. Initiation and propagation in the p-DCC/$AgSbF_6$/IBVE system is visualized to occur as follows:



To facilitate ionization of p-DCC, it was premixed with $AgSbF_6$ before the introduction of IBVE (see Experimental). The p-DCC dication $[(CH_3)_2C^{\oplus}-C_6H_4-C^{\oplus}(CH_3)_2]$ may also form during premixing.

IBVE is quite different from hydrocarbon olefins (e.g., α-methylstyrene); for instance, the former is a polar monomer while the latter are nonpolar, and by virtue of the resonance-stabilization of the ether oxygen the propagating carbocation derived from IBVE is much more stable than those from α-methylstyrene, isobutylene, etc. The high stability of the growing vinyl ether cation should be advantageous for quasiliving polymerizations. Although previous studies on IBVE polymerization suggest the involvement of long-lived cations [4, 5] or termination-free [6-8] propagations, "living" and/or "quasiliving" polymerizations have not yet been achieved. By applying the quasiliving technique, we polymerized IBVE with the p-DCC/$AgSbF_6$ initiating system under a variety of conditions and defined optimum reaction parameters for quasiliving polymerization of this monomer.

EXPERIMENTAL

Materials

Commercial IBVE (GAF Corp.) was washed with 10% aqueous sodium hydroxide and water, dried overnight over sodium sulfate, and freshly distilled at least twice over calcium hydride under dry nitrogen. p-bis(α,α-Dimethyl chloromethyl)benzene (p-DCC) was prepared as reported [3, 9]. $AgSbF_6$ (Cationics Inc. and Alfa) was used as received; it was protected from light during storage and handling. n-Heptane (Aldrich) was washed successively with concentrated sulfuric acid, water, 10% aqueous sodium hydroxide, water, dried overnight over molecular sieves (3Å), and distilled at least twice over calcium hydride under dry nitrogen. Methylene chloride was used as described [3].

Procedures

All manipulations including transfers of chemicals were performed under dry nitrogen in a stainless steel enclosure. Polymerizations were carried out in the temperature range from -30 to -90°C in a 300-cm^3 three-neck, round-bottom flask equipped with a stirrer, a Teflon plug for monomer addition, and a serum cap for sampling. First p-DCC and $AgSbF_6$ solutions (200 cm^3 in total) were mixed and stirred for 1 min at the desired temperature. To this premixed initiator solution IBVE (mostly 25 vol% solution) was introduced continuously at a controlled flow rate (2.0-4.0 cm^3/min) through a precision solvent-metering pump (Beckman Model 110A) and a glass capillary outlet. The glass capillary effected a continuous, fine monomer stream (absence of dripping). Separate experiments showed that the length of premixing (1.0-20 min) did not influence subsequent polymerizations. At desired times known amounts of aliquots were withdrawn with a syringe from the reaction mixture and were injected into capped vials containing a few cm^3 methanol (quenching). After filtration and evaporation of volatiles, yields were determined gravimetrically. Duplicate experiments at -90°C showed a good reproducibility for $\overline{M}_n$ values (see open circles in Fig. 3).

The MWD was measured by gel permeation chromatography (GPC) on a Waters Associates 6000 A high pressure GPC chromatograph equipped with Microstyragel columns of 10^6, 10^5, 10^4, 10^3, and 500 Å; 0.2-0.4 cm^3 polymer solutions (0.5-1.0 wt%) in THF were used. $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ were calculated from GPC traces using polystyrene calibration. For several poly(IBVE) samples absolute $\overline{M}_n$ values were also determined by GPC/low-angle laser light scattering (LALLS) technique [10] on a Chromatix KMX-6 LALLS photometer connected in series with a Waters Associates 150-C ALC/GPC chromatograph (columns: 10^6, 10^5, 10^4, 10^3, 500, and 100 Å Microstyragel; eluent: THF). The differential refractive index (dn/dc) used for data processing was measured in THF at 35°C on a Chromatix KMX-16 laser differential refractometer. The absolute $\overline{M}_n$'s thus obtained were in close agreement with the corresponding values based on polystyrene calibration:

$\overline{M}_n$(absolute) $\times 10^{-4}$	7.61	5.41	4.69	3.08	1.97	1.33	0.64
$\overline{M}_n$(PSt calibration) $\times 10^{-4}$	7.01	5.71	4.66	3.06	1.80	1.06	0.73

Thus the use of $\overline{M}_n$'s determined by polystyrene calibration will not significantly affect the data and interpretation.

