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LIVING CARBOCATIONIC POLYMERIZATION. XXI. KINETIC AND MECHANISTIC STUDIES OF ISOBUTYLENE POLYMERIZATION INITIATED BY TRIMETHYLPENTYL ESTERS OF DIFFERENT ACIDS*

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ABSTRACT

To gain increased insight into the mechanism of living polymerization of isobutylene (IB) and specifically into the effect of the structure of the initiator on the rate, we have investigated the polymerization of IB initiated by eight 2,4,4-trimethylpentyl (TMP) esters $RCOO{-}C(CH_3)_2C(CH_3)_3$ where $R = {-}CCl_3$, ${-}CHCl_2$, ${-}CH_2C_6H_5$, ${-}CH_3$, ${-}CH(CH_3)_2$, ${-}C(CH_3)_3$, ${-}C_6H_5$, and ${-}CH{=}CHC_6H_5$ in conjunction with BCl_3 coinitiator using CH_3Cl diluent at −30°C. The rates decreased along the sequence of these substituents from very high values (with $R = {-}CCl_3$, ${-}CHCl_2$) to very

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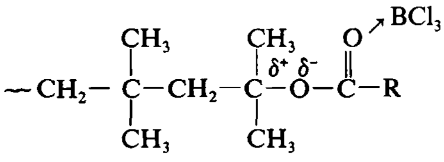
*A short preliminary report with the same title has appeared in *Polymer Preprints, 29*(2), 69 (1988).

low values (R = $-C(CH_3)_3$, $-C_6H_5$, $-CH{=}CHC_6H_5$). The trend of decreasing rates was interpreted in terms of inductive effects. According to conversion-time curves obtained with the five esters R = $-CH_2C_6H_5$, $-CH(CH_3)_2$, $-C(CH_3)_3$, $-C_6H_5$, and $-CH{=}CHC_6H_5$, propagation is first order in monomer and the apparent rate constants of propagation decrease along the above sequence, suggesting the presence of inductive effects and the absence of resonance effects. With highly electron-donating substituents, i.e., with R = $-CH(CH_3)_2$, $-C(CH_3)_3$, $-C_6H_5$, and $-CH{=}CHC_6H_5$, chain transfer to monomer is operational, the rates of which were found to be monomolecular (zero order in monomer). Chain transfer to monomer can be avoided by increasing the polarization of the C—O bond by using slightly electron-donating or strongly withdrawing substituents (R = $-CH_2C_6H_5$, $-CH_3$ or $-CHCl_2$, $-CCl_3$) or by the use of CH_2Cl_2; both measures also result in enhanced propagation rate constants. Solvent polarity critically affects the stability of the growing chain end. By decreasing the polarity of the solvent, the decomposition temperature of the growing site decreases, leading to termination. Quenching studies have been carried out with model compounds as well as with polymerization systems and both kinds of experiments indicated the exclusion formation of t-chloro endgroups.

INTRODUCTION

Great strides have been made in living carbocationic polymerization LC$^+$Pzn of olefins since the opening of this field some four years ago [1–3]. According to the original proposition [1], LC$^+$Pzn of IB induced by certain ester · BCl_3 complexes proceeds by monomer insertion into the alkyl-oxygen bond of the growing complex:



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}\overset{\delta^+\ \delta^-}{-O-}\overset{O \nearrow BCl_3}{\overset{\|}{C}}-R$$

The purpose of the present investigation was to deepen our insight into the mechanism of LC$^+$Pzn's, specifically to study the effect of the R group on the rate of LC$^+$Pzn of IB. We postulated that inductive and resonance effects of R will influence the polarization of the C—O bond and thus will control the rates [2]. Electron-withdrawing R groups (e.g., —CCl_3, —$CHCl_2$, —CH_2Cl) and groups capable of exerting resonance effects (e.g., —C_6H_5, —$CH{=}CHC_6H_5$) were expected to enhance the rates, while electron-donating substituents (e.g., —CH_3, —$CH(CH_3)_2$, —$C(CH_3)_3$) were anticipated to be retarders.

Against this background, the rates of IB polymerization have been determined by changing R (i.e., the acid moiety of the ester) but otherwise keeping the other system variables constant: RCOO—$C(CH_3)_2$-$CH_2C(CH_3)_3$/BCl_3/IB/CH_3Cl/−30°C. 2,4,4-Trimethylpentyl (TMP) esters have been used as initiators because their structure is essentially identical to that of the growing chain end. Thus the high initial rates with tertiary benzylic ester initiators [4, 5] are avoided. The results substantiated our expectations in regard to inductive effects but held surprises in that resonance effects were found to be absent. Analysis of these phenomena is of great value for fine tuning of LC$^+$Pzn systems and for the design of efficient initiating systems for the synthesis of block copolymers, functionalized polymers, etc. [6, 7].

EXPERIMENTAL

The source and purity of IB, CH_3Cl, CH_2Cl_2, C_2H_5Cl, *n*-hexane, and BCl_3, together with polymerization conditions and characterization methods (GPC, NMR), have been described [1].

TMP-trichloroacetate (Cl_3CCOO—TMP), TMP-dichloroacetate (Cl_2CHCOO—TMP), TMP-acetate (CH_3COO—TMP), and TMP-phenylacetate ($C_6H_5CH_2COO$—TMP) were synthesized from TMP-2-ol and the corresponding acid chloride in diethyl ether using *N,N*-dimethylaniline as catalyst. General procedures have been described [1]. TMP—isobutyrate ($(CH_3)_2CHCOO$—TMP), TMP-pivalate ($C(CH_3)_3COO$—TMP), TMP—benzoate (C_6H_5COO—TMP), and TMP—cinnamate ($C_6H_5CH{=}CHCOO$—TMP) have been synthesized according to the following general procedure: 9.5 g (0.073 mol) TMP-2-ol and 9.81 g (0.0803 mol) 4-dimethylaminopyridine were dissolved in 130 mL benzene, and 30 mL benzene was distilled off to dry the solution (azeotropic drying). While refluxing, 0.069 mol acid chloride was added dropwise and the reaction mixture was refluxed for 3–7 days. After workup [1], the crude product was chromatographed on neutral Al_3O_3 (activity III) and afforded upon elution with *n*-pentane pure TMP-ester.

