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LIVING CARBOCATIONIC POLYMERIZATION OF STYRENE IN THE PRESENCE OF PROTON TRAP

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ABSTRACT

The living polymerization of styrene was achieved with the 2,4,4-trimethyl-2-pentyl chloride/$TiCl_4$/MeCl:methylcyclohexane 40:60 v:v/ −80°C polymerization system in the presence of di-*tert*-butylpyridine in concentrations comparable to the concentration of protic impurities. It was determined that the living nature of the polymerization is not due to carbocation stabilization. The polymerization is second order in $TiCl_4$. Side reactions, namely polymerization by direct initiation and intermolecular alkylation, are operational, and a careful selection of experimental conditions is necessary to minimize their effect and obtain apparently living behavior. Polymerization by direct initiation can be minimized by increasing the initiator concentration, and intermolecular alkylation can be reduced by quenching the polymerization system when the conversion reaches close to 100%.

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INTRODUCTION

Recently we reported the living polymerization of isobutylene (IB) coinitiated with $TiCl_4$ or BCl_3 in the presence of proton trap di-*tert*-butylpyridine (DTBP) in concentrations comparable to the concentration of protic impurities in the system [1, 2]. We have confirmed that the living nature of the polymerization is not due to carbocation stabilization. We have also demonstrated that the living nature of the polymerization using electron donors in place of the proton trap is similarly not due to carbocation stabilization. We suggested that the main function of the externally added electron donors (EDs) and the sole purpose of DTBP in the polymerization of IB is to trap protic impurities in the polymerization system. We proposed that the polymerization of IB coinitiated with $TiCl_4$ or BCl_3 is living due to the absence of chain transfer and reversible termination. In the absence of a proton trap, induced chain transfer prevents living polymerization with $TiCl_4$. With BCl_3, fast polymerization by the protic impurities occurs, masking the much slower living polymerization, and the monomer is essentially consumed by this process unless protic impurities are scavenged.

We have extended our studies to the polymerization of styrenic monomers, and in the present publication we report on results obtained with styrene.

EXPERIMENTAL

Materials

The synthesis of 5-*tert*-butyl-1,3-dicumyl-methyl ether (*t*-BudiCUOMe) has been described [1]. 2,4,4-Trimethyl-2-pentyl chloride (TMPCl) was obtained from 2,4,4-trimethyl-pentene-1 (Aldrich) by hydrochlorination. Styrene (Aldrich) was purified by washing it with 10% aqueous sodium hydroxide solution, followed by distilled water until neutral. After drying over $MgSO_4$, the styrene was distilled at a reduced pressure. Traces of water remaining after treatment with $MgSO_4$ were removed by adding dibutylmagnesium (DBM) (Lithco) as a 14 wt% heptane solution to styrene. In a nitrogen-filled glove box, 5 mL DBM solution was injected into 500 mL styrene. The appearance of a pale yellow color indicated monomer dryness. During the subsequent vacuum distillation, the first fraction containing the heptane solvent was discarded. Methyl chloride (MeCl, Linde) was dried by passing the gas through in-line gas-purifier columns packed with BaO/Drierite, and it was condensed in the cold bath of the glove box prior to polymerization. Methylcyclohexane (MeChx, Aldrich) was refluxed for 2 days with concentrated sulfuric acid. It was washed with distilled water until neutral, dried over Molecular Sieves, refluxed, and distilled from CaH_2 under nitrogen atmosphere. Titanium tetrachloride (Aldrich) and the proton trap, 2,6-di-*tert*-butylpyridine (DTBP, 99.1% by GC, Aldrich), were used as received.

Procedures

All polymerizations were carried out under a dry nitrogen atmosphere in a MBraun 150-M glove box (Innovative Technology Inc. Newburyport, Massachusetts). The moisture level inside the glove box was kept under 1.0 ppm by continuous circulation of the internal nitrogen atmosphere through the MB 150-M gas purification system. Large (75 mL) test tubes were used as polymerization reactors for kinetic experiments. In the styrene homopolymerization experiments the reaction components were added into the test tubes in the following sequence: 1) solvents (methylcyclohexane and methyl chloride); 2) initiator (*t*-BudiCUOMe or TMPCl from master solutions); 3) proton trap (DTBP) (from master solution); 4) coinitiator (titanium tetrachloride); 5) monomer (styrene in 20 vol% solution). After adding the last component, the reaction mixture was stirred vigorously by a vortex stirrer, then placed back into the temperature-controlled heptane bath. After predetermined time intervals, polymerizations were terminated by adding prechilled methanol. The polymers were purified by repeated dissolution-precipitation in dichloromethane/methanol, and dried *in vacuo* prior to GPC measurements.

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 five μ-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The flow rate (THF) was 1.0 mL/min. Narrow MWD polystyrene samples (Polysciences) were used as calibration standards. For data acquisition and computing, a Waters Baseline chromatography workstation was used. NMR measurements were carried out by a Bruker 270 MHz instrument.

RESULTS AND DISCUSSION

The living polymerization of styrene using $TiCl_4$ as coinitiator was recently reported in the combined presence of the "electron donor" dimethyl acetamide (DMA) and the proton trap DTBP [3]. Using the Incremental Monomer Addition (IMA) technique, intermolecular alkylation was reported, and therefore the AMI (All Monomer In) technique was used to diagnose the living nature of the polymerization. This technique, however, does not provide sufficient proof for the living character of the polymerization [1, 4]. Experiments in the presence of DTBP but in the absence of DMA led to higher than theoretical molecular weights and were explained by weaker carbocation stabilization by DTBP compared to DMA.