^{1}H-NMR spectra (~20 wt% polymers in CCl_4) were recorded on a Varian Associates T-60 NMR spectrometer at room temperature.

Parallel with quasiliving experiments "control" runs were also carried out in CH_2Cl_2 at -90 or -50°C in culture tubes with Teflon-lined screw caps ($[IBVE]_0 = 0.20$ $\underline{M}$, $[p\text{-DCC}]_0 = 0.50\text{-}1.0$ m$\underline{M}$, $[AgSbF_6]_0 = 2.0$ m$\underline{M}$, time = 10 min). In these runs the monomer solution was added in one dose to a premixed p-DCC/$AgSbF_6$ charge (premixing 1.0 min). At -90°C neither p-DCC nor $AgSbF_6$ alone induced IBVE polymerization; however, quantitative polymer yield was obtained when the monomer solution was added to a premixed p-DCC/$AgSbF_6$ solution. At -50°C considerable polymerization

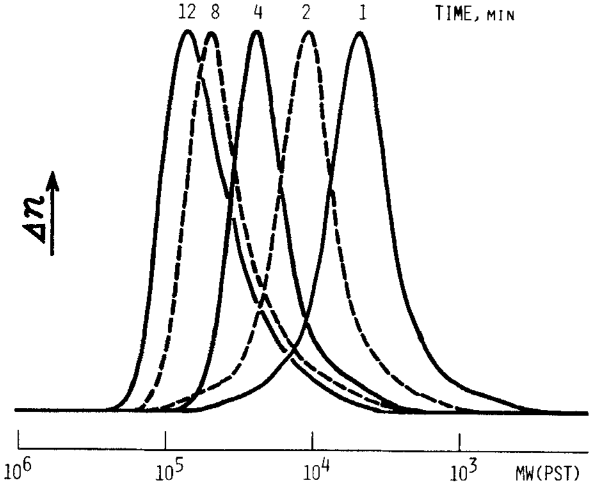


FIG. 1. MWD of poly(IBVE) obtained in CH_2Cl_2 at -90°C: $[p\text{-DCC}]_0$ = 0.50 mM; $[AgSbF_6]_0$ = 1.1 mM; IBVE addition rate = 0.76 g/min.

occurred with $AgSbF_6$ alone even in the absence of p-DCC. A premixed p-DCC/$AgSbF_6$ solution also gave 100% polymer yield.

RESULTS AND DISCUSSION

IBVE Polymerization in CH_2Cl_2 at -90°and -70° C: $\overline{M}_n$ and MWD

IBVE was polymerized by introducing the monomer as a steady and continuous stream into a premixed p-DCC/$AgSbF_6$ system in CH_2Cl_2 at -70 and -90°C. The silver salt was in slight stoichiometric excess over the p-DCC ($[AgSbF_6]_0/[p\text{-DCC}]_0$ = 2.3). In all experiments polymer yields at any time were in good agreement with the total weight of added IBVE, indicating consistently quantitative monomer conversions. The products obtained were sticky semisolids.

Figures 1 and 2 show typical GPC traces of poly(IBVE)'s obtained at different reaction times. The MWD's are narrow and are shifting toward higher molecular weights with time; no significant broadening can be observed.

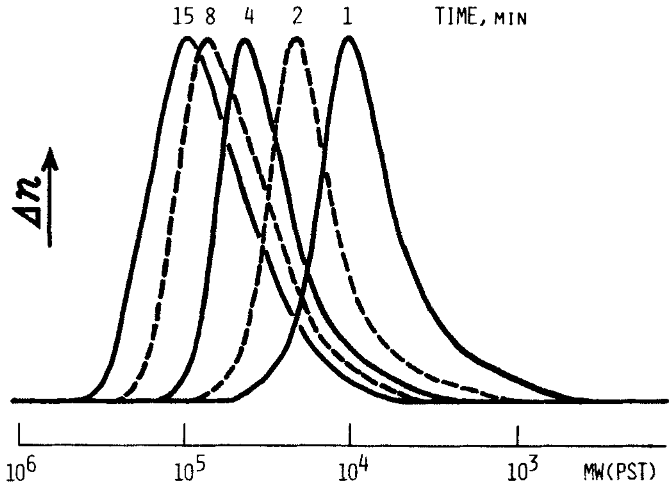


FIG. 2. MWD of poly(IBVE) obtained in CH_2Cl_2 at -70°C: $[p\text{-DCC}]_0 = 0.50$ mM; $[AgSbF_6]_0 = 1.1$ mM; IBVE addition rate = 0.77 g/min.

