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LIVING CARBOCATIONIC POLYMERIZATION OF ISOBUTYLENE WITH BLOCKED BIFUNCTIONAL INITIATORS IN THE PRESENCE OF DI-*tert*-BUTYLPYRIDINE AS A PROTON TRAP

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ABSTRACT

The polymerization of isobutylene (IB) has been studied using 5-*tert*-butyl-1,3-dicumyl-chloride, 5-*tert*-butyl-1,3-dicumyl-methyl ether, and 5-*tert*-butyl-1,3-dicumyl-acetate initiators in the absence and presence of 2,6-di-*tert*-butylpyridine (DTBP) as a proton trap. It is demonstrated that living polymerization can be achieved in the IB/initiator/$TiCl_4$/methylchloride-*n*-hexane (40:60 v:v)/DTBP/−80°C system, and that polymers with close to a Poisson molecular weight distribution can be obtained in the presence of a proton trap in concentrations only slightly higher than the concentration of protic impurities in the system. The polymerization rate is a first-order function of the monomer concentration and is not affected by the excess amount of DTBP added, which indicates that the living nature of the polymerization is not due to carbocation stabilization.

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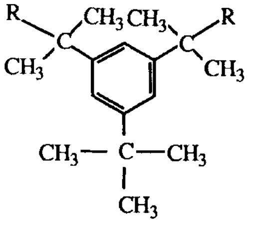
INTRODUCTION

It has been reported that many initiating systems that induce nonliving IB polymerizations and/or give relatively broad MWD PIBs in the presence of suitable *in situ* formed or externally added electron donors (EDs) give rise to living polymerizations and yield narrow MWD products [1, 2]. The effect of EDs on IB polymerization has been explained by carbocation stabilization through the EDs [1, 2]. We recently investigated the polymerization of isobutylene coinitiated with BCl_3 or $TiCl_4$ in the presence of EDs [3], and we showed that the excess free base (relative to the coinitiator) prevents IB polymerization, i.e., the effective species are the Lewis acid/ED complexes. Furthermore, experiments carried out with the proton trap 2,6-di-*tert*-butylpyridine indicated that their proton scavenging function and not carbocation stabilization may be responsible for the narrow molecular weight distribution products obtained in the BCl_3 coinitiated polymerization of isobutylene [3].

The purpose of this paper is to study the validity of this proposition for $TiCl_4$ coinitiated IB polymerization and to gain further insight into the underlying mechanism.

A second objective of the present investigation was to compare the initiating properties of three bifunctional initiators for the preparation of well-defined PIBs.



R = Cl (a), 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)-benzene
R = OMe (b), 5-*tert*-butyl-1,3-bis(1-methoxy-1-methylethyl)-benzene
R = OAc (c), 5-*tert*-butyl-1,3-bis(1-acetoxy-1-methylethyl)-benzene

EXPERIMENTAL

Materials

5-tert-Butyl-1,3-bis(1-chloro-1-methylethyl)-benzene. 3,5-Dicarboxyl-1-*tert*-butylbenzene (Amoco Chemicals Co.) (200 g, 0.9 mol) was esterified by refluxing for 48 h in methanol (1000 mL, 24.7 mol) in the presence of H_2SO_4 (38 mL). The mixture was cooled to room temperature and stored at 0°C overnight. The solid was filtered, washed with water until neutral, and dried at 50°C. The dimethyl-5-*tert*-butyl-1,3-benzene dicarboxylate was recrystallized from methanol. Yield: 151 g (71%). The dimethylester (20 g, 0.08 mol) dissolved in 200 mL anhydrous diethylether was added dropwise to a Grignard-reagent solution prepared from 9.72 g magnesium turnings (0.4 mol) and 24.8 mL iodomethane (0.4 mol). Addition was carried out while stirring the reaction mixture under nitrogen atmosphere at 0-5°C. After stirring for an additional 15 h, the charge was slowly added to a stirred

NH_4Cl-ice mixture containing 22 g NH_4Cl and 200 g ice. The product was extracted with diethyl ether and dried over anhydrous $MgSO_4$. The solvent was evaporated and the product was purified by recrystallization from ethyl acetate. Yield: 18.8 g (93%). The melting point of the 5-*tert*-butyl-1,3-bis(1-hydroxy-1-methylethyl)-benzene produced was 120–122°C. Chlorination of the diol was carried out by treating 10 g (0.04 mol) starting material with 100 mL HCl at 0°C. After stirring for 3 h, 100 mL methylene chloride was added to the reaction mixture, and the stirring was continued for an additional 30 min. The organic layer was separated, dried over anhydrous $MgSO_4$, and the solvent was evaporated at 0°C. Yield: 11.2 g (98%). The melting point of the white crystals of 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)-benzene was 62°C.

Synthesis of *5-tert-butyl-1,3-bis(1-methoxy-1-methylethyl)-benzene* was carried out as described by Wang and coworkers [4].

5-tert-Butyl-1,3-bis(1-acetoxy-1-methylethyl)-benzene was synthesized from the corresponding diol 5-*tert*-butyl-1,3-bis(1-hydroxy-1-methylethyl)-benzene by using 4-dimethylaminopyridine as catalyst [5]: 5-*tert*-butyl-1,3-bis(1-hydroxy-1-methylethyl)-benzene (25 g, 0.1 mol), acetic anhydride (Aldrich) (20 mL, 0.21 mol), triethylamine (Aldrich) (20 mL, 0.15 mol), and 0.5 g (0.004 mol) *N*-dimethylaminopyridine (Aldrich) were mixed in a 100-mL round-bottom flask, and the reaction mixture was shaken for 20 h at room temperature. The solution was neutralized with 2 *N* NaOH and extracted with diethylether. Shaking the ethereal phase with 1 *N* HCl, drying, and evaporation gave 92% (3.07 g) of 5-*tert*-butyl-1,3-bis(1-acetoxy-1-methylethyl)-benzene.