Based on the results with IB, we hypothesize that the main function of DMA and the sole purpose of DTBP in the polymerization of styrene is similar, i.e., to trap protic impurities in the polymerization system, and that the living polymerization of styrene could be achieved using DTBP alone. We interpreted the results of Kaszas et al. [3] on the basis of postpolymerization intermolecular alkylation. Therefore we carried out polymerization experiments measuring conversions with different polymerization times using the reported polymerization conditions. According to the results in Fig. 1, conversion is essentially complete in 4 minutes. The molecular weights (Fig. 2)follow the theoretical M_n-conversion line up to this point but start to increase with longer times, a clear indication of intermolecular alkylation. The rate of alkylation can be expressed by

$$-d[\mathrm{P}]/dt = k_a[\mathrm{P}^+]([\mathrm{M}]_0 - [\mathrm{M}]) \tag{1}$$

where k_a is the rate constant of aklylation, and [M], $[\mathrm{P}^+]$, and [P] are the concentrations of monomer, polymer cation, and polymer (dormant and active), respectively. Using the first-order Eq. (2) where k_p is the rate constant of propagation,

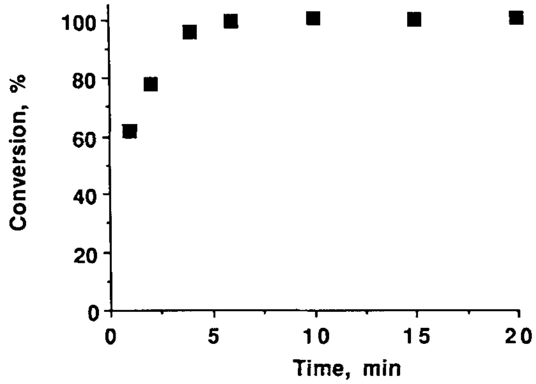

FIG. 1. Conversion vs time plot in the polymerization of styrene at high monomer concentration. $[M]_0 = 1.75$ M; [TMPCl] = 4.44×10^{-3} M; [$TiCl_4$] = 8.28×10^{-2} M; [DTBP] = 8×10^{-3} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −80°C.

$$-d[M]/dt = k_p[P^+][M] \tag{2}$$

and assuming that $[P^+]$ is constant and negligible compared to [P], Eq. (1) can be integrated:

$$[P] = [I]_0 - k_a[M]_0[P^+]t + (k_a/k_p)[M]_0(1 - \exp\{-k_p[P^+]t\}] \tag{3}$$

where $[I]_0$ is the initiator concentration.

In line with Eq. (3), the intermolecular alkylation proceeds at a close to constant rate (2%/min, Fig. 3) when the exponential third term in Eq. (3) is negligible compared to the second linear term, i.e., around 100% conversion. When a significant number of polymer chains disappeared, the assumption $[P^+]$ = constant is no longer valid and the rate of alkylation will decrease. It is important to note

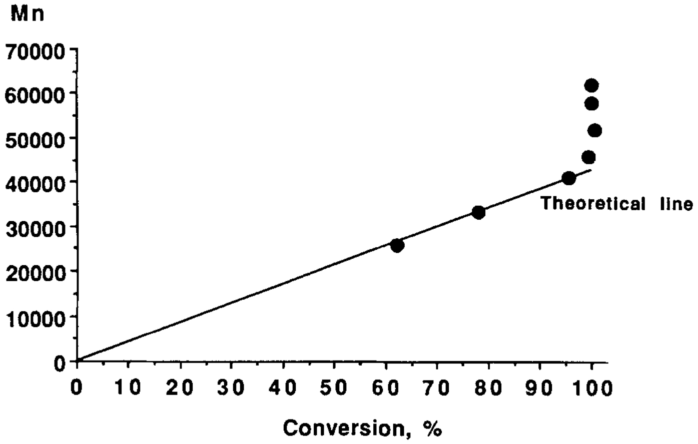

FIG. 2. M_n vs conversion plot in the polymerization of styrene at high monomer concentration. $[M]_0 = 1.75$ M; [TMPCl] = 4.44×10^{-3} M; [$TiCl_4$] = 8.28×10^{-2} M; [DTBP] = 8×10^{-3} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −80°C.

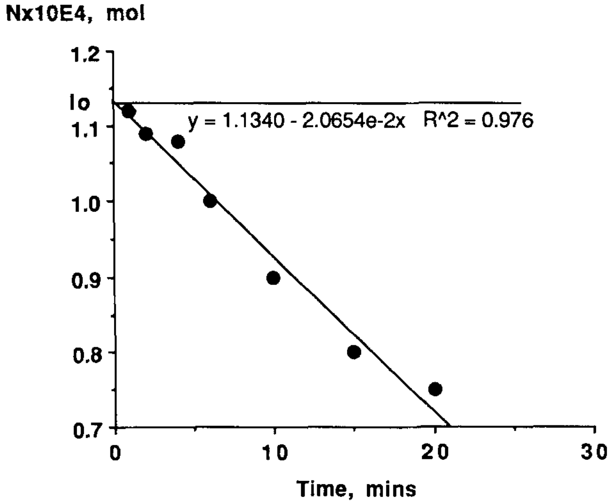

FIG. 3. The number of moles of polystyrene-time plot. $[M]_0$ = 1.75 M; [TMPCl] = 4.44×10^{-3} M; $[TiCl_4]$ = 8.28×10^{-2} M; [DTBP] = 8×10^{-3} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −80°C.

that alkylation also takes place while the polymerization is in progress, but its extent is negligible according to Fig. 3.

