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ELECTRON DONORS AS COLORIMETRIC INDICATORS OF PROTIC IMPURITY REMOVAL IN LIVING CATIONIC POLYMERIZATION OF ISOBUTYLENE

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ABSTRACT

Various tertiary amines including octyl-*p*-(dimethylamino)benzoate, *N*,*N*-dimethyl-*m*-toluidine, ethyl-*p*-(dimethylamino)benzoate, and quinoline were examined as external electron donors in the living cationic polymerization of isobutylene using a 1,3-*bis*(2-chloro-2-propyl)-5-*tert*-butylbenzene (*t*-Bu-*m*-DCC)/ED/$TiCl_4$ initiating system in hexane/methyl chloride cosolvents. These aromatic amines were observed to retard the rate of polymerization and, when added to the polymerization reaction in excess of the concentration of protic impurities, were observed to form vividly colored complexes with $TiCl_4$. Under these conditions, initiation by protic impurities was suppressed, and the polymerizations were living as demonstrated by linearity of first-order kinetic and $\overline{M}_n$ vs conversion plots, and absence of unsaturation at the polyisobutylene chain ends. When the concentration of amine was below that of protic impurities, the polymerizations were colorless and nonliving; thus these amines yield a colorimetric indication of protic impurity elimination. GPC chromatograms also demonstrated that the elimination of initiation by protic impurities coincided with the color change.

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These results support a mechanism in which the major role of the electron donor in $TiCl_4$-coinitiated systems is to remove protic impurities from the system.

INTRODUCTION

Living polymerizations are defined as polyaddition reactions that proceed with the virtual exclusion of termination and chain transfer [1]. The living cationic polymerization of isobutylene (IB) was first reported by Kennedy et al. for polymerizations utilizing *tert*-alkyl ester [2, 3] or ether [4, 5] initiators in conjunction with BCl_3 or $TiCl_4$ Lewis acids. The $TiCl_4$-based systems were shown to initiate efficiently in moderately nonpolar media in which the formed polyisobutylene (PIB) remained soluble, thus enabling the synthesis of high molecular weight PIBs (up to $\overline{M}_n$ = 126,000 g/mole) with narrow molecular weight distributions (MWD) ($\overline{M}_w/\overline{M}_n$ = 1.1) [4]. Kaszas et al. [6] later reported that living cationic polymerization of IB, producing products of narrow MWD, could also be achieved by the addition of external electron donors (ED) to the polymerization medium. In a subsequent paper [7], these same authors showed that the mechanism of polymerization could be interpreted in terms of a conventional polymerization with reversible activation-deactivation of the growing chain ends. The livingness of the earlier systems was attributed to the in-situ formation of electron pair donors derived from the Lewis acid and the polar acetoxy or methoxy groups of the initiator molecules. They proposed that the electron pair donors (whether formed in situ or purposefully added externally) participate in the formation and stabilization of the propagating carbocation center, thereby suppressing termination and transfer reactions.

Recently, Faust et al. [8] challenged this "carbocation stabilization" mechanism and proposed that the only role of the ED is to remove protic impurities from the polymerization mixtures, and that the polymerizations are inherently living due to the absence of chain transfer and the operation of a chain-end, activation-deactivation equilibrium. This proposition resulted from observations of polymerizations employing 2,6-di-*tert*-butylpyridine (DTBP) as an externally added electron donor. DTBP has been shown to be incapable of complexation with carbocations due to steric hindrance, but to exhibit highly specific reactivity toward protons. They reported that IB polymerizations at −80°C initiated with 1,3-*bis*(2-chloro-2-propyl)-5-*tert*-butylbenzene (*t*-Bu-*m*-DCC)/$TiCl_4$ in the presence of DTBP as ED were free of termination and chain transfer, and that the polymerization rate was independent of the DTBP concentration.