$\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ values calculated from these data were plotted against W_{IBVE}, the cumulative weight of IBVE added to the initiating system (Figs. 3 and 4). At both temperatures $\overline{M}_n$ increases steadily with W_{IBVE} and, more importantly, $\overline{M}_n$ versus W_{IBVE} plots are linear over a wide range of W_{IBVE} and pass through the origin. $\overline{M}_w/\overline{M}_n$ values range from 1.4 to 1.7, i.e., they are within experimental variation of the theoretical value of 1.5 expected for a two-headed quasiliving species. With increasing W_{IBVE} the $\overline{M}_n$ versus W_{IBVE} plots tend to deviate from the straight lines.

These results demonstrate that quasiliving polymerization of IBVE can be achieved by the use of CH_2Cl_2 solvent at -70 and -90°C. This novel quasiliving system enables the synthesis of poly(IBVE)'s with controlled (and high) molecular weights and rather narrow MWD; these achievements cannot be attained by conventional IBVE polymerizations because of unavoidable and frequent chain-transfer reactions [6].

Figure 3 shows the $\overline{M}_n$ versus W_{IBVE} relationships obtained over monomer-addition rates of 0.38 to 1.68 g/min; $\overline{M}_n$ increases linearly with W_{IBVE} (< 10 g) and the data give a single straight line passing

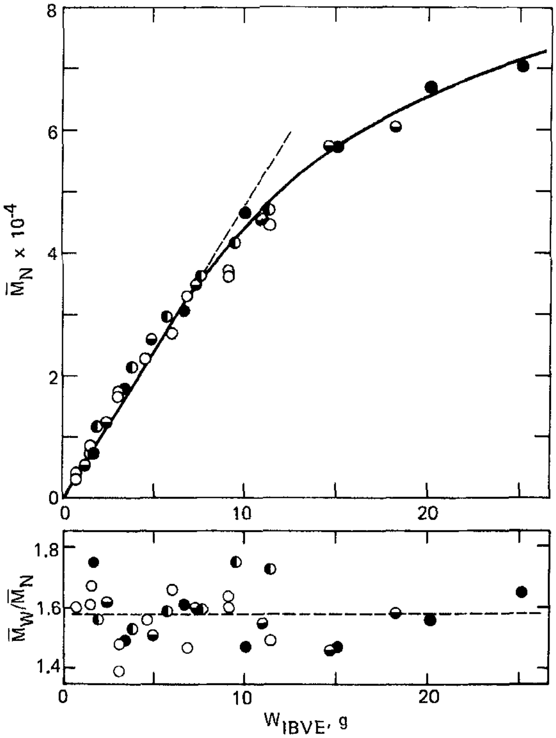


FIG. 3. $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ as functions of monomer input W_{IBVE} in CH_2Cl_2 at -90°C: $[p\text{-DCC}]_0 = 0.50$ mM; $[AgSbF_6]_0 = 1.1$ mM. IBVE addition rate (g/min): (◐) 0.38, (○) 0.76, (◒) 1.22, (●) 1.68.

through the origin. The monomer-addition rate does not seem to affect the $\overline{M}_n$-W_{IBVE} relationship provided the monomer is added slowly and continuously to an initiator charge. Although the maintaining of very low monomer concentration throughout the quasiliving polymerization is mandatory [1], it is of interest that quasiliving conditions of IBVE polymerization can be attained over this range of monomer-addition rates.