Methyl chloride and isobutylene were dried in the gaseous state by passing them through in-line gas-purifier columns packed with BaO/Drierite. They were condensed in the cold bath of a glove box prior to polymerization. Methylcyclohexane and *n*-hexane were refluxed for 24 h with concentrated sulfuric acid, washed neutral with distilled water, dried for 48 h on Molecular Sieves, refluxed for 24 h, and distilled from CaH_2 under nitrogen atmosphere. Molecular weights and MWDs were not sensitive to the solvent drying procedure in the presence of DTBP. Only this standardized procedure resulted in reproducible results in the absence of DTBP. Titanium tetrachloride, 2,6-di-*tert*-butylpyridine (DTBP, 99.1% by GC, Aldrich), and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 99.9% by GC, Aldrich) were used as received.

Procedures

Polymerizations were carried out in a MBraun 150M stainless steel glove box (Innovative Technology Inc.) equipped with a gas purification system (15 lb Molecular Sieves and 11 lb copper catalyst, with automatic regeneration program) under dry nitrogen atmosphere (H_2O and O_2 less than 1 ppm). The moisture content in the glove box was monitored by an MBraun moisture analyzer. Total volume of the reaction mixture was 25 mL. The addition sequence of the reactants was as follows: solvent mixture (40/60 v/v methylchloride/*n*-hexane), monomer (IB), initiator, proton trap (DTBP), coinitiator ($TiCl_4$). By using the AMI (all monomer in) technique, parallel runs were killed with prechilled methanol at increasing reaction times. IMA (incremental monomer addition) experiments were also carried out for diagnostic purposes. Molecular weights were measured using a Waters HPLC system equipped with Model 510 HPLC pump, Model 410 differential refractometer, Model 486 tunable UV/Vis detector, Model 712 sample processor, and a series of five ultrastyragel columns (500, 10^3, 10^4, 10^5, and 100 Å). A calibration curve made with well-characterized PIB standards obtained by living carbocationic polymerization was used. Representative samples were also measured by a GPC on-line differential viscometer (Viscotek Co.) using the universal calibration curve obtained with PSt standards. NMR measurements were carried out by a Bruker 270 MHz multinuclear spectroscope equipped with a temperature controller.

RESULTS AND DISCUSSION

It has been reported that PIB with a molecular weight in excess of 100,000 can be prepared by living polymerization (IMA technique) using the *p*-dicumyl methyl ether/$TiCl_4$ initiating system in a nonpolar solvent mixture (CH_3Cl:*n*-hexane, 40:60 v:v) at −80°C [6]. Although the lifetime of the growing species with this system is increased substantially by the use of low temperature and a nonpolar solvent mixture, it has also been reported that in the absence of monomer the living chain

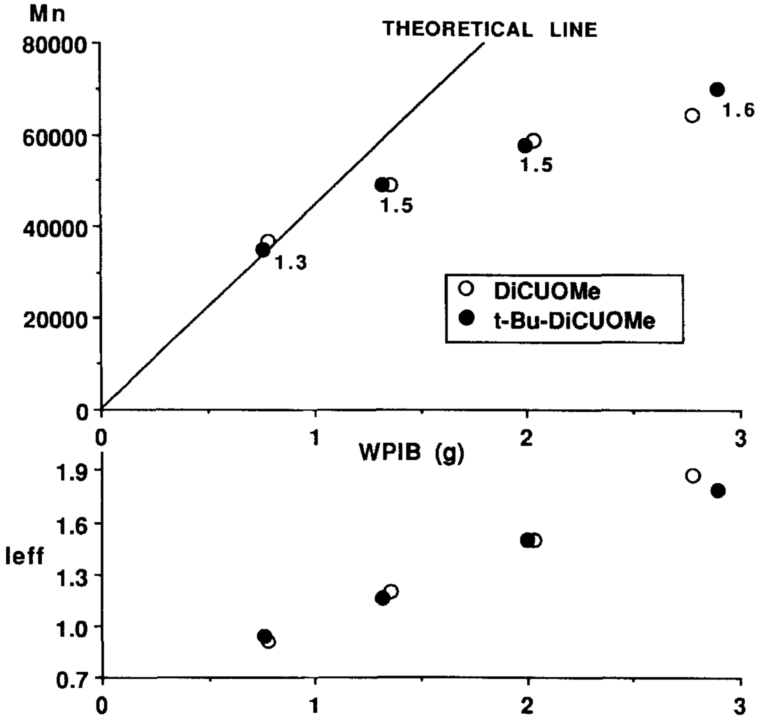


FIG. 1. Polymerization of IB initiated with 1,4-dicumyl-methylether and 5-*tert*-butyl-1,3-dicumyl-methylether. IMA technique. Time between monomer additions: 30 min. [DiCuOMe] = [*t*-Bu-DiCuOMe] = $9.25 \times 10^{-4} M$; [$TiCl_4$] = $3.6 \times 10^{-2} M$; V_0 = 25 mL. Solvent: CH_3CL:*n*-hexane, 40:60 v:v. Temperature: −80°C. I_{eff} = [polymer]/[initiator]. The numbers are MWD values.