In forced termination studies the charges and the TMP—ester · BCl_3 model compound in CH_2Cl_2 were quenched by the addition of prechilled methanol or pyridine (wet quenching), or without the addition of any quenching agent by increasing the temperature of the system to ambient and thus decomposing the active complexes (thermal quenching). The ^1H-NMR and IR spectra of the decomposition products of the TMP—ester · BCl_3 model compounds were taken in the original CH_2Cl_2 solutions without further purification.

RESULTS AND DISCUSSION

Demonstration of Living Polymerization

Orienting research on the rate of LC^+Pzn of IB induced by RCOO—TMP/BCl_3 complexes showed two extremes: the rates were either very high, i.e., with R = CCl_3—, $CHCl_2$—, CH_3— conversions were complete within a few minutes, or were very low, i.e., with R = $(CH_3)_2CH$—, $(CH_3)_3C$—, C_6H_5—, $C_6H_5CH{=}CH$— conversions reached ~90% within 2–4 days. Due to the high rates, the living nature of the CH_3COO—TMP/BCl_3/IB/CH_3Cl/−30°C system had to be demonstrated by the incremental monomer addition (IMA) technique [1]. In the present study we have determined the rates of IB polymerization initiated by TMP esters of seven acids, i.e., with RCOO—TMPs where R = CCl_3—, $CHCl_2$—, $C_6H_5CH_2$—, $(CH_3)_2CH$—, $(CH_3)_3C$—, C_6H_5—, C_6H_5—CH=CH—, while the other variables were kept constant: RCOO—TMP/BCl_3/IB/CH_3Cl/−30°C. Two types of control experiments were also carried out, one in the absence of added initiator (BCl_3/IB/CH_3Cl/−30°C) and one using TMP-chloride in place of the TMP-esters at the same concentration (TMPCl/BCl_3/CH_3Cl/−30°C). The results of these control runs, shown in Table 1, suggest that TMPCl is not an efficient initiator: the PIB molecular weights and conversions were similar in the presence and in the absence of TMPCl. With the various TMP—esters, depending on the specific R group, we have obtained much faster as well as much slower polymerizations than in the control runs. Evidently uncontrolled initiation (i.e., by protogenic impurities) is absent in the presence of TMP—esters, which suggests that these esters may function as proton traps in these experiments.

TABLE 1. Control Polymerization Experiments: $BCl_3/IB/CH_3Cl/-30°C$[a]

Added initiator	Polymerization time	Conversion, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
–	30 min	6	36 000	2.0
TMPCl	30 min	9	34 000	2.3
–	6 h	100	32 000	2.8
TMPCl	6 h	100	34 000	2.7

[a] $[IB] = 0.94$ mol/L, $[BCl_3] = 5.1 \times 10^{-2}$ mol/L, $[TMPCl] = 5.6 \times 10^{-3}$ mol/L.

As expected, very high rates were obtained with $R = CCl_3-$ and *$CHCl_2-$ so that conversion-time plots could not be obtained and the* living nature of these polymerizations had to be proven by $\bar{M}_n$ versus W_{PIB} (weight of polymer formed) plots using the IMA technique [1]. Figures 1 and 2 show the data. The inserts show that the number of moles of PIB formed (N) is constant throughout the run and that $N = [I_0]$ (= initial initiator concentration). The same results were obtained by the IMA and conventional techniques and by adding the IB to premixed initiator/coinitiator systems. Not too surprisingly, these results are essentially identical to those obtained with TMP-acetate, $R = CH_3-$ [1].

In contrast to these systems, the rates obtained by $C_6H_5CH_2COO-TMP$ were sufficiently low to construct $\bar{M}_n$ versus % conversion plots. Figure 3 shows the results of these experiments together with those obtained by the IMA technique (see also Fig. 4). Evidently living polymerizations proceed with the $C_6H_5CH_2COO-TMP/BCl_3$ combination as well.

The charges analyzed in Figs. 1-3 became hazy (heterogeneous) at $\bar{M}_n \approx 5000$. The appearance of heterogeneity also depends on MWD: If the MWD is broad, haziness may appear at a lower $\bar{M}_n$.

Polymerizations were much slower with the other four TMP—esters, i.e., $R = C_6H_5CH{=}CH-$, C_6H_5-, $(CH_3)_3C-$, and $(CH_3)_2CH-$. Figure 4 shows the $\bar{M}_n$-% conversion plots obtained with these initiators. The charges were homogeneous up to ~90% conversions where they became cloudy, indicating the onset of polymer precipitation due to the