Number of Polymer Chains

The quasiliving character of IBVE polymerization is further supported by quantitative analyses. Figure 5 illustrates changes in N, the number of poly(IBVE) chains produced per unit initiator (p-DCC), as a function of W_{IBVE}. N is defined by

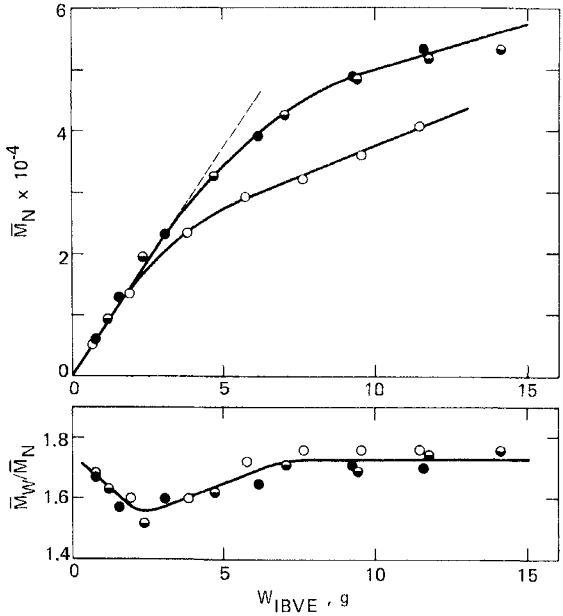


FIG. 4. $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ as functions of monomer input W_{IBVE} in CH_2Cl_2 at -70°C: $[p\text{-DCC}]_0$ = 0.50 mM; $[AgSbF_6]_0$ = 1.1 mM. IBVE addition rate (g/min): (○) 0.38, (◒) 0.59, (●) 0.77.

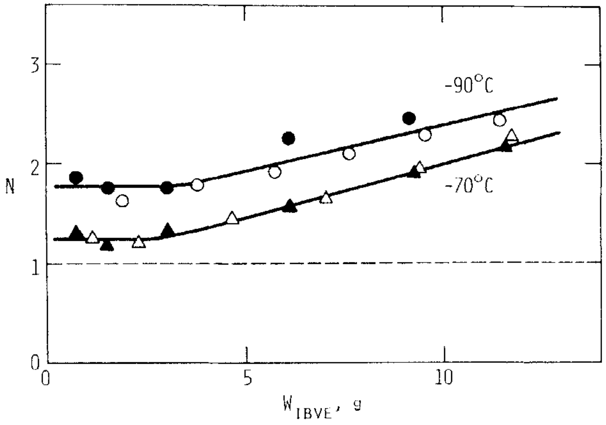


FIG. 5. Relationships between monomer input W_{IBVE} and N, the number of poly(IBVE) chains produced per unit p-DCC molecule, in CH_2Cl_2 at -90 and -70°C: $[p\text{-DCC}]_0$ = 0.50 mM; $[AgSbF_6]_0$ = 1.1 mM. IBVE addition rate (g/min): (○) 0.38, (●) 0.76, (△) 0.59, (▲) 0.77.

$$N = \frac{W}{\overline{M}_n[\text{p-DCC}]_0} \tag{1}$$

where W represents the cumulative weight of IBVE added to 1 dm^3 charge and $[\text{p-DCC}]_0$ is the initial concentration of p-DCC. Ideal living systems give N equal to unity throughout the experiment. At -70 and -90°C the N values obtained were close to unity and remained constant during the early stages of the polymerizations; however, N increased gradually later with increasing W_{IBVE}, probably due to chain transfer. The trends of these data, i.e., agreement with theory during the early stages of the experiment and deviation later, reflect those shown in Figs. 3 and 4 and indicate quasiliving conditions up to ~3 g IBVE.

Effect of p-DCC Concentration

In quasiliving polymerizations, $\overline{M}_n$ obeys

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

Thus the effect of $[\text{p-DCC}]_0$ on $\overline{M}_n$ versus W_{IBVE} plots was studied at -90°C. Figure 6 gives the results. $\overline{M}_n$ increased linearly with W_{IBVE} at all p-DCC concentrations and the plots passed through the origin, although deviations from linearity appeared during the later stages of the reactions. The slopes of linear portions of the plots were inversely proportional to $[\text{p-DCC}]_0$, which is consistent with Eq. (2) and provides further support for the existence of quasiliving polymerization at lower temperatures. Similar results were obtained for -70°C.