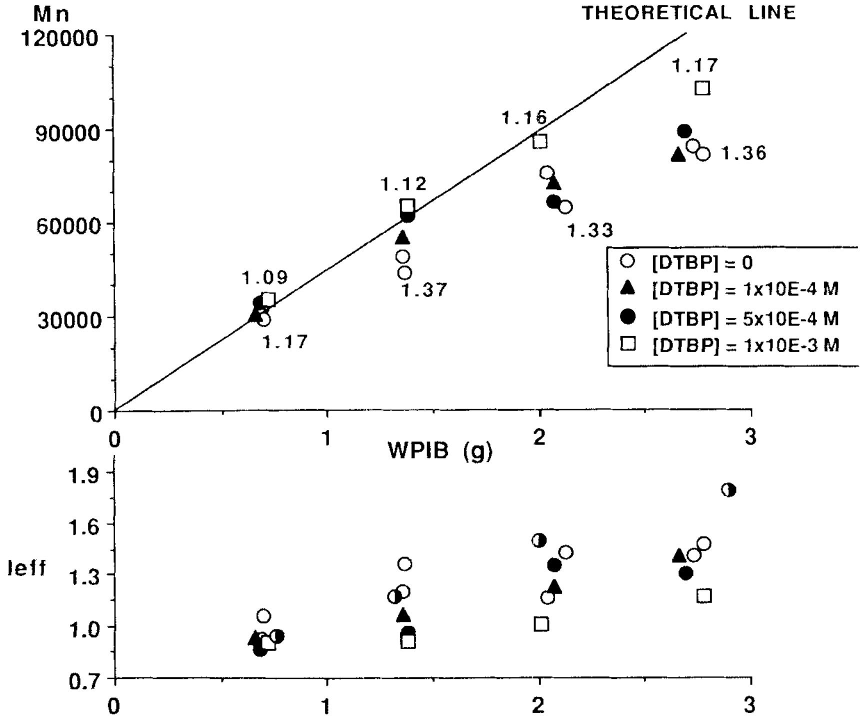


FIG. 2. Polymerization of IB initiated with 5-*tert*-butyl-1,3-dicumyl-methylether in the presence of DTBP. IMA technique. Time between monomer additions: 30 min. [*t*-Bu-DiCuOMe] = 9.25×10^{-4} *M*; [$TiCl_4$] = 3.6×10^{-2} *M*; V_0 = 25 mL. Solvent: CH_3CL: *n*-hexane, 40:60 v:v. Temperature: −80°C (◑ from Fig. 1). The numbers are MWD values.

ends undergo irreversible side reactions. Our investigations indicated that this side reaction is proton elimination from the growing center which results in chain transfer to monomer upon further monomer addition. It was diagnosed by a curved M_n versus weight of PIB formed plot obtained by the IMA technique when the time between monomer additions were increased to 30 min to observe complete monomer conversions after each monomer increment (Fig. 1). Furthermore, it suggests that the chain transfer process is gegenion assisted (zero order in monomer). Chain transfer to monomer also results in broadening of the molecular weight distribution. That the chain transfer is not due to intramolecular alkylation is shown by the parallel curve obtained with the 5-*tert*-butyl-1,3-dicumyl-methylether (a blocked difunctional initiator)/$TiCl_4$ initiating system.

When the polymerization experiments are carried out in the presence of a proton trap (DTBP), deviations from the theoretical line decrease with increasing DTBP concentration. At [DTBP] = 1×10^{-3} mol/L, close to theoretical molecular weights and narrow MWDs are observed (Fig. 2). Under these conditions, protic initiation is prevented, as evidenced by the negligible amount of polymer (3 wt%) formed in the control runs, i.e., in the absence of initiator. The fact that theoretical molecular weights are observed is not a sufficient indication of living polymerization, especially in the presence of bases capable of trapping the eliminated proton

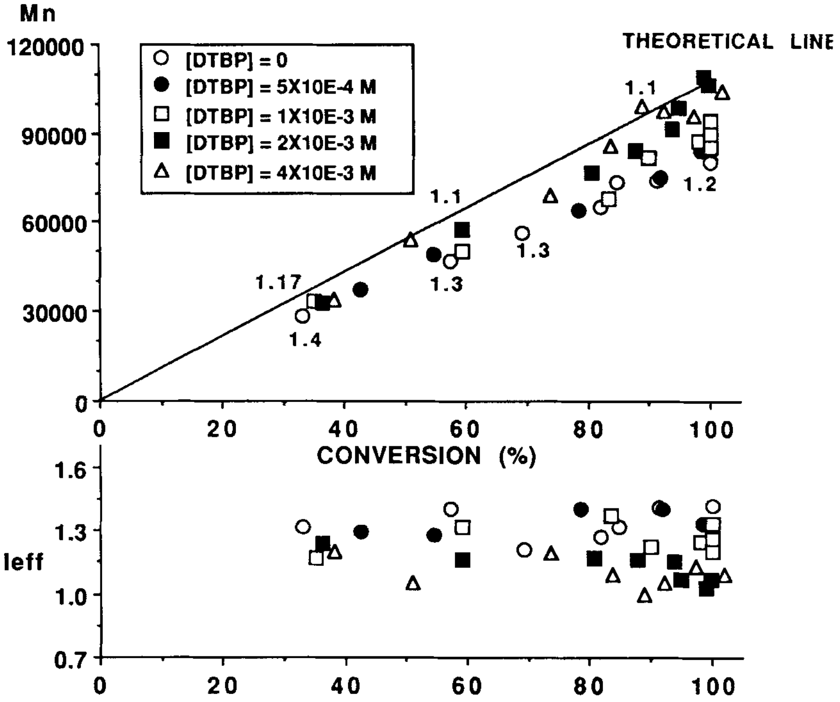


FIG. 3. Polymerization of IB with 5-*tert*-butyl-1,3-dicumyl-methylether as initiator in the presence of proton trap DTBP. AMI technique. $[IB]_0 = 2.04$ *M*. [*t*-Bu-DiCuOMe] = 1×10^{-3} *M*; $[TiCl_4] = 3.6 \times 10^{-2}$ *M*; $V_0 = 25$ mL. Solvent: CH_3Cl:*n*-hexane, 40:60 v:v. Temperature: −80°C. The numbers are MWD values.