In the presence of DMA a substantial portion of $TiCl_4$ is complexed, reducing the $TiCl_4$ concentration, which leads to reduced rates. According to this interpretation, the linear M_n-W_p (weight of polymer) curve reported in Ref. 3 in the simultaneous presence of DMA and DTBP can be explained by the decreased polymerization as well as decreased alkylation rate due to the decreased $TiCl_4$ concentrations.

In the light of these new results, we have decided to do a further study on the polymerization of styrene in the presence of a proton trap.

Experimentation started with control experiments, i.e., polymerizations carried out in the absence of initiator. The results are plotted in Fig. 4 as conversion-time, in Fig. 5 as ln ($[M]_0/[M]$) versus time, and in Fig. 6 as M_n-conversion plots. In the absence of DTBP, bimodal distributions were obtained, indicating at least two different growing centers. In the presence of DTBP the molecular weight distribution is monomodal. The conversion-time plots (Fig. 4) are similar in the [DTBP] = 2×10^{-3} to 8×10^{-3} M concentration range, while in the absence of DTBP the polymerization rate is significantly higher due to initiation from protic impurities. This is similar to the results obtained with IB in the presence of $\sim 2 \times 10^{-3}$ M DTBP where polymerization initiated by protic impurities is prevented. In the absence of DTBP the ln ($[M]_0/[M]$) versus time plot is linear; apparently the polymerization is first order in monomer. Increasing the DTBP concentration above 2×10^{-3} M had no effect on the rates or the molecular weights. In the presence of $>2 \times 10^{-3}$ M DTBP, polymer formation is most probably due to direct initiation [5], and the conversion-time and the ln ($[M]_0/[M]$) versus time plot is slightly curved although it could still be fitted linearly. Polystyrene formation due to direct initiation is slow (5-10%/30 minutes) and should be negligible compared to polymeriza-

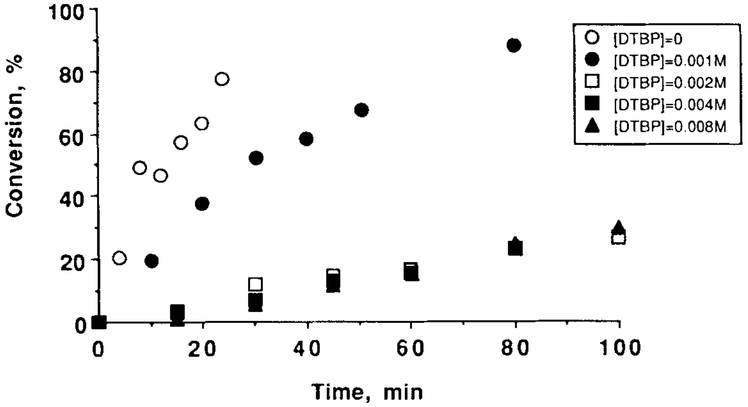

FIG. 4. Conversion time plot for the polymerization of styrene in the absence and presence of proton trap. $[M]_0 = 0.35$ M; $[TiCl_4] = 3.64 \times 10^{-2}$ M. Solvent: MeCl/MeChx 40/60 v/v mixture. −90°C.

tion by controlled initiation provided the concentration of initiator is not very low. Indeed, the rate of polymerization initiated by 5-*tert*-butyl-1,3-dicumyl-methyl ether, even at a relatively low concentration (8.96×10^{-4} M), is much higher (Fig. 7), and consequently polymer formation is essentially from the initiator. The polymerization rate decreases with decreasing $TiCl_4$ concentration and is lower in the presence of DTBP, which prevents initiation from protic impurities. The M_n-

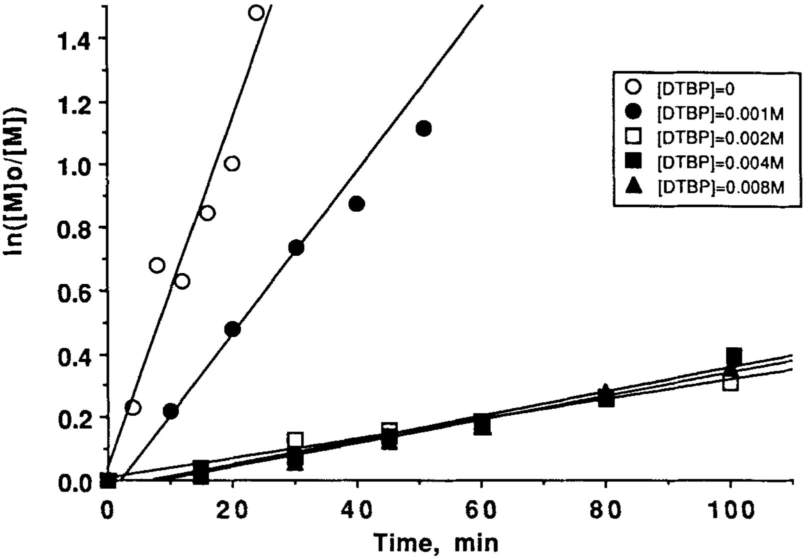

FIG. 5. ln $([M]_0/[M])$ vs time plot for the polymerization of styrene in the absence and presence of proton trap. $[M]_0 = 0.35$ M; $[TiCl_4] = 3.64 \times 10^{-2}$ M. Solvent: MeCl/MeChx 40/60 v/v mixture. −90°C.