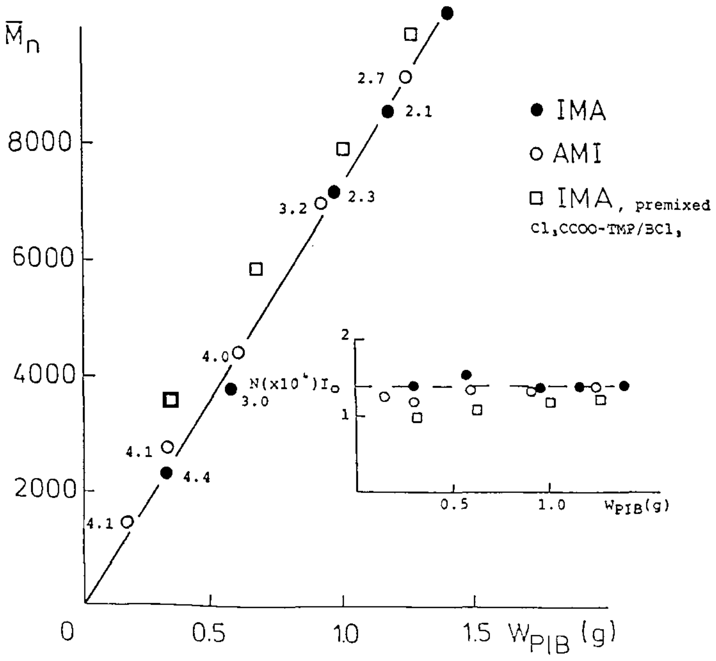


FIG. 1. $\overline{M}_n$ and $W_{PIB'}$ and N versus W_{PIB} plots obtained with the Cl_3COO—TMP/BCl_3/IB/CH_3Cl/−30°C system. ($[I_0] = 5.6 \times 10^{-3}$ *M*, $[BCl_3] = 5.1 \times 10^{-2}$ *M*. Numbers indicate $\overline{M}_w/\overline{M}_n$ values.)

formation of relatively high $\overline{M}_n$ PIB. The data are close to theoretical up to ~50% conversion; however, beyond this level they start to deviate from the theoretical and suggest the onset of chain transfer to monomer. According to ^{1}H-NMR spectroscopy, both *exo-* and *endo*-olefinic protons are present in the polymers, which also indicates chain transfer (see also later). As expected [8], the molecular weight distributions (MWD) exhibit a broadening tendency from $\overline{M}_w/\overline{M}_n = 1.2$ below ~50% conversion to $\overline{M}_w/\overline{M}_n = 1.5$ at close to 100% conversion. By lowering the temperature to −50°C, some improvement is obtained, i.e., the data points follow the theoretical line up to ~60% conversion (see Fig. 5).

Comments about the broad MWDs, particularly with R = CCl_3— and $CHCl_2$—, by one of the reviewer's prompts us to point out that living polymers need not be monodisperse and that narrow MWD is not a criterion for livingness. The fact that the MWDs do narrow with progressing polymerization indicates a living system. While the cause of the broad MWDs observed is unknown, several possibilities may explain it: 1) Broad MWDs appear right at the onset of the polymerizations (1st sample); however, further growth (2nd, 3rd, etc. samples) yields close to monodisperse polymer. A simple calculation illustrates this: If a living polymer of $\overline{M}_n = 2000$ and $\overline{M}_w/\overline{M}_n = 4.4$ grows to give a product of $\overline{M}_n = 3000$ and $\overline{M}_w/\overline{M}_n = 3.0$, then growth must have occurred by the incorporation of 1000 g/mol close to monodisperse material (cf. Fig. 1). Similarly, if a living polymer of $\overline{M}_n = 3000$ and $\overline{M}_w/\overline{M}_n = 2.7$ grows to $\overline{M}_n = 4000$ and $\overline{M}_w/\overline{M}_n = 2.1$, then growth must have involved 1000 g/mol monodisperse polymer (cf. Fig. 3). 2) Broad MWDs may arise by relatively slow initiation (i.e., slow cation generation or cationation). In the systems under investigation, relatively slow cation generation would

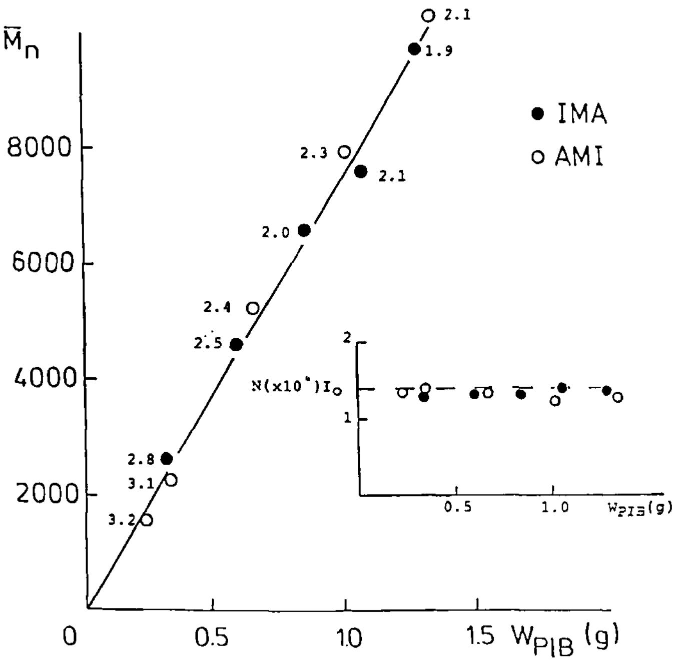


FIG. 2. $\overline{M}_n$ and W_{PIB}, and N versus W_{PIB} plots obtained with the $Cl_2CHCOO-TMP/BCl_3/IB/CH_3Cl/-30°C$ system. ($[I_0] = 5.6 \times 10^{-3}$ M, $[BCl_3] = 5.1 \times 10^{-2}$ M. Numbers indicate $\overline{M}_w/\overline{M}_n$ values.)

mean slow dormant $\rightleftharpoons$ living equilibration. By increasing the ionicity of the growing center (e.g., in the presence of less nucleophilic counteranions), the rate of propagation will increase while the rate of the dormant $\rightleftharpoons$ living process would decrease. Broad MWDs cannot be due to slow monomer cationation because cationation and propagation are essentially identical processes with the TMP—esters. But even if cationation were slow relative to propagation, the limiting MWD would be $\bar{M}_w/\bar{M}_n \approx 1.4$ [8]. 3) Broad MWDs may also be due to a multiplicity of growing centers with dissimilar ionicites, inadequate reactor control (insufficient stirring, heat jumps), etc.