before initiation of a new polymer chain. It has been established [7] that DTBP, a hindered pyridine, exhibits extraordinary specificity toward protons owed to its very high basicity coupled with nonnucleophilicity due to steric hindrance. Accordingly, it reacts with HCl but not with BF_3 or CH_3I. The specificity toward protons has been exploited in cationic macromolecular engineering to obtain high efficiency blocking and grafting by aborting gegenion-assisted chain transfer in the polymerization of α-methylstyrene and isobutylene [8, 9]. When this terminative proton entrapment occurs and initiation is instantaneous, molecular weights cannot deviate from the theoretical molecular weights although the polymerization is not living. The observed narrow MWDs are insufficient albeit strong indications that the polymerization is living and terminative chain transfer does not occur. Under these conditions, proof for living polymerization can only be obtained by additional kinetic measurements, i.e., in living polymerization the growing center concentration remains constant. We have measured M_n-conversion and time-conversion data for the 5-*tert*-butyl-1,3-dicumyl-methylether/$TiCl_4$/IB/methylchloride-*n*-hexane (40:60 v:v)/DTBP/−80°C system and plotted them in Fig. 3 and as ln $[M_0]/[M]$ vs time on Fig. 4. The molecular weight-conversion plots (Fig. 3) are similar to the M_n-W_{PIB} plots obtained with the IMA technique (Fig. 2). In the absence of DTBP, molecular weights deviate from the theoretical line even in the presence of the

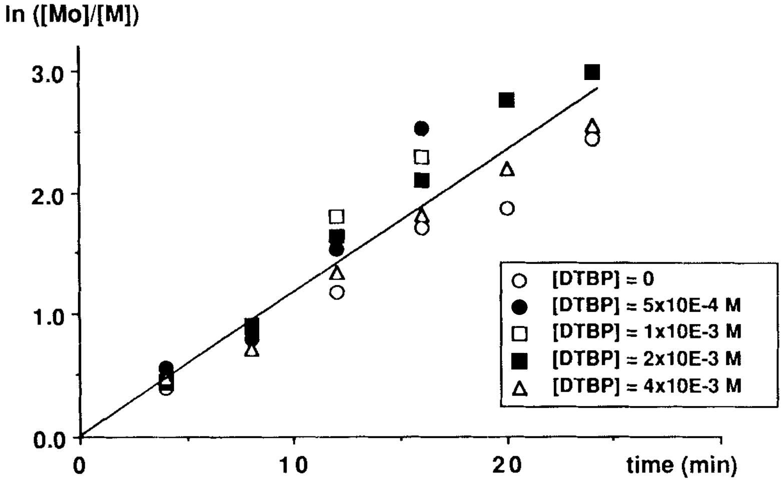


FIG. 4. Polymerization of IB with 5-*tert*-butyl-1,3-dicumyl-methylether as initiator in the presence of proton trap DTBP. AMI technique. $[IB]_0 = 2.04\ M$. [*t*-Bu-DiCuOMe] = $1 \times 10^{-3}\ M$; $[TiCl_4] = 3.6 \times 10^{-2}\ M$; $V_0 = 25$ mL. Solvent: CH_3Cl:*n*-hexane, 40;60 v:v. Temperature: −80°C.

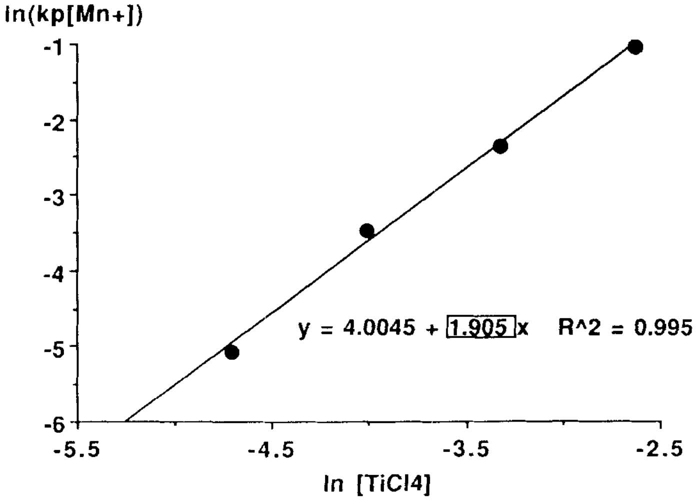


FIG. 5. Reaction order of $TiCl_4$ in the polymerization of isobutylene by the 5-*tert*-butyl-1,3-dicumyl-methylether. Solvent: $TiCl_4/CH_3Cl$:*n*-hexane, 40:60 v:v. Temperature: −80°C. With a corrected $[TiCl_4]$ (assuming instantaneous chlorination of the initiator and that the $TiCl_3OMe$ is inert), the order is 1.73.