Initiation Efficiency

Since we employed p-DCC as the initiator, GPC analysis with dual [ultraviolet (UV) and refractive index (RI)] detectors enabled us to examine quantitatively the incorporation of the aromatic fragment of the initiator into poly(IBVE) by Kennedy and Smith's method based on [3]

$$\frac{(UV/RI)_m}{(UV/RI)_x} = \frac{(MW)_x}{(MW)_m} \tag{3}$$

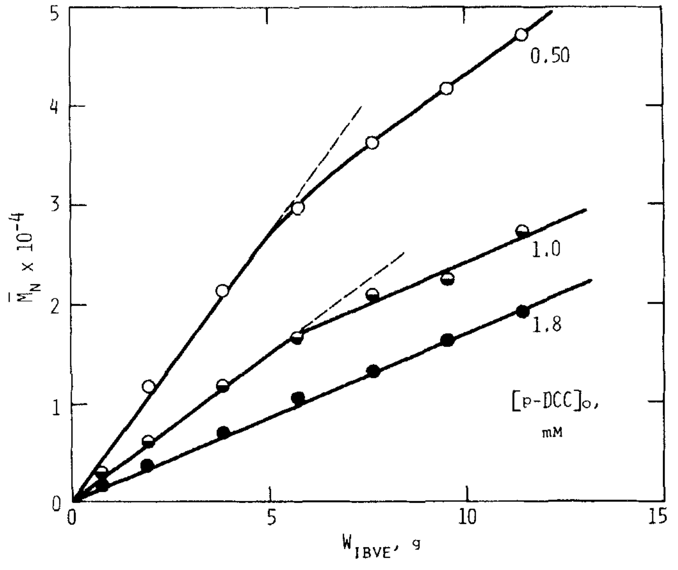


FIG. 6. Effect of $[\text{p-DCC}]_0$ on $\bar{M}_n$-W_{IBVE} relationships in CH_2Cl_2 at -90°C: $[\text{p-DCC}]_0$ as indicated; $[AgSbF_6]_0/[\text{p-DCC}]_0$ = 2.3; IBVE addition rate = 0.38 g/min.

where $(UV/RI)_x$ represents the ratio of UV and RI detector responses at an elution volume x, $(MW)_x$ is the molecular weight at x, and $(UV/RI)_m$ and $(MW)_m$ are reference values taken at x = m. If a poly(IBVE) molecule carries one p-DCC fragment (or p-DCC fragments are distributed uniformly in polymers regardless of their molecular weights), the plot of $(UV/RI)_m/(UV/RI)_x$ against $(MW)_x/(MW)_m$ at various x's should result in a straight line passing through the origin and having a unit slope [3]. Plots of Eq. (3) were constructed for poly(IBVE) samples obtained at -70°C (20 samples) and -90°C (17 samples) and they all yielded straight lines passing through the origin with the following slopes:

0.98 ± 0.02 at -70°C
0.97 ± 0.03 at -90°C

Furthermore, the ^{1}H-NMR spectrum of a poly(IBVE) ($\bar{M}_n$ = 3600) obtained at -90°C under quasiliving conditions exhibit a sharp

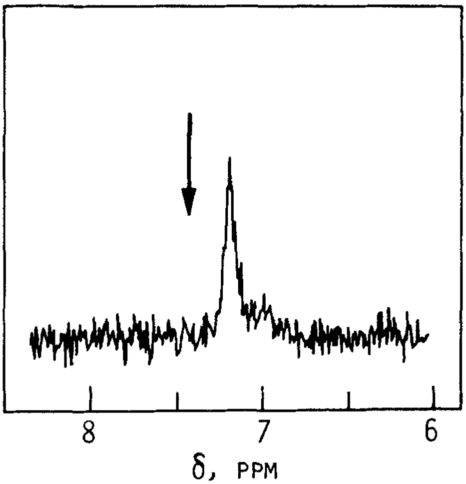


FIG. 7. ^{1}H-NMR spectrum (aromatic region) of poly(IBVE) formed in CH_2Cl_2 at -90°C: $[\text{p-DCC}]_0$ = 2.0 mM; $[AgSbF_6]_0$ = 4.5 mM; IBVE addition rate = 0.38 g/min; time = 5.0 min; $\overline{M}_n$ (GPC) = 3600. The arrow shows the position of aromatic absorption for p-DCC.

aromatic resonance at δ7.20 ppm (Fig. 7), characteristic of a p-DCC unit incorporated into a polymer chain [3]. Signals due to unreacted p-DCC (singlet at δ7.42 ppm) were absent.