Kinetic Investigations

The low rates obtained with RCOO—TMP initiators where R = C_6H_5—, C_6H_5—CH=CH—, $(CH_3)_3C$—, $(CH_3)_2CH$—, and $C_6H_5CH_2$— enabled us to construct conversion-time plots and thus to calculate kinet-

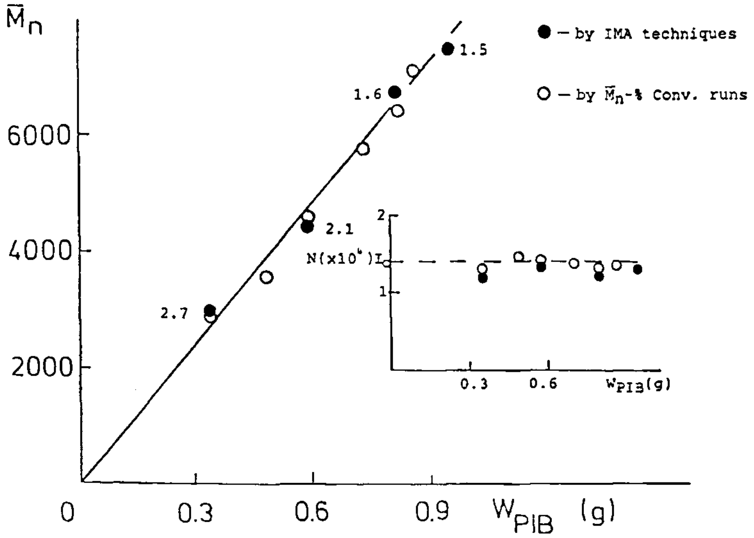


FIG. 3. $\bar{M}_n$ and W_{PIB} and N versus W_{PIB} plots obtained with the C_6H_5-CH_2COO—TMP/BCl_3/IB/CH_3Cl/−30°C system. ($[I_0] = 5.6 \times 10^{-3}$ M, $[BCl_3] = 5.1 \times 10^{-2}$ M. Numbers indicate $\bar{M}_w/\bar{M}_n$ values.)

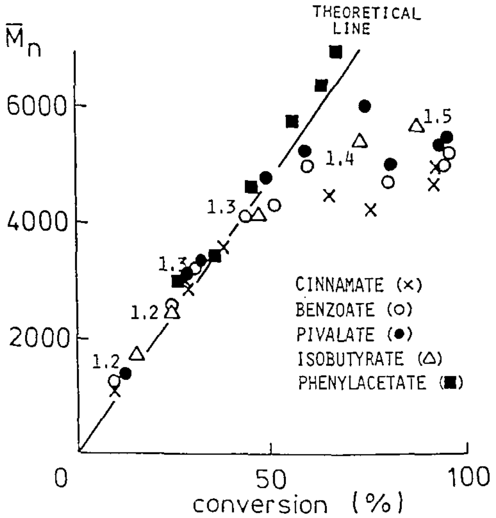


FIG. 4. $\overline{M}_n$ versus conversion plot for the polymerization of IB with the RCOO—TMP/BCl_3/CH_3Cl/−30°C system. ($[I_0]$ = 5.6 × 10^{-3} M, $[BCl_3]$ = 5.1 × 10^{-2} M. Numbers indicate $\overline{M}_w/\overline{M}_n$ values.)

ic parameters. Figure 6 shows first-order plots for experiments at −30°C. The linearity of the plots indicates that propagation is first order in monomer and that the active center concentration is constant. The numbers in the figure indicate the apparent propagation rate constants ($k_p^A = k_p \cdot A$, where $A = [\overline{M}_n^+]/[I_0]$). Since the MWD's are reasonably narrow ($\overline{M}_w/\overline{M}_n$ = 1.2–1.5, see Fig. 4), dormant species are either absent ($k_p^A = k_p$) or the exchange between the dormant and growing centers is faster than propagation.

Table 2 summarizes k_p^A's obtained with the different TMP—esters together with the pK's of the corresponding acids. The k_p^A's range from 10^3–10^{-3} L · mol^{-1} · s^{-1}, indicating the very different ionicity (from very high to very low) of the growing species. The high rates were estimated from available percent conversion–time data and compared to rates obtained with the TMP—phenylacetate. Surprisingly, the k_p^A's obtained with TMP—cinnamate and benzoate are relatively low. These esters were expected to yield high k_p^A's on account of resonance stabilization of their anionic moiety. The high pK values of benzoic and cinnamic acids are due to resonance stabilization of their anions, and a corresponding high k_p^A

value was expected of their TMP—esters due to resonance stabilization of the aromatic counteranions. The low k_p^A's suggest the absence of this effect, which in turn points to nonionic species in these polymerizations.

Chain Transfer Studies

The relatively slow polymerizations exhibit chain transfer to monomer (cf. deviation from the theoretical line in Figs. 4 and 5). It was of interest to gain further insight into the nature of chain transfer processes in these systems.