We have performed detailed investigations of the living cationic polymerization of isobutylene, conducted in the presence of three structurally similar, amine-based EDs: pyridine [9, 10] and 2,4-dimethylpyridine (DMP) [11, 12], which both complex with $TiCl_4$, and DTBP, which is proposed to be noncomplexing. Polymerizations utilizing pyridine as an electron donor, 1,4-*bis*(2-chloro-2-propyl)benzene (DCC) or similar tertiary alkyl chloride as the initiator, and $TiCl_4$ as the coinitiator in a 60/40 (v/v) hexane/methyl chloride cosolvent system were found to be living and to produce nearly monodisperse PIBs ($\overline{M}_w/\overline{M}_n$ = 1.1) with predictable molecular weights up to $\overline{M}_n$ = 110,000 g/mole. This system was used to synthesize a variety of well-defined structures, such as block copolymers [13-15] and multi-arm star-branched polymers [16], and it was subjected to detailed kinetic investigations [10]. However, the polymerizations were observed to be heterogeneous due to partial precipitation of the $TiCl_4$:pyridine complex. This prompted development of a new system which produced homogeneous polymerizations [12] based on DMP as externally added ED. It should be noted that the word "homogeneous" indicates solubility of the $TiCl_4$:DMP complex; however, onium salts due to proton scavenging are often still observed, depending on the prevailing protic impurity concentration. It is noteworthy that both the heterogeneous and homogeneous polymerization systems produced living cationic polymerizations with similar characteristics, i.e., the two complexing EDs functioned in the same manner regardless of solubility of the formed $TiCl_4$:ED complex. Kinetic results obtained with DMP [12] were essentially identical to, and thus validated, the results obtained earlier with pyridine.

During our search for EDs that produce soluble complexes in IB polymerizations conducted in mixed hydrocarbon/chlorinated hydrocarbon media, a family of amine-based EDs (Scheme 1), including octyl *p*-(dimethylamino)benzoate (ODAB), ethyl *p*-(dimethylamino)benzoate (EDAB), *N*,*N*-dimethyl-*m*-toluidine (DMMT), and quinoline, was discovered that not only produced homogeneous reactions, but colored ones as well. In this paper we show how these EDs can be used as colorimetric indicators of exhaustive proton scavenging, and thereby confirm the existence of appropriate conditions for living carbocationic polymerization.

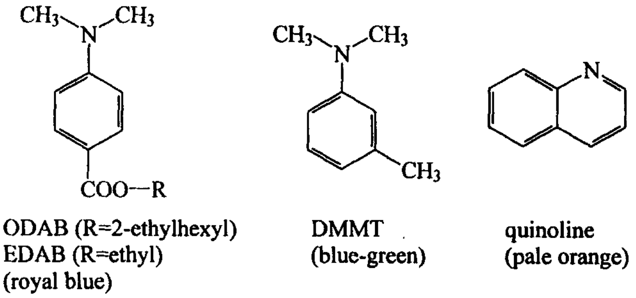
EXPERIMENTAL

Materials

2-Ethylhexyl *p*-(dimethylamino)benzoate (ODAB), ethyl *p*-(dimethylamino)benzoate (EDAB), and *N*,*N*-dimethyl-*m*-toluidine (DMMT) were used as received from First Chemical Co., Pascagoula, MS. Quinoline was used as received from Aldrich Chemical Co. The preparation and purity of all other materials have been previously reported [10].

Procedures

Polymerizations were carried out in a glove box under dry nitrogen. Specific reaction conditions are listed in the figure captions and tables. A representative procedure used to construct a single first-order plot for a polymerization conducted



SCHEME 1. Various tertiary amines used as electron donors in living isobutylene polymerization. Color refers to complex with $TiCl_4$.

at −80°C was as follows: 600 mL hexane, 400 mL methyl chloride, 1.09 mole (86 mL) IB, 1.35 × 10^{-3} mole (0.387 g) *t*-Bu-*m*-DCC, and 2 × 10^{-3} mole (0.556 mL) ODAB were added sequentially to a chilled 2000 mL three-necked round-bottomed flask equipped with a mechanical stirrer. Methyl chloride and IB were condensed into chilled graduated cylinders before addition to the flask. The mixture was stirred 0.5 hour; then 50 mL portions were transferred to 25 × 200 mm chilled culture tubes via a 50-mL volumetric pipette, and the tubes were capped with Teflon-lined screw caps. With vigorous shaking, 1.35 × 10^{-3} mol (0.148 mL) $TiCl_4$ (not chilled) was injected using a Hamilton CR-700 constant rate syringe into each culture tube to commence polymerization. Polymerization was terminated by the injection of 10 mL of pre-chilled methanol.

The terminated polymer solutions were removed from the dry box and immediately precipitated into approximately 100 mL methanol contained in pre-weighed 8 oz glass jars. The methanol was allowed to evaporate into the atmosphere, and the remaining precipitate was washed three times by pouring approximately 100 mL methanol into the jars, swirling the solution, and then decanting off the methanol. The beakers containing the polymer were then placed in a vacuum oven at 50°C until a constant weight was obtained. The fractional yield (Y) of polymer was determined gravimetrically, and the quantity $[M]_0/[M]$ was calculated as $1/(1 - Y)$.