These GPC and NMR analyses indicate quantitative initiation by p-DCC in polymerizations at -70 and -90° C. These data also suggest the formation of bifunctional quasiliving poly(IBVE) cations.

Effect of Temperature in CH_2Cl_2

Figure 8 shows $\overline{M}_n$ versus W_{IBVE} plots obtained with poly(IBVE)'s prepared at higher temperatures (-30 and -50° C) in CH_2Cl_2 but otherwise under the same conditions as those prepared at -70 and -90° C. At -30° C $\overline{M}_n$ increased with W_{IBVE}, but its values were an order of magnitude smaller than those expected from $[\text{p-DCC}]_0$ (cf. Eq. 2) and the plot could no longer be back-extrapolated to the origin. $\overline{M}_n$ versus W_{IBVE} plots for -50° C increase steadily but nonlinearly; $\overline{M}_n$'s were higher than those obtained at -30° C at the same W_{IBVE}.

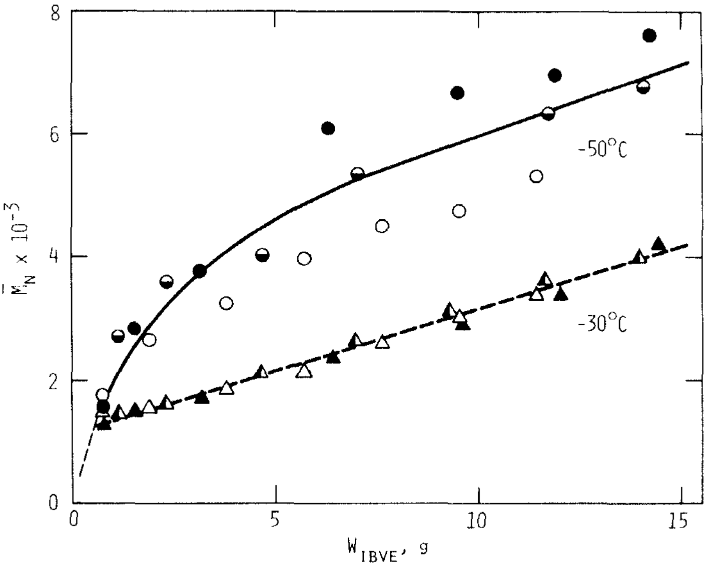


FIG. 8. $\bar{M}_n$-W_{IBVE} relationships in CH_2Cl_2 at -50°C (—) and at -30°C (- - -): $[p\text{-DCC}]_0 = 0.50$ mM; $[AgSbF_6]_0 = 1.1$ mM. IBVE addition rate (g/min): (○) 0.38, (◒) 0.59, (●) 0.79, (△) 0.38, (◭) 0.58, (▲) 0.80.

However, at both temperatures MWD's were narrow ($\bar{M}_w/\bar{M}_n = 1.4$-$1.6$), i.e., within the experimental error of the expected value of 1.5. These data, coupled with the observed increases in $\bar{M}_n$ values, suggest the presence of long-lived propagating species, but also show that satisfactory quasiliving conditions do not prevail at -30 and -50°C.

From the data given in Fig. 8, the number of polymer chains (N, Eq. 1) was calculated and compared with those obtained in experiments carried out at -70 and -90°C (Fig. 9). In contrast to the nearly ideal values at -70 and -90°C, i.e., N close to unity and almost constant, the N values for the higher temperatures were much higher than unity and increased steeply with W_{IBVE}. These trends indicate an increasing contribution of chain transfer at higher temperatures.