The number-average degree of polymerization, assuming bimolecular chain transfer to monomer with no termination and instantaneous initiation, can be expressed by

$$\overline{DP}_n = \frac{[M_0] - [M]}{[I_0] + \frac{k_{tr2,M}}{k_p}([M_0] - [M])}, \qquad (1)$$

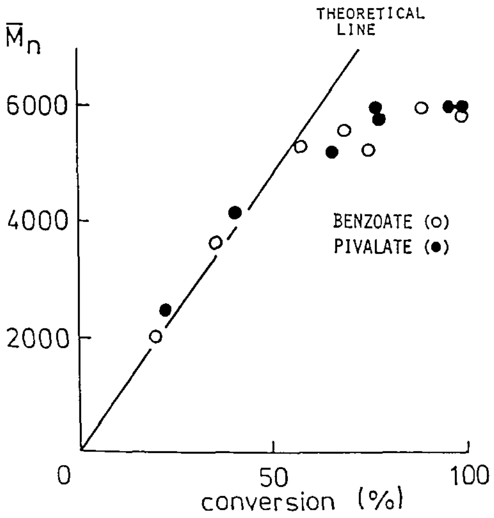


FIG. 5. $\overline{M}_n$ versus conversion plot for the polymerization of IB with the RCOO—TMP/BCl_3/CH_3Cl/−50°C system. ($[I_0] = 5.6 \times 10^{-3}$ M, $[BCl_3] = 5.1 \times 10^{-2}$ M. Numbers indicate $\overline{M}_w/\overline{M}_n$ values.)

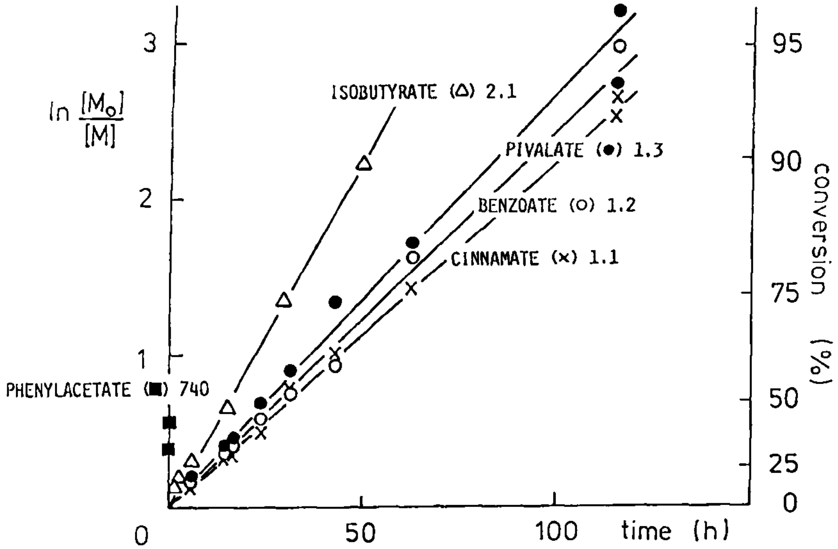


FIG. 6. Determination of apparent k_p's ($\times 10^{-3}$ in L · mol^{-1} · s^{-1}) in the RCOO—TMP/BCl_3/IB/CH_3Cl/−30°C systems.

where $[M_0]$ and $[M]$ are the initial and final monomer concentrations, and $[I_0]$ is the initial initiator concentration. And similarly, assuming monomolecular chain transfer to monomer:

$$\overline{DP}_n = \frac{[M_0] - [M]}{[I_0] + \frac{k_{tr1,M}}{k_p} \ln \frac{[M_0]}{[M]}}. \tag{2}$$

Equations (1) and (2) can be rewritten as

$$\frac{[M_0] - [M]}{\overline{DP}_n} = [I_o] + \frac{k_{tr2,M}}{k_p}([M_0] - [M]) \tag{3}$$

and

$$\frac{[M_0] - [M]}{\overline{DP}_n} = [I_o] + \frac{k_{tr1,M}}{k_p} \ln \frac{[M_0]}{[M]}. \tag{4}$$

TABLE 2. Polymerization Rate–Acid Strength Relationship

TMP-ester	Polymerization rate (k_p^A (L · mol^{-} · s^{-1}))	Acid strength, pK
Cinnamate	1.1×10^{-3}	4.44
Benzoate	1.2×10^{-3}	4.19
Pivalate	1.3×10^{-3}	5.03
Isobutyrate	2.1×10^{-3}	4.84
Phenylacetate	7.4×10^{-1}	4.28
Acetate	~ 10	4.75
Dichloroacetate	$\sim 10^{2-3}$	1.48
Trichloroacetate	$\sim 10^{2-3}$	0.7

A linear plot of Eq. (3) would indicate bimolecular (or direct) chain transfer to monomer, whereas a linear plot of Eq. (4) would suggest monomolecular chain transfer to monomer (i.e., the rate-determining step is proton expulsion from the growing chain end) [1]. This kinetic treatment is similar to the one published earlier [1] for instantaneous initiation and complete conversion (i.e., $[M] = 0$), except that at complete conversion Eq. (4) becomes undefined. For this reason the absence of bimolecular chain transfer could not be proven directly for extremely fast polymerizations [1]. While the plot corresponding to Eq. (3), shown in Fig. 7, did not give linear relationships, that corresponding to Eq. (4), seen in Fig. 8, yielded straight lines with intercepts ($\sim 5 \times 10^{-3}$ mol/L) in good agreement with $[I_0]$ ($= 5.6 \times 10^{-3}$ mol/L). According to these results, chain transfer to monomer is monomolecular, i.e., zero order in monomer. Similar conclusions have been derived earlier [1].