RESULTS AND DISCUSSION

The kinetics of the living polymerization of isobutylene, initiated by *t*-Bu-*m*-DCC/$TiCl_4$ in hexane/methyl chloride (60/40 v/v) cosolvents and utilizing a series of amine-based EDs which produce colored $TiCl_4$:ED complexes, were determined by gravimetrically monitoring yield as a function of reaction time. The monomer (1M) and polymerization volume (50 mL) were held constant in all cases, and $TiCl_4$ was always the final component to be added. It should be noted that, in direct contrast to the previously reported pyridine-based system, the present EDs formed soluble complexes with $TiCl_4$; therefore, the polymerization mixtures were essentially homogeneous with respect to all components.

The data were interpreted in terms of the kinetic rate law for a chain polymerization in which the number of growing species is a constant:

$$r_p = -\frac{d[M]}{dt} = k_p[R^+][M] = k_{app}[M] \tag{1}$$

Here, r_p is the rate of polymerization, k_p is the second-order rate constant for propagation, $[R^+]$ is the concentration of instantaneously actively growing species (constant), k_{app} is the apparent first-order rate constant for propagation, and [M] is the concentration of monomer. First-order kinetic plots, $\ln([M]_0/[M])$ vs time (linearity = no termination), and plots of $\overline{M}_n$ vs conversion (linearity = no chain transfer) were utilized to demonstrate livingness. Living polymerization was observed and will be demonstrated for all of the colorimetric EDs; however, due to length considerations, only ODAB, which is representative, will be discussed in detail.

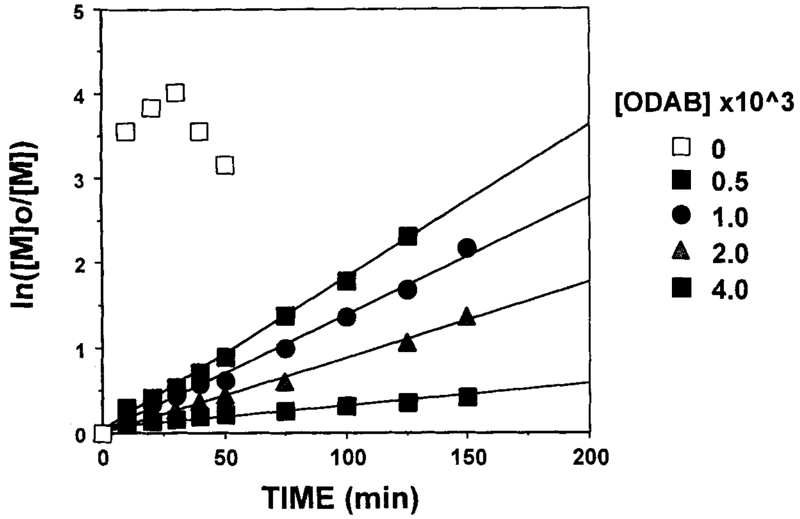


FIG. 1. Effect of ODAB concentration on the rate of IB polymerization at −70°C. $[IB]_0$ = 1 M; $[t\text{-bu-}m\text{-DCC}]_0 = 1.0 \times 10^{-3}$ M; $[TiCl_4]_0 = 2 \times 10^{-2}$ M; hexane/MeCl = 60/40 (v/v).

Effect of ODAB on Rate of Polymerization

The effect of the concentration of ODAB on the rate of polymerization at −70°C was determined by measuring the first-order kinetic behavior of the polymerizations conducted using various ODAB concentrations while holding $[IB]_0$, $[t\text{-Bu-}m\text{-DCC}]_0$, and $[TiCl_4]_0$ constant at 1.0, 1×10^{-3}, and 2×10^{-2} M, respectively. The first-order kinetic plots ($\ln([M]_0/[M])$ vs time) for the resulting polymerizations are shown in Fig. 1, and the k_{app}s extracted from the slopes of the lines are listed in Table 1. The data demonstrate that the addition of ODAB caused a significant

TABLE 1. Color of Reaction Medium and Apparent Rate Constant for Isobutylene Polymerizations Initiated by $TiCl_4$ in the Presence of ODAB[a]