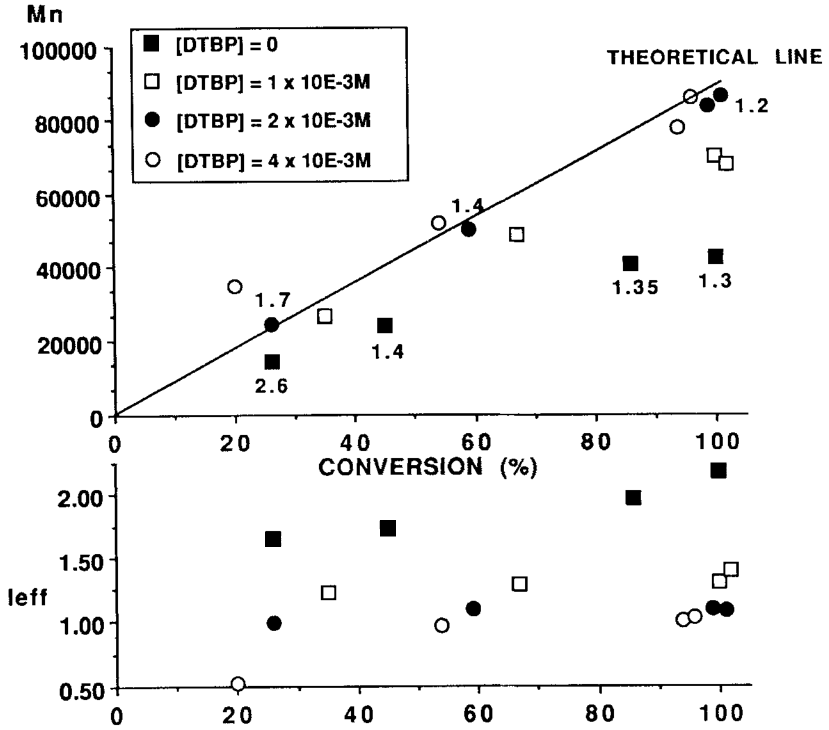


FIG. 6. Polymerization of IB with 5-*tert*-butyl-1,3-dicumyl-methylether as initiator in the presence of proton trap DTBP. AMI technique. $[IB]_0 = 1.54\ M$. [*t*-Bu-DiCuOMe] = $9.24 \times 10^{-4}\ M$; $[TiCl_4] = 3.6 \times 10^{-2}\ M$; $V_0 = 25$ mL. Solvent: CH_3Cl:MeCH, 40:60 v:v. Temperature: −80°C. The numbers are MWD values.

monomer although the initiator efficiencies (I_{eff} = [polymer]/[initiator]) are somewhat lower than in the IMA experiments. Deviations from the theoretical line decrease with increasing DTBP concentration. At $[DTBP] \geq 2 \times 10^{-3}$ mol/L, close to theoretical molecular weights and narrow MWDs are observed.

Polymerization rates measured at different $TiCl_4$ concentrations are plotted as $\ln (k_p[M_n^+])$ vs $\ln [TiCl_4]$ (Fig. 5). The close to second-order behavior suggests that $TiCl_4$ forms bimolecular associates (or bimolecular complex gegenions). This is in agreement with published results that $TiCl_4$ exists in nonpolar solvents as a dimer through chlorine bridges [10, 11]. Chain transfer to monomer in the absence of DTBP is more evident when the methyl chloride-methylcyclohexane solvent mixture is used (Fig. 6). The polymerization rate (Fig. 7) is similar to that of the corresponding methyl chloride-*n*-hexane solvent mixture (Fig. 4). In both solvent systems, polymerization rates remain unchanged by the addition of DTBP. Results similar to Figs. 3 and 4 have been obtained with the 5-*tert*-butyl-1,3-dicumyl-chloride/$TiCl_4$ initiating system (Figs. 8 and 9). Contrary to earlier published results [2, 12], the propagation is apparently first order in monomer according to Figs. 4, 7, and 9, and the $\ln [M_0]/[M]$-time curves are linear in the entire measured conversion range (<95%). Importantly, the same linearity is obtained within experimental error in the presence and absence of DTBP.

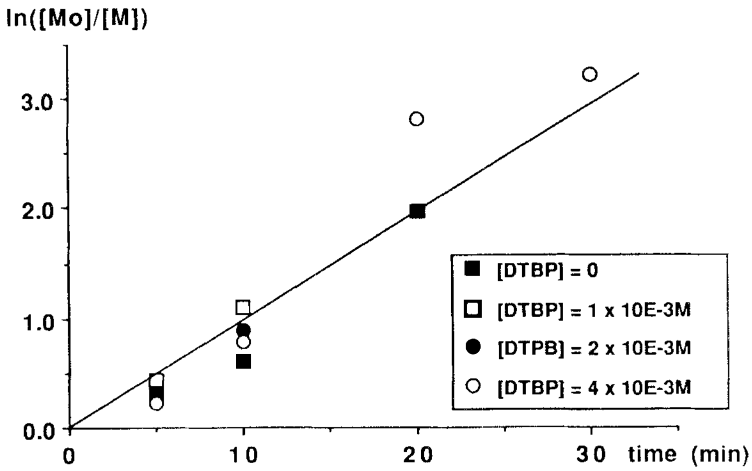


FIG. 7. Polymerization of IB with 5-*tert*-butyl-1,3-dicumyl-methylether as initiator in the presence of proton trap DTBP. AMI technique. $[IB]_0 = 1.54$ *M*. [*t*-Bu-DiCuOMe] = 9.24×10^{-4} *M*; $[TiCl_4] = 3.6 \times 10^{-2}$ *M*; $V_0 = 25$ mL. Solvent: CH_3Cl:MeCH, 40:60 v:v. Temperature: −80°C.

The polymerization of IB in the presence of DTBP has already been investigated with the cumyl chloride/BCl_3 and the $H_2O/AlCl_3$ systems [13, 14]. Under the experimental conditions studied by the authors, DTPB did not interfere with nonprotic initiation, but with the cumyl chloride/BCl_3 system it was able to abstract a proton from the propagating $\sim C^+(CH_3)_2$ center. These observations can be reconciled with our observations by considering the much lower temperatures and the nonpolar solvent mixture used in the present investigation. From the IMA (100% conversions and narrow MWDs) and AMI experiments (linear ln $[M_0]/[M]$ vs time curve), it is clear that in our system the concentration of growing centers remains constant. The supplemental linearity of the M_n-W_{PIB} and M_n-conversion plots proves living polymerization. Gegenion-assisted proton elimination from the growing PIB chain end is absent, and DTBP does not abstract a proton from the growing PIB chain end due to either lessened cationic character or steric hindrance, which implies a tighter ion pair. That the living nature of the polymerization is a result of carbocation stabilization by the proton trap is highly unlikely due to steric hindrance. DTBP is reportedly ineffective in mediating living polymerization of vinyl ethers since it is unable to stabilize the growing carbocations due to steric factors [15]. Notwithstanding, if carbocation stabilization by DTBP takes place in the polymerization of IB, the rate of the polymerization should decrease with increasing DTBP concentration. The experimental results (Figs. 4, 7, and 9) show that the rate of polymerization remains unchanged in the [DTPB] = 0–4 × 10^{-3} mol/L range; consequently, carbocation stabilization does not occur.