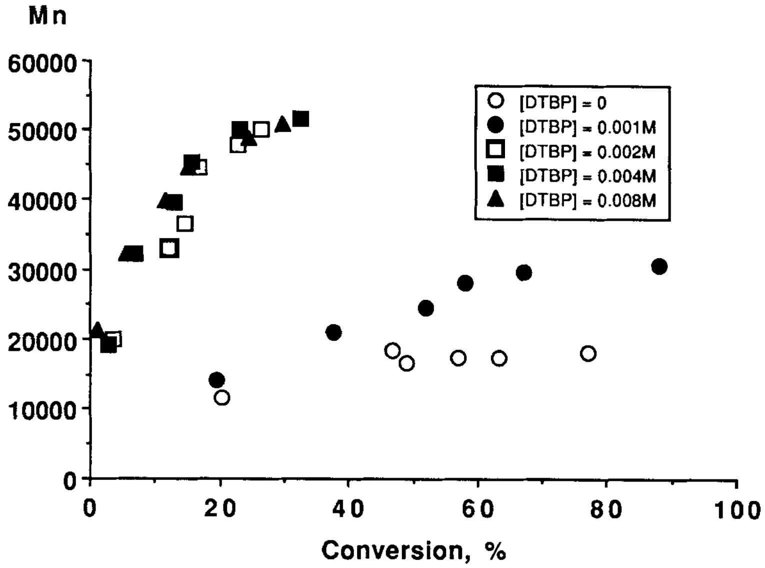

FIG. 6. Molecular weight vs conversion plot for the homopolymerization of styrene in the absence and presence of proton trap. $[M]_0$ = 0.35 M; $[TiCl_4]$ = 3.64×10^{-2} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −90°C.

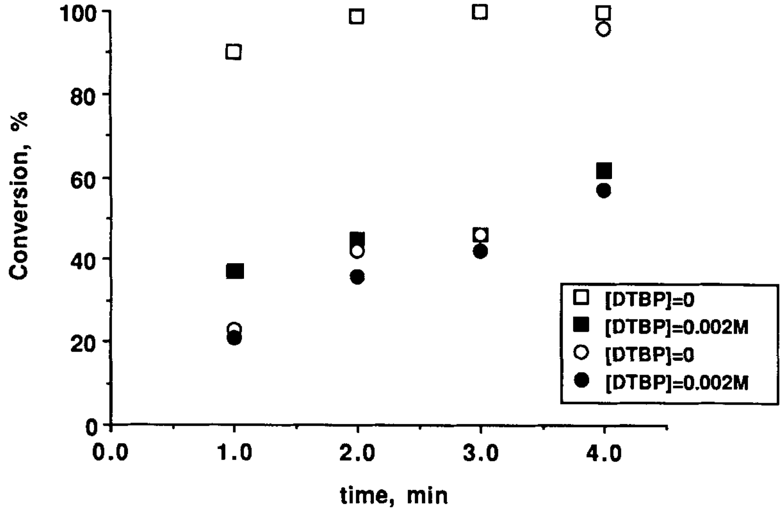

FIG. 7. Conversion vs time plot for the polymerization of styrene with the *t*-BudiCUOMe/$TiCl_4$/CH_3Cl:MeChx, 40:60 v:v/ −80°C system in the presence and absence of proton trap (DTBP). $[M]_0$ = 0.35 M; $[I]_0$ = 8.96×10^{-4} M; $[TiCl_4]$ = 3.6×10^{-2} M (□, ■) and 1.8×10^{-2} M (○, ●).

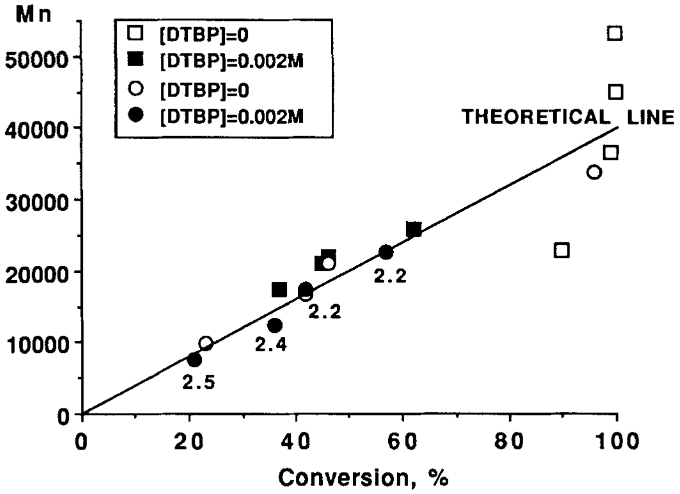

FIG. 8. Molecular weight vs conversion plot for the polymerization of styrene with the *t*-BudiCUOMe/$TiCl_4$/CH_3Cl:MeChx, 40:60 v:v/ −80°C system in the presence and absence of proton trap (DTBP). The numbers are MWD values. $[M]_0$ = 0.35 M; $[I]_0$ = 8.96 × 10^{-4} M; [$TiCl_4$] = 3.6 × 10^{-2} M (□, ■) and 1.8 × 10^{-2} M (○, ●).

conversion plot is linear in the presence of DTBP and also in its absence with the lower $TiCl_4$ concentration. Controlled initiation is evidently much faster than initiation from protic impurities, and close to theoretical molecular weights are obtained even in the absence of DTBP. Using a higher $TiCl_4$ concentration, the molecular weight at higher conversion is lower than theoretical, i.e., the polymer concentration is higher than the concentration of initiator. At ~100% conversion, intermolecular alkylation becomes important as reflected in the higher than theoretical molecular weights which increase with increasing time. Representative MWD values are shown in Fig. 8 for polymers obtained in the presence of DTBP. In its absence the MWDs are bimodal and very broad.