The chain transfer constants $C_{tr1,M}\left(= \dfrac{k_{tr1,M}}{k_p}\right)$ decrease in the order as cinnamate > benzoate > pivalate > isobutyrate. The calculated apparent chain transfer rate constants $k^{A}_{tr1,M}$ ($= k_{tr1,M} \cdot A$) are very small ($\sim 10^{-6}$ L · mol^{-1} · s^{-1}) and do not change much along this series. The decrease in $C_{tr1,M}$ along this series is largely due to a corresponding increase in $k_p{}^{A}$'s in the reverse order.

In line with these observations, the question arises whether or not very slow chain transfer to monomer would also occur with the other TMP —esters as well but would remain undetected because it is masked by much faster propagation (larger k_p). Since C_M values less than $\sim 10^{-6}$ would be very difficult to determine by molecular weight differences between theoretical and observed values, we have studied the effect of R on $k_{tr1,M}$ by other means. It has been reported [1] that with the $CH_3COO{-}TMP/BCl_3$ system, monomolecular chain transfer to monomer becomes operational at −10°C; however, this rate is very low relative to that of propagation and can be detected only by the IMA technique after monomer depletion (i.e., in the absence of monomer the living chain ends slowly and spontaneously undergo proton elimination). We have carried out similar experiments with $CCl_3COO{-}TMP$ and $CHCl_2COO{-}TMP/BCl_3$ at −10°C, and Fig. 9 shows the results. Al-

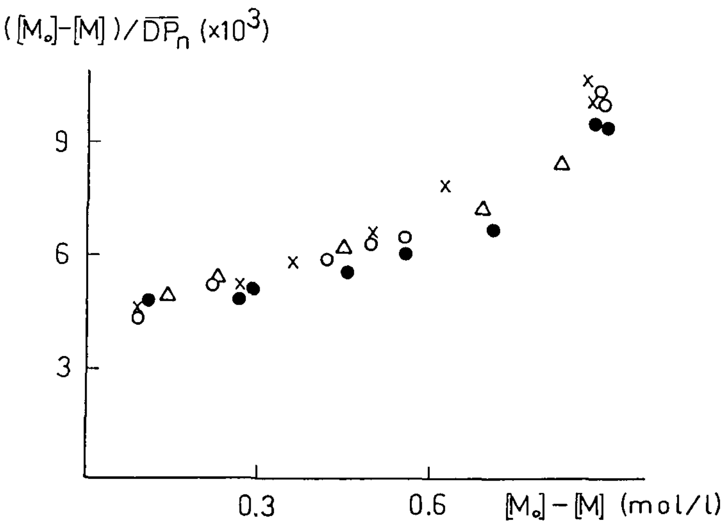


FIG. 7. Plot of Eq. (1) for the $RCOO{-}TMP/BCl_3/IB/CH_3Cl/{-}30°C$ system. R = $(CH_3)_3C{-}$ (•), $C_6H_5{-}$ (○), $C_6H_5{-}CH{=}CH{-}$ (×), $(CH_3)_2CH{-}$ (Δ).

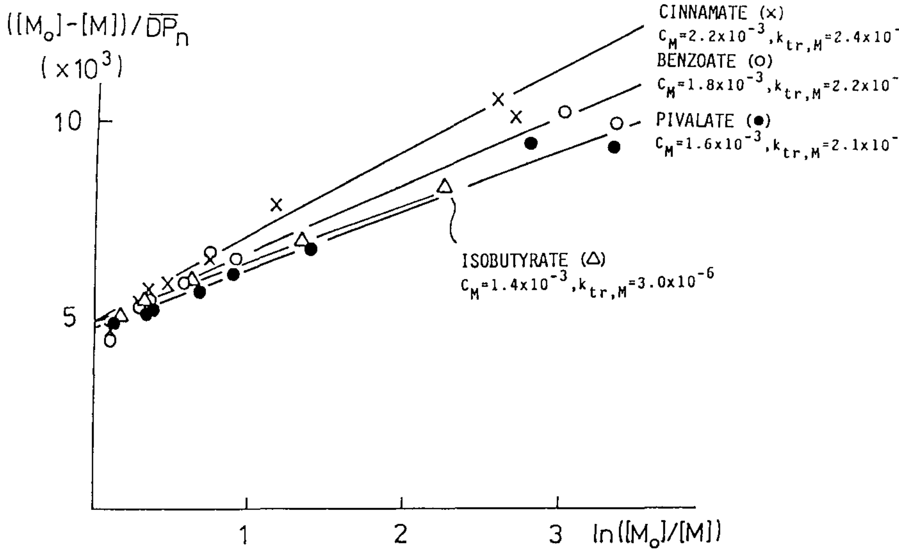


FIG. 8. Determination of C_M's and apparent $k_{tr,M}$'s in the RCOO—TMP/ BCl_3/IB/CH_3Cl/−30°C system. R = $(CH_3)_3C$— (•), C_6H_5— (○), C_6H_5—CH=CH— (×), $(CH_3)_2CH$— (Δ).

though polymerizations with these esters are much faster than with CH_3COO—TMP, proton elimination is perceptible in the absence of monomer, and its extent can be determined by the extent of deviation from the theoretical $\bar{M}_n$ versus W_{PIB} line. The $\bar{M}_n$ versus W_{PIB} plots obtained by the IMA technique with CCl_3COO—TMP and Cl_2CHCOO—TMP are close to theoretical, only the last point (after 2.5 h) start to deviate from theoretical. Relative to the CH_3COO—TMP system [1], not only C_M but also $k_{tr,M}$ decreases with the electron-withdrawing tendency of the R groups (i.e., with increasing ionicity of the growing center). Evidently the extent of chain transfer is determined by both the stability of the propagating PIB cation *and* the nucleophilicity of the counteranion.