^{1}H-NMR studies with the DTBMP/$TiCl_4$/nondried CH_2Cl_2 system confirmed the presence of protonated and unprotonated DTBMP at room temperature, and the concentration of protonated DTBMP (2.2×10^{-2} *M*) was in good agreement with the results of Karl-Fisher titration (1.7×10^{-2} *M*). Similar to earlier results of Sigwalt et al. [16] and of Moulis, Collomb, Gandini, and Cheradame [17], complex-

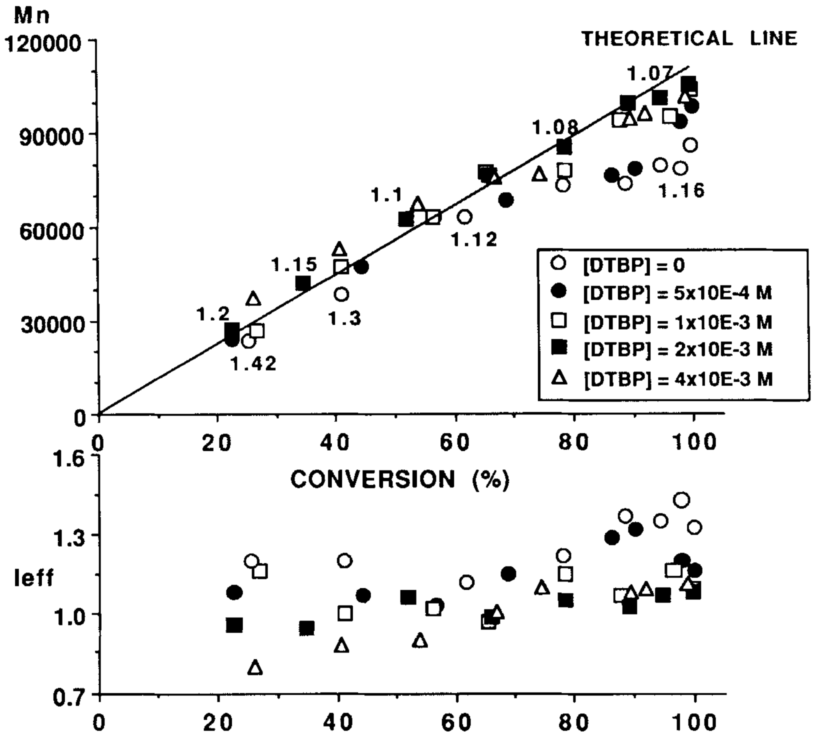


FIG. 8. Polymerization of IB with 5-*tert*-butyl-1,3-dicumyl-chloride as initiator in the presence of proton trap DTBP. AMI technique. $[IB]_0 = 2.04$ *M*. [*t*-Bu-DiCuCl] = 1 × 10^{-3} *M*; $[TiCl_4] = 3.6 \times 10^{-2}$ *M*; $V_0 = 25$ mL. Solvent: CH_3Cl:*n*-hexane, 40:60 v:v. Temperature: −80°C. The numbers are MWD values.

ation with $TiCl_4$ was not detected even when the temperature was decreased to −60°C. With the decrease of temperature, however, the resonances due to protonated DTBMP decreased and at −60°C completely disappeared (Fig. 10). Simultaneously, we observed a pale yellow precipitate. Consequently, the protonated DTBMP salt is insoluble at low temperatures.

Interestingly, the polymerization rate with the dichloride and dimethyl ether initiator appears to be the same in the absence and in the presence of DTBP. This leads us to conclude that polymerization takes place by the common gegenion $TiCl_5^-$, which has already been assumed to arise by fast chlorination of the methyl ether followed by $TiCl_4$ coinitiation [1, 2]. However, we dispute the beneficial effect of the "*in-situ* formed ED," $TiCl_3OMe$, in mediating living polymerization by carbocation stabilization [1, 2]. Its effect, if any, is negligible according to the same M_n-conversion and ln $[M_0]/[M]$-time plots using the chloride and methyl ether initiator in the absence (as well as in the presence) of DTBP. The MWDs are actually narrower with the dichloride initiator, and the narrowest reported MWDs have been obtained with the IMA technique in the presence of 2 × 10^{-3} mol/L DTBP (Fig. 11).

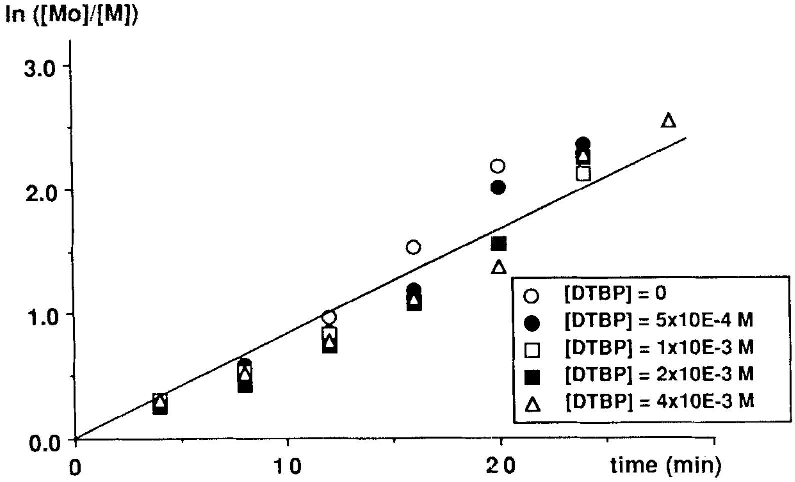


FIG. 9. Polymerization of IB with 5-*tert*-butyl-1,3-dicumyl-chloride as initiator in the presence of proton trap DTBP. AMI technique. $[IB]_0 = 2.04$ *M*. [*t*-Bu-DiCuCl] = 1 × 10^{-3} *M*; $[TiCl_4] = 3.6 \times 10^{-2}$ *M*; $V_0 = 25$ mL. Solvent: CH_3Cl:*n*-hexane, 40:60 v:v. Temperature: −80°C.