The observed linear molecular weight-conversion plot in the presence of DTBP is not a sufficient indication of living polymerization; it only reveals the absence of chain transfer to monomer. In the presence of bases, however, the eliminated proton is trapped before initiation of a new polymer chain. When this terminative proton entrapment or other termination reactions occur and initiation is instantaneous, theoretical molecular weights will be obtained although the polymerization is not living. Proof for living polymerization, as we discussed earlier [1], can only be obtained by additional kinetic measurements, i.e., in living polymerization the growing center concentration remains constant. The ln ($[M]_0/[M]$) versus time plot for the two $TiCl_4$ concentrations is shown in Fig. 9. While the data points corresponding to the lower $TiCl_4$ concentration can be fitted with a straight line starting at the origin and indicating the absence of terminative chain transfer up to ~60% conversion, terminative proton transfer is probably operational at the higher $TiCl_4$ concentration.

In the polymerization of isobutylene with the same system, we concluded [1] that the polymerization takes place by the common gegenion $TiCl_5^-$ or $Ti_2Cl_9^-$, which

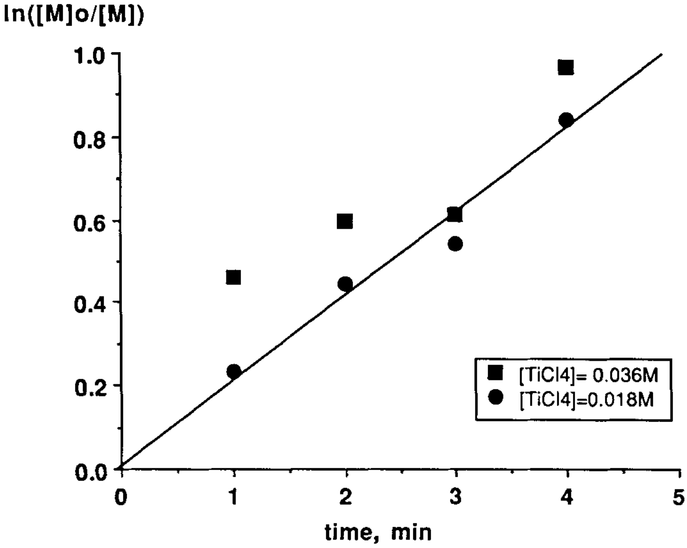

FIG. 9. In ($[M_0]/[M]$) vs time plot for the polymerization of styrene with the *t*-BudiCUOMe/$TiCl_4/CH_3Cl$:MeChx, 40:60 v:v/−80°C system in the presence of proton trap (DTBP). $[M]_0 = 0.35$ M; $[I]_0 = 8.96 \times 10^{-4}$ M; $[TiCl_4] = 3.6 \times 10^{-2}$ M (■) and 1.8×10^{-2} M (●).

arises by fast chlorination of the methyl ether followed by $TiCl_4$ coinitiation. Since the polymerization of styrene is much faster, this conclusion may not be valid. We also reported [4] that a high ionicity of an initiating species will not instantaneously decrease to a lower ionicity corresponding to the growing chain end structure. This can lead to side reactions similar to those which occur in conventional systems. It resulted in chain transfer to monomer at the early stage of the polymerization in the cumyl acetate/BCl_3/St/CH_3Cl/−30°C system [6]. For the above reasons and because of our interest in block copolymerization, further experiments were carried out using TMPCl as the initiator. Orienting copolymerization experiments were carried out under the same polymerization conditions. The dependence of copolymer composition on the comonomer feed composition is shown in Fig. 10a. From the extended Kelen-Tüdös plot (Fig. 10b), $r_{IB} = 5.9 \pm 1.8$ and $r_{St} = 5.7 \pm 1.9$ monomer reactivity ratios were obtained, indicating that both crossovers are slow.

From the reactivity ratios we anticipated that initiation with TMPCl may be slow. Figure 11 shows the conversion-time plots for the polymerization of styrene initiated with TMPCl at different $TiCl_4$ concentrations using 2×10^{-3} M DTBP. Coinitiator/initiator ratios ranged from 8 to 64. The polymerization rates are practically the same in the [DTBP] = 1-8 $\times 10^{-3}$ M concentration range at −80 or −90°C (Fig. 12). The rate in the absence of DTBP was somewhat higher due to simultaneous initiation from protic impurities. The M_n-conversion plot (Fig. 13) reveals that initiation is indeed slow: the molecular weights at low conversion are higher than theoretical and reach the theoretical line at ~20% conversion indepen-

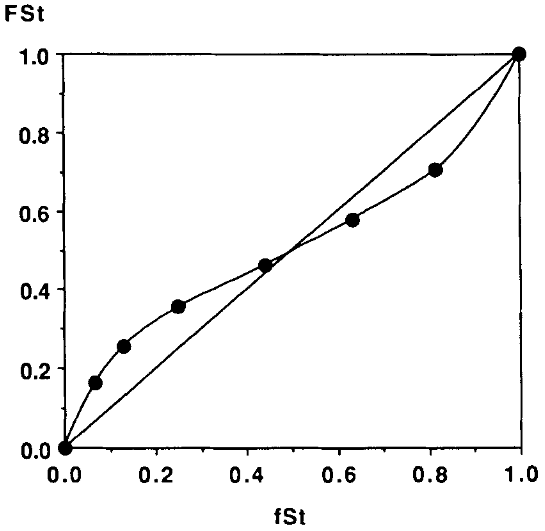

FIG. 10a. Dependence of copolymer composition (f_{St}) on the comonomer feed composition (F_{St}) in the copolymerization of IB with St by the *t*-BudiCUOMe/TiCl$_4$/Ch$_3$Cl: MeChx, 40:60 v:v/ − 80°C system in the presence of proton trap.