Effect of Solvent Polarity

The ionic character of the growing chain end and thus the propagation rate increases by increasing the polarity of the medium [1]; however, by increasing the polarity, the rate of chain transfer to monomer may also increase. Figure 10 shows $\bar{M}_n$ versus % conversion plots for $(CH_3)_3CCOO$—TMP and C_6H_5COO—TMP with CH_2Cl_2 solvent at −30 and −10°C. The corresponding first-order plots (not shown) were both linear and gave for both esters values ~10 times higher ($k_p{}^A \approx 1.25 \times 10^{-2} L \cdot mol^{-1} \cdot s^{-1}$) than those obtained by using CH_3Cl.

The data of the −30°C experiments do not show evidence for chain transfer to monomer (note the linearity of the $\bar{M}_n$ versus conversion plot up to >90%), which indicates that $k_{tr1,M}$ probably did not increase, or did not increase in proportion with the increase in k_p. At −10°C, chain transfer to monomer may be present as judged by the deviation from linearity of the $\bar{M}_n$ versus conversion plot.

It has been reported [1] that solvent polarity critically affects the rate of polymerization; for example, the use of polar solvent (CH_2Cl_2 or CH_3Cl) was necessary with the CH_3COO—TMP/BCl_3 system to obtain high polymerization rates. The rate of polymerization drastically decreased along the sequence CH_2Cl_2 > CH_3Cl > CH_2Cl_2-*n*-hexane 80/20 v/v > C_2H_5Cl > CH_2Cl/*n*-hexane 60/40 v/v > $CHCl_3$, and bimodal MWDs were obtained with the last four solvent systems by the IMA technique [1]. This observation was explained by assuming a living ⇌ dormant equilibrium and postulating that the equilibrium shifts to the left by increasing the polarity of the medium. We theorized that in view of

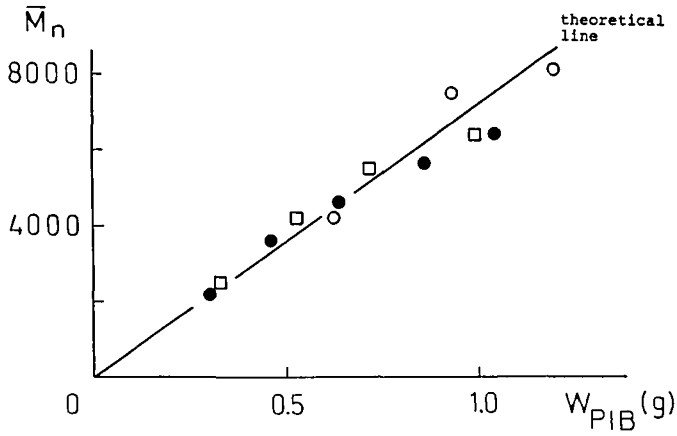


FIG. 9. $\bar{M}_n$ versus the weight of PIB formed in the Cl_3COO—TMP (●, IMA; ○, AMI) and Cl_2CHCOO—TMP (□, IMA)/BCl_3/IB/CH_2Cl_2/−10°C system. ($[I_0] = 5.6 \times 10^{-3} M$, $[BCl_3] = 5.1 \times 10^{-2} M$.)

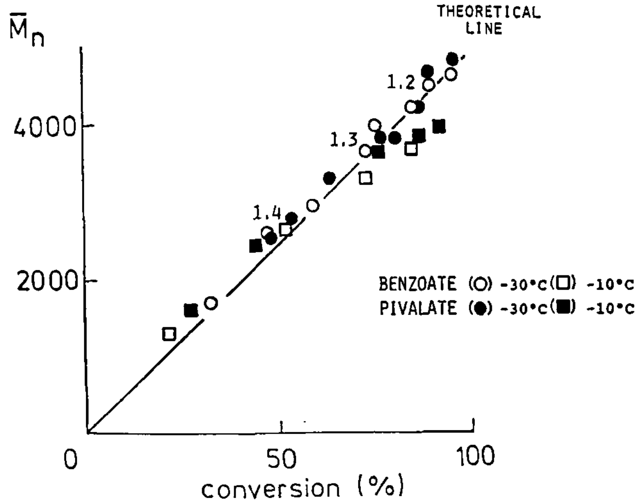


FIG. 10. $\bar{M}_n$ versus conversion plots for the polymerization of IB with the $C_6H_5COO-TMP$ and $(CH_3)_3CCOO-TMP/BCl_3/CH_2Cl_2/-30°$ and $-10°C$ system. (Numbers indicate $\bar{M}_w/\bar{M}_n$ values.)

the high activity of the $CHCl_2COO-TMP$ and $CCl_3COO-TMP/BCl_3$ systems, living polymerizations may also be obtained by the use of less polar solvents. Results obtained with the relatively less polar solvent C_2H_5Cl substantiated these expectations; the rates were so high that we were compelled to use the IMA technique to prove the living nature of these systems. Figure 11 shows the data. Conversions were complete after every monomer increment.

Encouraged by these results, further experiments have been carried out at −20 and −10°C. The data obtained in these experiments have been collected in Fig. 12. Unexpectedly, the rates decreased upon every monomer addition at these temperatures, and at −10°C the polymerization essentially stopped after the first increment. These results cannot be explained by the living $\rightleftharpoons$ dormant equilibrium, since in this case the structures of the initiator RCOO—TMP and the growing end are essentially identical and the position of the equilibrium should remain the same during propagation. According to this evidence, our earlier proposition that dormant esters are responsible for the decrease in polymerization rates and for the broadening of the MWD with decreasing solvent polarity has to be revised. In line with the results of this study, the species thought to be dormant esters are in fact *t*-chlorine-terminated polyisobutylenes which are unable to reinitiate the polymerization under the experimental conditions used.