With the 5-*tert*-butyl-1,3-dicumyl-acetate/$TiCl_4$ initiating complex, the ln $[M_0]/[M]$ versus time curves are not linear (Fig. 12). Apparently $k_p[M_n^+]$ (i.e., the first derivative of the curve) shows a steady increase. (Following the conclusions with the chloride and methyl ether initiator, it is reasonable to assume there is also first-order monomer dependency of propagation with the acetate system.) When the corresponding ln $[M_0]/[M]$ versus time curves for the three initiator for the absence of DTBP are plotted together (Fig. 13), it becomes evident that in about 20 min the first derivative of the curve corresponding to the acetate initiator and that

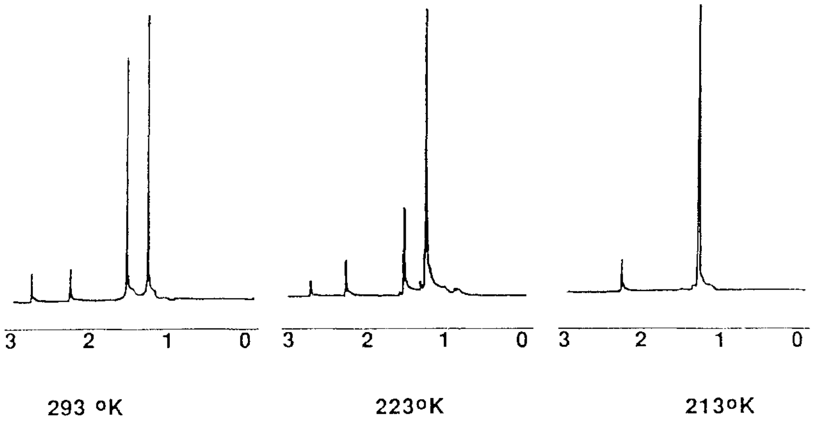


FIG. 10. ^{1}H-NMR spectra of 2,6-di-*tert*-butyl-4-methylpyridine/$TiCl_4$ system at different temperatures. Solvent: CH_2Cl_2/chloroform-*d*, 50v/50v.

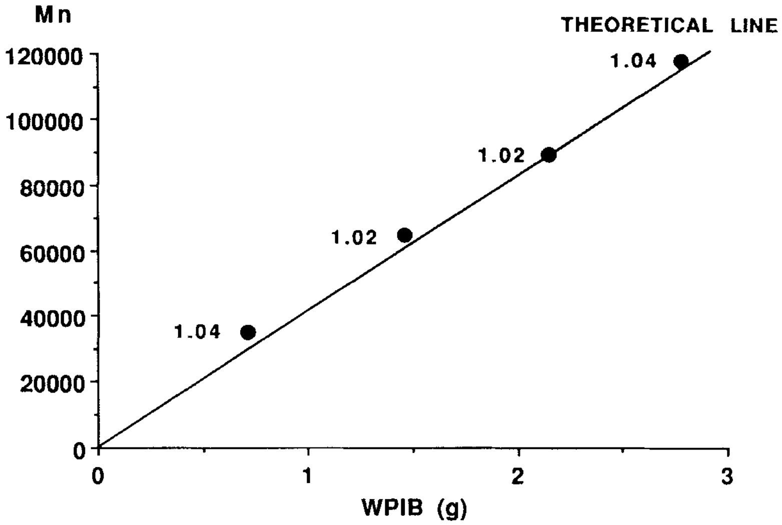


FIG. 11. Living polymerization of IB initiated with 5-*tert*-butyl-1,3-dicumyl-chloride. IMA technique (4 × 1 mL). Time elapsed between monomer additions: 30 min., [*t*-Bu-DiCuCl] = 1×10^{-3} *M*; [$TiCl_4$] = 3.6×10^{-2} *M*; V_0 = 25 mL; [DTBP] = 1×10^{-3} *M*. Solvent: CH_3Cl:*n*-hexane, 40:60 v:v. Temperature: −80°C. The numbers are MWD values.

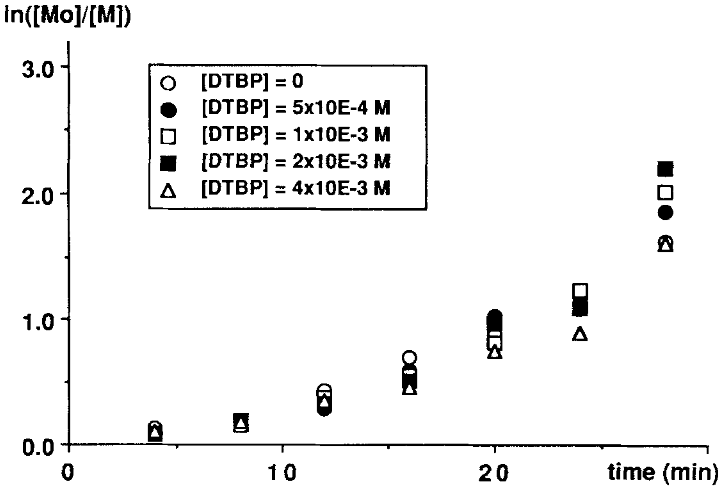


FIG. 12. The effect of DTBP concentration on the rate of IB polymerization initiated with 5-*tert*-butyl-1,3-dicumyl-acetate. AMI technique. $[IB]_0$ = 2.04 *M*. [*t*-Bu-DiCuOAc] = 1×10^{-3} *M*; [$TiCl_4$] = 3.6×10^{-2} *M*; V_0 = 25 mL. Solvent: CH_3Cl:*n*-hexane, 40:60 v:v. Temperature: −80°C.