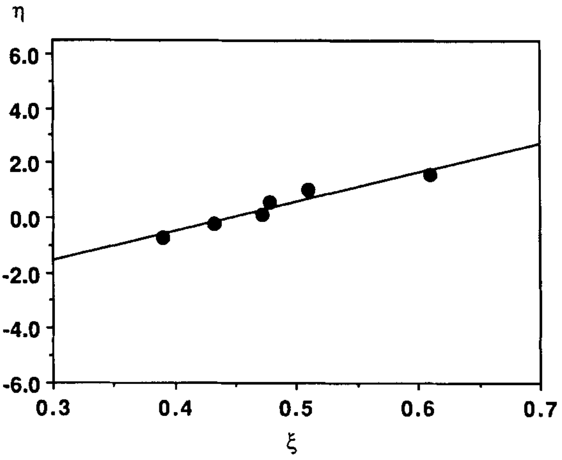

FIG. 10b. Determination of reactivity ratios by the Kelen–Tüdös method for the copolymerization of IB with St by the *t*-BudiCUOMe/TiCl$_4$/Ch$_3$Cl:MeChx, 40:60 v:v/ − 80°C system in the presence of proton trap.

dently of the coinitiator concentration. Above ~20% conversion the molecular weights are close to but somewhat lower than theoretical. This may indicate that at [TMPCl] = 1×10^{-3} M the polymerization by direct initiation (5–10%/30 minutes at [TiCl$_4$] = 3.64×10^{-2} M) is no longer negligible. The ln ([M]$_0$/[M]) versus time plot is shown in Fig. 14 for the three highest coinitiator concentrations. The points

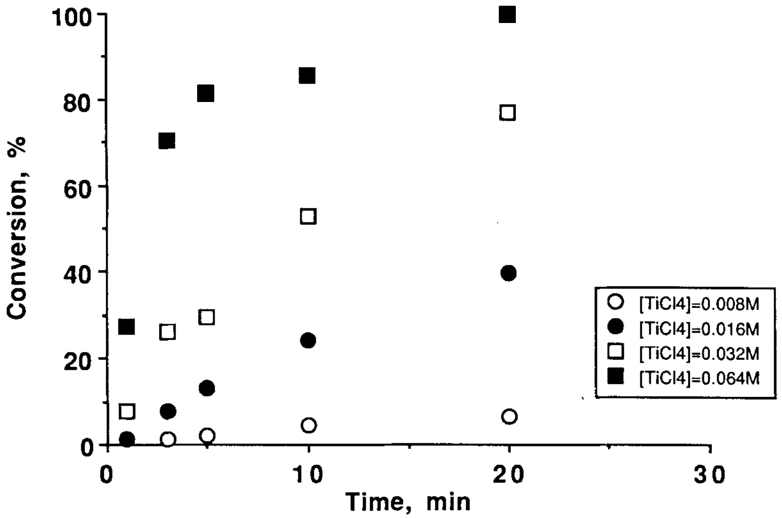

FIG. 11. Conversion vs time plot in the polymerization of styrene at different coinitiator concentrations in the presence of proton trap. $[M]_0$ = 0.35 M; [TMPCl] = 1×10^{-3} M; [DTBP] = 2×10^{-3} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −80°C.

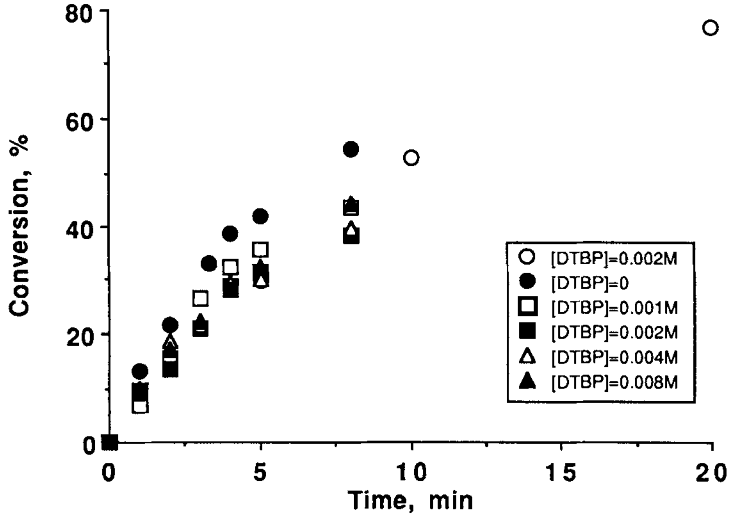

FIG. 12. Conversion vs time plot for the polymerization of styrene in the presence of proton trap. $[M]_0$ = 0.35 M; [TMPCl] = 1×10^{-3} M; $[TiCl_4]$ = 3.64×10^{-2} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −90°C. (○ $[TiCl_4]$ = 3.2×10^{-2} M; −80°C.) In the (○) experiments, $[TiCl_4]$ and temperature were different from the rest of the experiments. All other parameters were the same.