Effect of Solvent Polarity

IBVE polymerizations were also carried out in a nonpolar solvent, n-heptane, at -70 and -50°C. Since $AgSbF_6$ is sparingly soluble in

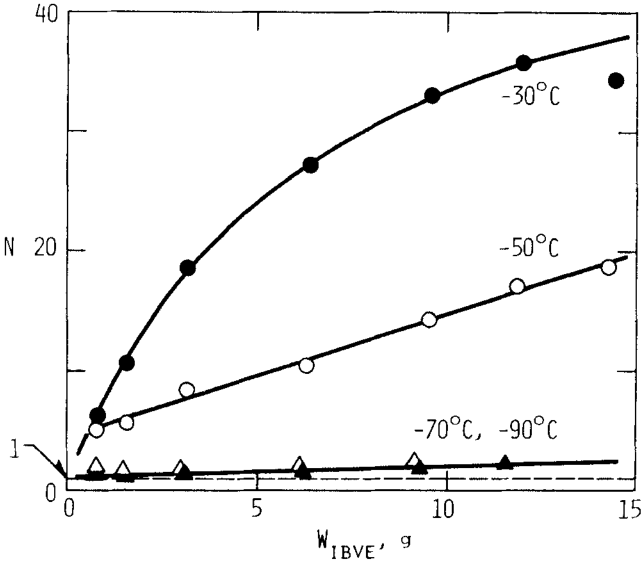


FIG. 9. Effect of temperature on the number of polymer chains (N) in CH_2Cl_2: $[p\text{-DCC}]_0 = 0.50$ mM; $[AgSbF_6]_0 = 1.1$ mM; IBVE addition rate = 0.76 - 0.80 g/min. Temperature (°C): (●) -30, (○) - 50, (▲) -70, (△) -90.

nonpolar solvents, the salt was dissolved in a small amount (5 cm^3) of CH_2Cl_2 and premixed with a p-DCC solution (195 cm^3) in n-heptane (see Experimental). Figure 10 shows representative results at -70°C and corresponding data using CH_2Cl_2 for comparison. In n-heptane the $\overline{M}_n$ versus W_{IBVE} plot shows a steeply rising phase followed by a much slower rising stage. Importantly, the N values are less than unity at the beginning of the reaction, but increase steadily with W_{IBVE} and finally exceed unity. This is in contrast to the results obtained with CH_2Cl_2 where N was close to but always larger than unity. N values smaller than unity indicate that in nonpolar media initiation is slow due to incomplete ionization of the initiator system during premixing.

At -50°C (Fig. 11), $\overline{M}_n$'s remain unchanged with increasing W_{IBVE} and $\overline{M}_w/\overline{M}_n \approx 2.0$. Evidently the polymerization in n-heptane at -50°C involves neither quasiliving nor long-lived propagating species but follows a conventional chain-transfer-dominated course.

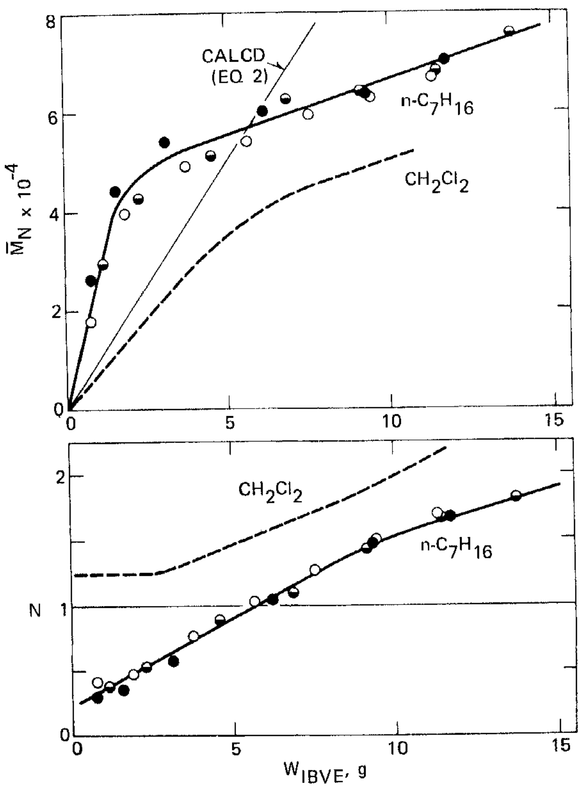


FIG. 10. $\overline{M}_n$ and N as functions of monomer input W_{IBVE} in n-heptane at -70°C: $[\text{p-DCC}]_0$ = 0.50 mM; $[AgSbF_6]_0$ = 1.1 mM. IBVE addition rate (g/min): (○) 0.38, (◒) 0.57, (●) 0.78. The dashed lines show the data obtained in CH_2Cl_2 under the same conditions (from Figs. 4 and 5).