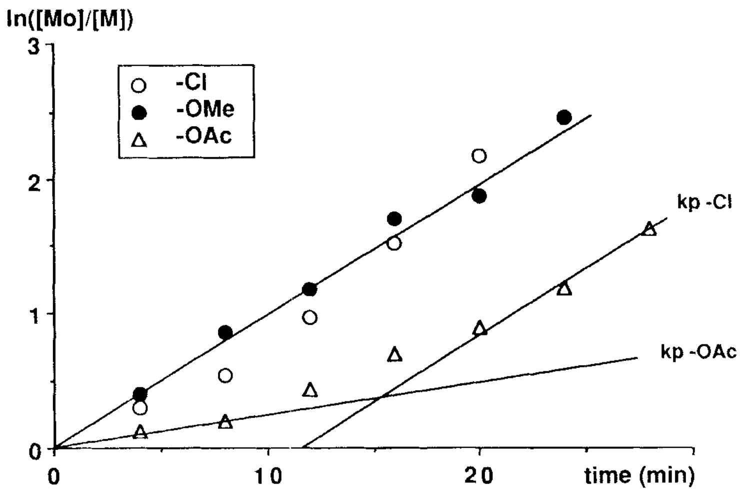


FIG. 13. Comparison of the rate of IB polymerization initiated with 5-*tert*-butyl-1,3-dicumyl-chloride, -methylether, and -acetate. AMI technique. $[\mathrm{IB}]_0 = 2.04$ *M*. [t-Bu-DiCuCl] = [t-Bu-DiCuOMe] = [t-Bu-DiCuOAc] = 1×10^{-3} *M*; $[\mathrm{TiCl_4}] = 3.6 \times 10^{-2}$ *M*; V_0 = 25 mL. Solvent: $\mathrm{CH_3Cl}$:*n*-hexane, 40:60 v:v. Temperature: −80°C.

of the dichloride become equal. The nonlinearity of the ln ($[\mathrm{M_0}]/[\mathrm{M}]$) versus time plot can also be caused by slow initiation, as the reviewer rightfully pointed out. Indeed, the starting initiating efficiencies are ~70% and they increase somewhat, which might indicate slow initiation, but they do not account for the threefold rate increase during polymerization. Evidently a slow chlorination of the growing PIB chain end takes place, followed by reinitiation by the excess $\mathrm{TiCl_4}$. The polymerization can be visualized by the following kinetic scheme:

$$\frac{d[\mathrm{M}]}{dt} = (k_{p,\mathrm{OAc}}[\mathrm{M}^+_{\mathrm{O,Ac}}] + k_{p,\mathrm{Cl}}[\mathrm{M}^+_{\mathrm{Cl}}])[\mathrm{M}] \tag{1}$$

if $[\mathrm{TiCl_4}]$ = constant:

$$\mathrm{M}^+_{\mathrm{OAc}} \xrightarrow{k_t} \mathrm{M}^+_{\mathrm{Cl}}$$

thus

$$[\mathrm{M}^+_{\mathrm{OAc}}] = [\mathrm{M}^+_{\mathrm{OAc}}]_0 \exp(-k_t t) \tag{2}$$

Substituting (2) into (1):

$$\frac{d[\mathrm{M}]}{\mathrm{M}} = \frac{d(\ln[\mathrm{M_0}]/[\mathrm{M}])}{dt}$$

$$= k_{p,\mathrm{OAc}}[\mathrm{M}^+_{\mathrm{OAc}}]_0 \exp(-k_t t) + k_{p,\mathrm{Cl}}[\mathrm{M}^+_{\mathrm{OAc}}]_0[1 - \exp(-k_t t)]dt$$

Since the TMPOAc/$\mathrm{TiCl_4}$ system does not initiate IB polymerization or at best is a very inefficient initiating system [18] under the same experimental conditions, i.e., methylchloride-*n*-hexane (40:60 v:v)/−80°C, we conclude that the polymerization is ionic and there is no termination by reforming of the PIB ester. Furthermore, although the MWDs are broader (1.5–1.25), the absence of bimodal MWDs reveals that there is an exchange of the gegenions $\mathrm{TiCl_5^-}$ and $\mathrm{TiCl_4OAc^-}$ between growing

PIB chain ends. This type of exchange has been postulated to explain monomodal MWDs in the polymerization of isobutylene with the cumyl acetate-cumyl propionate complex initiating systems [9], but was later rescinded [2] and replaced with the theory of instantaneous chlorination of the initiator. Our results seem to support the earlier proposition and to contradict the latter one.

CONCLUSIONS

We suggest that the sole purpose of DTBP is to trap protogenic impurities in the polymerization system. This is in line with the earlier observation with BCl_3, which has been confirmed for the $TiCl_4$ system in this study, that DTPB is required in concentrations comparable with the concentration of protic impurities i.e., $\sim 10^{-3}$ mol/L in the system. Similarly, we hypothesize that proton trapping is the main function of the externally added EDs. We conclude that the polymerization of IB coinitiated with $TiCl_4$ in the presence of a proton trap is living due to the absence of chain transfer and reversible termination, and is not the result of carbocation stabilization. In the absence of a proton trap, however, induced chain transfer prevents living polymerization. Although a proposition has already been presented [3] to account for the broad MWDs caused by protogenic impurities in the ester/ BCl_3 living polymerization system, further research is needed to clearly identify why the presence of protogenic impurities leads to nonliving character.

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Note Added in Proof. The $TiCl_4$ order for polymerization by 5-*tert*-butyl-1,3-dicumyl-chloride/CH_3Cl:MeCH, 40:60 v:v/ −80°C has been determined and found to be 2.19.