Figure 12 shows that only negligible amounts of polymer have formed with $CH_3COO-TMP$ at −10 and −20°C. Essentially similar results have been obtained with the rather nonpolar CH_3Cl/n-hexane 60/40 v/v mixture at −40°C. Evidently termination (the decomposition temperature of the growing complex) is strongly dependent on solvent polarity and is reduced in a less polar medium. Conversions are reduced along the series R = $CCl_3-, > CHCl_2-, > CH_3-$, which suggests that termination (i.e., the decomposition temperature) increases by reducing the electron-withdrawing character of the R— substituents. These observations are in line with those of Gerrard and Wheelans [10] according to which the *t*-butyl acetate · BCl_3 complex starts to decompose at about −25°C in the absence of solvent, but in *n*-pentene at −10°C it decomposes immedi-

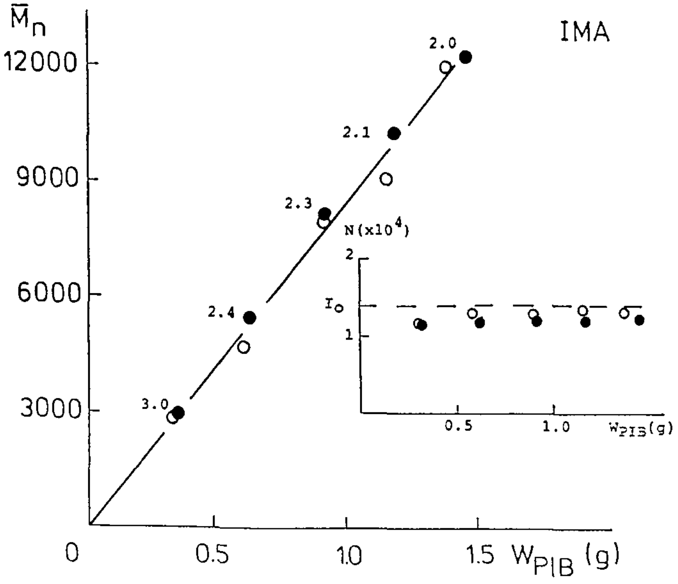


FIG. 11. $\bar{M}_n$ and W_{PIB}, and N versus W_{PIB} plots obtained with the $Cl_3COO-TMP$ (○) and $Cl_2CHCOO-TMP$ (•)/$BCl_3/IB/C_2H_5Cl/-30°C$ systems. ($[I_0] = 5.6 \times 10^{-3}$ *M*, $[BCl_3] = 5.1 \times 10^{-2}$ *M*. Numbers indicate $\bar{M}_w/\bar{M}_n$ values.)

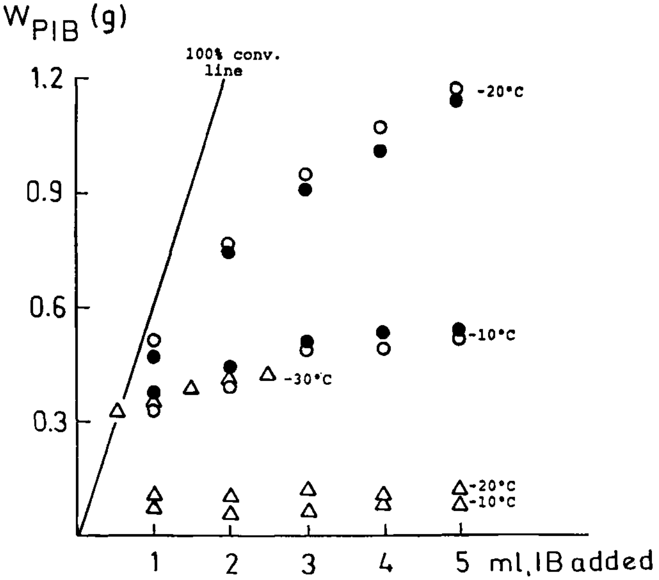


FIG. 12. Weight of PIB formed versus IB added with $Cl_3CCOO-TMP$ (•), $Cl_2CHCOO-TMP$ (O), and $CH_3COO-TMP$ (Δ)/BCl_3/IB/C_2H_5Cl systems at different temperatures.

ately. We have reported [1] the absence of decomposition at −10°C in the more polar solvent CH_2Cl_2.

Forced Termination Studies

It was of interest to investigate the structure of the end groups obtained by the use of the seven TMP—ester/BCl_3 initiating systems. Thus the nature of forced termination was investigated by model studies, that is, by adding methanol or pyridine to TMP—ester/BCl_3 systems, or by raising the temperature of the TMP—ester/BCl_3 complex prepared at −30°C to above its decomposition temperature. (The TMP—ester/BCl_3 complex is regarded to mimic the growing polymer end.) The structure of the surviving species was determined by ^{1}H-NMR and IR spectroscopies. According to the results of these 21 model experiments, the only species that arose upon both wet or thermal quenching was TMP—Cl. The results of model studies have subsequently been corroborated by polymerization studies in which polymerizations were quenched with methanol or pyridine. According to ^{1}H-NMR spectroscopy, in the absence of chain transfer to monomer, *t*-chlorine terminated PIBs have been invariably obtained with both quenching agents. In the presence of chain transfer to monomer, that is, in experiments reported in Figs. 4 and 5, ^{1}H-NMR spectroscopy indicated 3 kinds of termini: $-CH_2C(CH_3)=CH_2$ and $-CH=C(CH_3)_2$ due to proton expulsion (chain transfer to monomer) and $-CH_2C(CH_3)_2Cl$ due to termination.

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