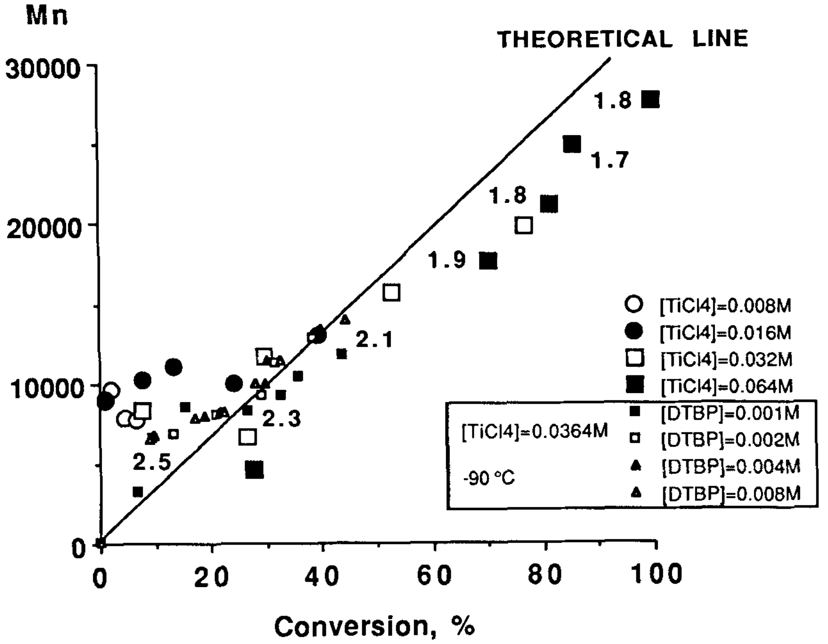

FIG. 13. M_n vs conversion plot in the polymerization of styrene at different coinitiator concentrations in the presence of proton trap. The numbers are MWD values. $[M]_0$ = 0.35 M; [TMPCl] = 1 × 10^{-3} M; [DTBP] = 2 × 10^{-3} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −80°C.

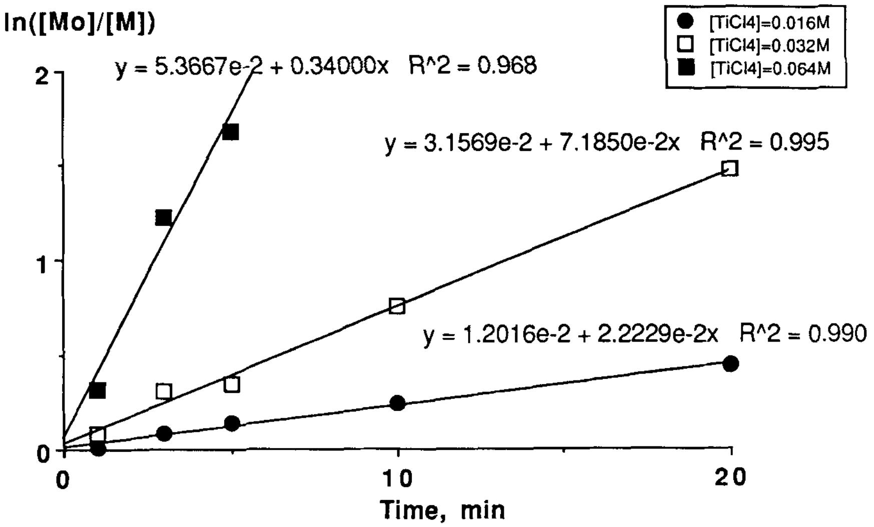

FIG. 14. Time dependence of ln $([M_0]/[M])$ in the polymerization of styrene at different coinitiator concentrations in the presence of initiator and proton trap. $[M]_0$ = 0.35 M; [TMPCl] = 1 × 10^{-3} M; [DTBP] = 2 × 10^{-3} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −80°C.

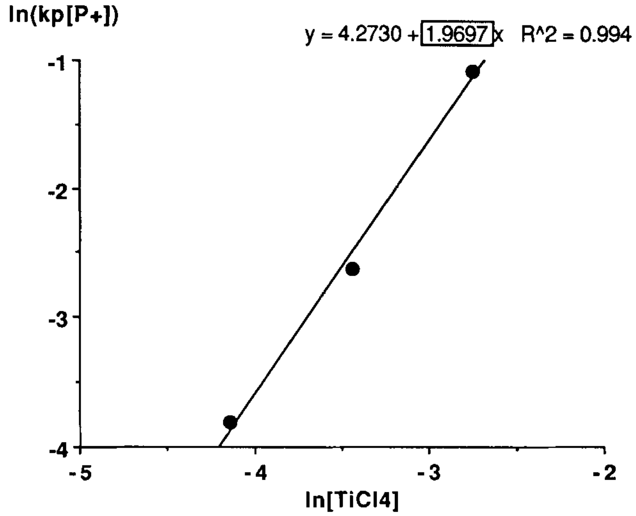

FIG. 15. ln ($k_p[P^+]$) vs ln [$TiCl_4$] diagnostic plot to determine $TiCl_4$ order in the polymerization of styrene. $[M]_0$ = 0.35 M; [TMPCl] = 1 × 10^{-3} M; [DTBP] = 2 × 10^{-3} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −80°C.

for the lowest $TiCl_4$ concentration are not shown since the initiator efficiencies are substantially below 100% due to slow initiation and increasing with increasing conversion. Consequently, the growing center concentration increases and the ln ($[M]_0/[M]$) versus time plot will not be linear. For the [$TiCl_4$] = 1.6 × 10^{-3} M concentration, although all data points are shown, only the last two were used to create the linearity. From the slopes, $k_p[M_n^+]$ values are obtained from which the order of $TiCl_4$ can be obtained by plotting ln ($k_p[M_n^+]$ versus ln [$TiCl_4$] (Fig. 15). According to Fig. 15, the polymerization of styrene is close to second order in $TiCl_4$. Second-order $TiCl_4$ dependency was also obtained with IB [1] under the same conditions, i.e., in MeCl/MeChx (40/60 v/v) at −80°C. In agreement with published results, we suggested [1] that $TiCl_4$ forms bimolecular associates and/or bimolecular complex gegenions.