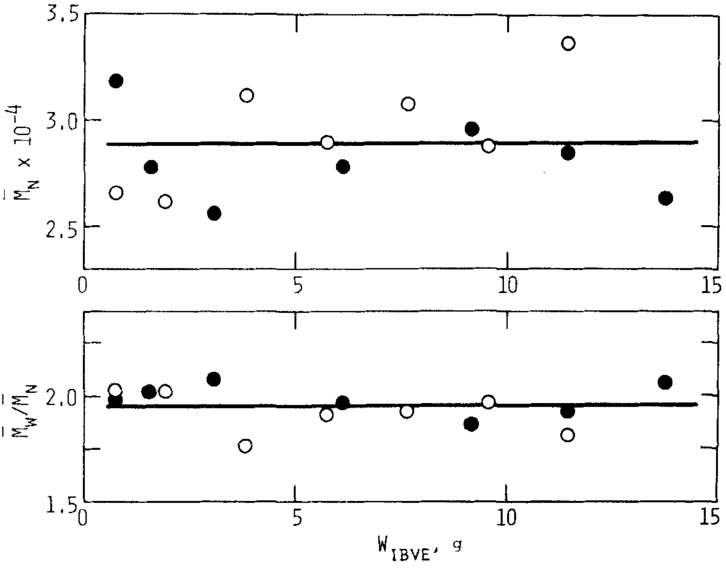


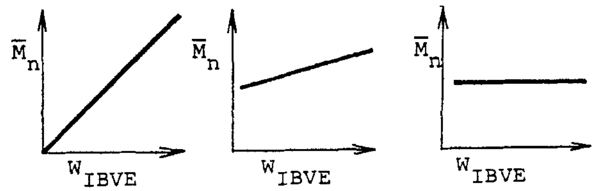
FIG. 11. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ as functions of monomer input W_{IBVE} in n-heptane at -50°C: $[\text{p-DCC}]_0 = 0.50$ mM; $[\text{AgSbF}_6]_0 = 1.1$ mM. IBVE addition rate (g/min): (○) 0.38, (●) 0.76.

TABLE 1

$\bar{M}_n$-W_{IBVE} Relationships under a Variety of Conditions[a]

Solvent	Temperature, °C -90	 -70	 -50	 -30
CH_2Cl_2	○	○	△	△
n-C_7H_{16}	—	△	×	—

[a] Key: ○ △ ×



CONCLUSIONS

Table 1 summarizes $\overline{M}_n$-W_{IBVE} relationships obtained under a variety of conditions in this work. The observed relationships are classified into three categories: 1) (○) linear $\overline{M}_n$-W_{IBVE} plot passing through the origin and extending over a wide range of W_{IBVE}; plots like this indicate quasiliving polymerizations; 2) (×) $\overline{M}_n$ independent of W_{IBVE}; plots like this indicate conventional transfer-dominant polymerizations; and 3) (△) intermediate case between 1) and 2), where $\overline{M}_n$ increases linearly with W_{IBVE} but $\overline{M}_n$-W_{IBVE} plots do not pass through the origin; in this case, quasiliving conditions may be attained only at the very beginning of the reaction.

Inspection of Table 1 shows that quasiliving conditions for IBVE polymerizations are optimum in polar solvents (CH_2Cl_2) at lower temperatures (-70 and -90°C). Evidently irreversible transfer and/or termination reactions are "frozen out" at low temperatures and fast initiation and/or reionization of dormant (halogenated) growing ends is promoted in polar media.

The presence of the ether oxygen in the monomer may or may not be advantageous for quasiliving polymerizations of vinyl ethers in general and IBVE in particular. Vinyl ether carbocations are highly stable and may undergo terminationless polymerization [4-8]; however, these monomers are strongly nucleophilic and highly prone to frequent chain transfer to monomer [6]. The attainment of quasiliving polymerization of IBVE, as demonstrated above, implies that the quasiliving technique overcomes this drawback most likely by promoting the reversibility of chain transfer to monomer.

In conclusion, optimum conditions for the quasiliving cationic polymerization of IBVE by the p-DCC/$AgSbF_6$ initiating system have been established. Application of this new quasiliving process to the synthesis of block polymers is the subject of a subsequent publication [11].

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