$[t\text{-bu-}m\text{-DCC}]_0$ (M) × 10^3	[ODAB] (M) × 10^3	Color (Blue)	$[TiCl_4]_0$ (M) × 10^2	k_{app} (s^{-1}) × 10^4
1	0.5	No	2	3.0
	1	No		2.3
	2	Yes		1.5
	4	Yes		0.42
2.5	1	No	5	12
	2	Yes		7.3
	5	Yes		4.0

[a] [IB] = 1 M; hexane/MeCl 60/40 (v/v); −70°C.

reduction in the rate of polymerization (filled symbols) as compared to a control polymerization in the absence of ODAB (hollow squares). This reduction in the rate is primarily due to the elimination of initiation by protic impurities (HA) which, when operative, results in very fast and uncontrolled polymerizations. The slopes of the lines in Fig. 1 also show that an increase in the concentration of electron donor caused a simultaneous decrease in the rate of polymerization. Similar behavior has been previously reported [10, 12], and it reflects a second cause for the reduction in rate compared to the control polymerization. Namely, upon elimination of protic initiation, further reductions in rate occur as a result of complexation of the Lewis acid by the ED; thus, a fraction of the overall $TiCl_4$ concentration is rendered unavailable for coinitiation of the polymerization due to formation of the complex. Since the concentration of uncomplexed $TiCl_4$ has a very strong influence on the rate of polymerization, with a kinetic order of around 2 for polymerizations in which $TiCl_4$:ED is on the order of 10:1 [10, 12], even small changes in its concentration result in a pronounced effect on the rate of polymerization as shown in Fig. 1.

The linearity of the plots in Fig. 1 demonstrates that essentially no termination occurred within the studied lifetimes of the polymerizations. To also establish the absence of chain transfer, and thus provide evidence for livingness of the polymerizations, $\overline{M}_n$ vs conversion plots were constructed for these same polymerizations, and ^{1}H-NMR analysis was performed on a low molecular weight sample ($\overline{M}_n$ = 4800 g/mole) to establish the absence of unsaturation at the chain ends. As shown in Fig. 2, it is clear that no chain transfer occurred for any of the polymerizations in which [ODAB] > 1 × 10^{-3} M, as evidenced by the linearity of the plots obtained and their excellent agreement with the theoretical line. Likewise, as shown in Fig. 3, ^{1}H-NMR analysis of the $\overline{M}_n$ = 4800 g/mole sample, produced using [ODAB] = 2.6 × 10^{-3} M, failed to reveal any peaks in the 4.0–7.0 ppm range, indicating

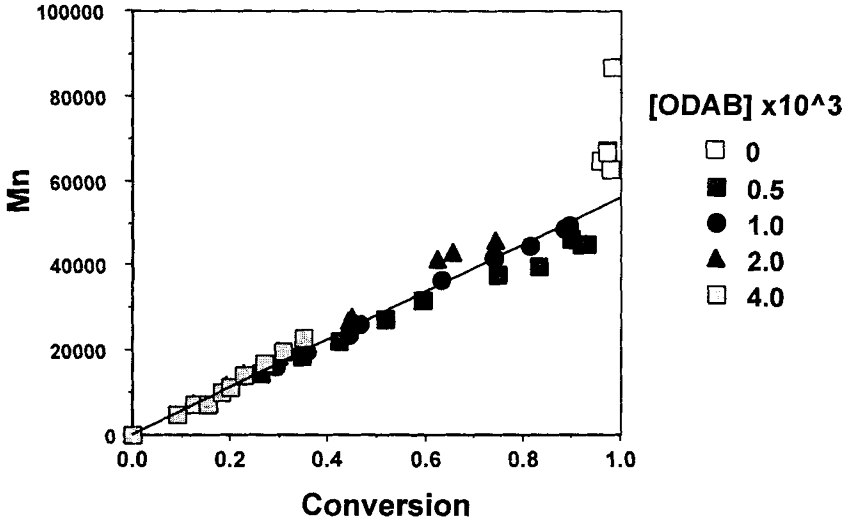


FIG. 2. $\overline{M}_n$ vs conversion plots for IB polymerizations at −70°C with varying ODAB concentrations. Line is theoretical. $[IB]_0$ = 1 M; $[t\text{-bu-}m\text{-DCC}]_0$ = 1.0 × 10^{-3} M; $[TiCl_4]_0$ = 2 × 10^{-2} M; hexane/MeCl = 60/40 (v/v).