If direct initiation is responsible for the somewhat lower than theoretical molecular weights at [TMPCl] = 1 × 10^{-3} M, the TMPCl concentration can be increased to increase the ratio of controlled versus uncontrolled polymerization in order to obtain theoretical molecular weights. Figure 16 shows the conversion-time plot for the polymerization when the TMPCl concentration is doubled to 2 × 10^{-3} M. Polymerization rates remained unchanged in the [DTBP] = 1–8 × 10^{-3} M concentration range. Importantly the molecular weights (Fig. 17) are theoretical above ~20% conversion.

Representative samples were examined by ^{13}C-NMR spectroscopy. According to the phenyl C-1 carbon signal for determining stereoregularity, the product is atactic polystyrene.

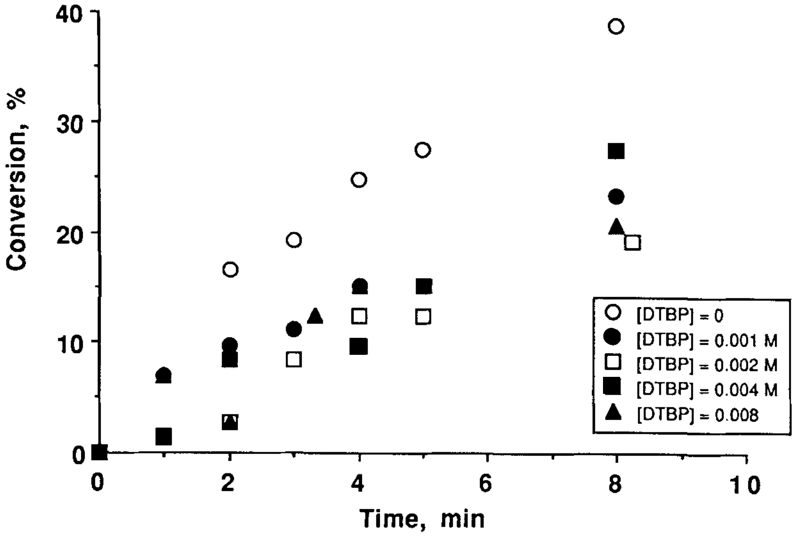

FIG. 16. Conversion vs time plot for the homopolymerization of styrene in the absence and presence of proton trap. $[M]_0$ = 0.35 M; [TMPCl] = 2 × 10^{-3} M; $[TiCl_4]$ = 1.6 × 10^{-2} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −90°C.

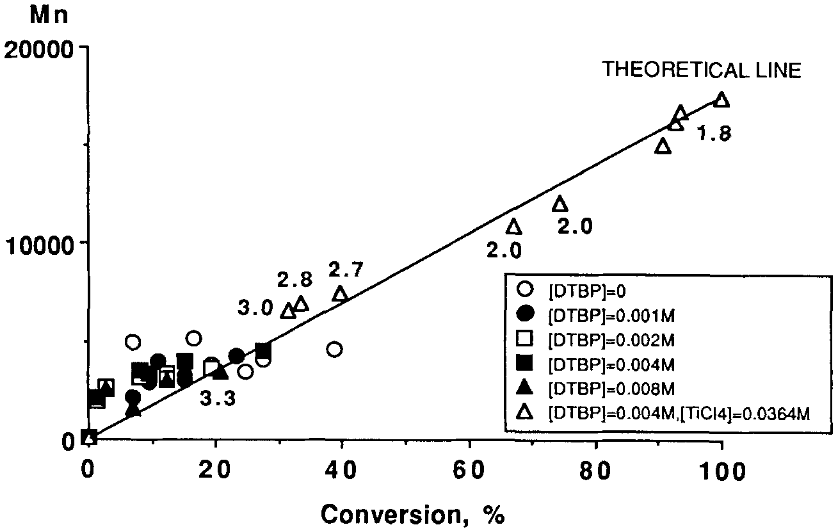

FIG. 17. Molecular weight vs conversion plot for the polymerization of styrene in the absence and presence of DTBP. The numbers are MWD values. $[M]_0$ = 0.35 M; [TMPCl] = 2 × 10^{-3} M; $[TiCl_4]$ = 1.6 × 10^{-2} M. Solvent: MeCl/MeChx 40/60 v/v mixture. −90°C.

CONCLUSIONS

The living polymerization of styrene can be achieved with the TMPCl/$TiCl_4$/MeCl:MeChx 40:60 v:v/−80°C polymerization system in the presence of DTBP which prevents initiation from protic impurities. The polymerization rate is not affected by the excess amount of DTBP added, consequently the living nature of the polymerization is not due to carbocation stabilization. Side reactions, namely polymerization by direct initiation and intermolecular alkylation, however, are operational, and a careful selection of experimental conditions are necessary to minimize their effect and obtain apparently living behavior. Polymerization by direct initiation can be minimized by increasing the initiator concentration, and intermolecular alkylation can be reduced by quenching the polymerization system when the conversion reaches close to 100%.

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