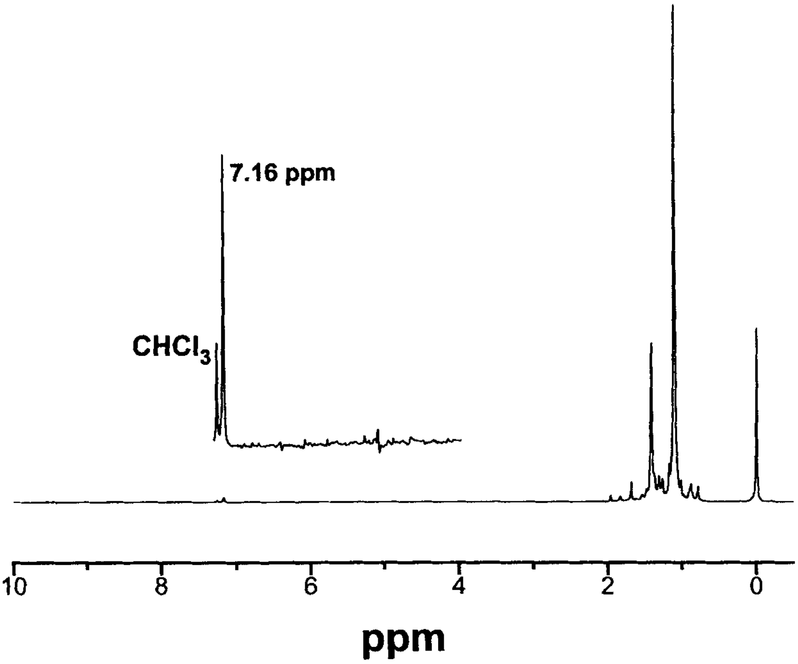


FIG. 3. ^{1}H-NMR spectrum of polyisobutylene with $\overline{M}_n$ = 4800 g/mole. Expanded region shows aromatic initiator resonance at 7.16 ppm, but no olefinic resonances in the range 4.5–5.3 ppm that would result from chain transfer reactions. $[IB]_0$ = 1 M; $[t\text{-bu-}m\text{-DCC}]_0 = 1.2 \times 10^{-2}$ M; [ODAB] = 2.6×10^{-3} M; $[TiCl_4]_0 = 2.4 \times 10^{-1}$ M; hexane/MeCl = 60/40 (v/v).

the absence of unsaturated end groups. It was observed however, that for the polymerization with [ODAB] = 0.5×10^{-3} M, the experimentally determined number-average molecular weights were lower than predicted by the theoretical line (Fig. 2), particularly at high monomer conversions. This was attributed to initiation by protic impurities, in addition to initiation due to the purposefully added initiator *t*-Bu-*m*-DCC. This resulted in a higher number of initiating species and thus an overall molecular weight lower than predicted. In addition, the formed polymers were observed to have a bimodal distribution due to the two different types of initiating species as will be discussed in the following section.

Demonstration of Colorimetric Indication of Protic Impurity Removal

For the polymerizations described in the previous section, it is significant that all polymerizations carried out at [ODAB] greater than 1×10^{-3} M were intensely colored (brilliant royal blue) whereas those polymerizations carried out at [ODAB] $\leq 1 \times 10^{-3}$ M were colorless. The color observed in the polymerizations at the higher ODAB concentrations was attributed to a soluble $TiCl_4$:ODAB complex. Two possible explanations initially presented themselves for the absence of color at low [ODAB]. Most likely, the absence of color indicated decomposition of the complex by protic impurities (HA) resulting in the formation of onium salts. Thus, the onset of persistent color indicated that the [ODAB] had exceeded that of protic impurities, i.e., at these higher concentrations there was sufficient ODAB to scavenge all HA and provide a $TiCl_4$:ODAB complex yielding a colored polymerization solution. This conclusion was even further supported by the observations at low [ODAB] of 1) a faint color upon $TiCl_4$ addition which almost immediately dissipated, and 2) the appearance of a slight precipitate that very much resembled the onium salts which have been observed to precipitate out of pyridine- or DMP-containing polymerization mixtures at the same temperature. It remained a possibility, however, that since [HA] ≅ chain end concentration ([CE]), the transition from colorless to colored solutions as the [ODAB] was increased could coincide with [ODAB] = [CE] rather than [ODAB] = [HA]. Thus, a new series of polymerizations was carried out in which first-order kinetics were measured for IB polymerizations at −70°C using various ODAB concentrations while holding $[IB]_0$, $[t\text{-Bu-}m\text{-DCC}]_0$, and $[TiCl_4]_0$ constant at 1.0, 2.5×10^{-3}, and 5×10^{-2} M, respectively, i.e., conditions yielding [CE] five times greater than [HA].

First-order plots constructed for the resulting polymerizations were linear and passed through the origin, and the resulting k_{app}s are listed in Table 1. $\overline{M}_n$ vs conversion plots constructed from the same polymerizations were linear and all fell on the theoretical line, demonstrating that in fact all of the polymerizations were living. As shown by the k_{app}s listed in Table 1, it was observed that this series of experiments resulted in the same lowering of rate with increasing [ODAB]. However, of greatest interest in Table 1 is the fact that the color change again occurred at [ODAB] $> 1 \times 10^{-3}$ M. This fact confirms that the onset of color corresponds to ODAB concentrations which exceed [HA] and provides corroboration of the proposed mechanism in which the dominant role of the ED in $TiCl_4$-based polymerization systems is to remove protic impurities from the system.

To further corroborate the proton scavenging mechanism, a comparison of GPC traces for the PIBs obtained in both of the previously described series of polymerizations was performed. Figure 4 shows representative GPC curves (solid

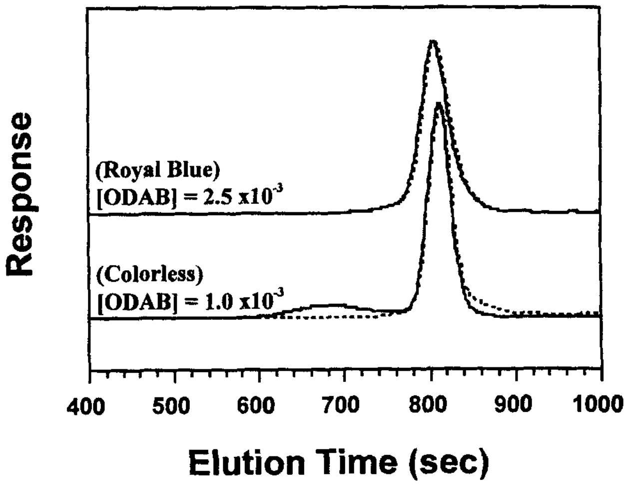


FIG. 4. GPC traces demonstrating effect of [ODAB] on MWD at −70°C. Dashed lines = UV detector response; solid lines = RI detector response. $[IB]_0$ = 1 M; $[t\text{-bu-}m\text{-DCC}]_0 = 1.0 \times 10^{-3}$ M; $[TiCl_4]_0 = 2 \times 10^{-2}$ M; hexane/MeCl = 60/40 (v/v).

lines = RI; dashed lines = UV) for PIBs produced with [ODAB] > [HA] and [ODAB] < [HA]. Note that the polymerization at the lower ODAB concentration, which was colorless, yielded two peaks using an RI detector but only one using a UV detector. The broad, high molecular weight peak (left-hand peak), which was observed solely in the RI, is due to initiation by protic impurities (i.e., water). Since these PIBs were initiated by protons, they have no chromophore in their structure and do not show up in the UV trace. In contrast, the narrow, lower molecular weight peak, which is due to initiation by the purposefully added initiator (*t*-Bu-*m*-DCC), was observed using either detector because the aromatic initiator residue serves as a UV chromophore. Of greatest significance in Fig. 4, however, is the fact that the peak due to HA initiation was observed to disappear for the polymerizations in which [ODAB] > 1×10^{-3} M. This threshold of [ODAB] at which HA initiation was eliminated is coincident with the observed onset of color in the polymerizations, thus demonstrating that ODAB indeed serves to colorimetrically indicate exhaustive proton scavenging in the polymerizations.

Demonstration of Living Polymerization and Comparison of Colorimetric EDs

The effect of the colorimetric EDs on the polymerization of IB at −70°C was determined by measuring the first-order kinetic behavior of polymerizations conducted in the presence of the various EDs while holding $[IB]_0$, $[t\text{-Bu-}m\text{-DCC}]_0$, $[TiCl_4]_0$, and [ED] constant at 1.0, 1×10^{-3}, 2×10^{-2}, and 2.5×10^{-3} M, respectively. A colored polymerization medium was obtained for every electron donor (ODAB, EDAB = brilliant royal blue; DMMT = blue-green; quinoline = orange). It is noteworthy that a very slight precipitate was observed using ODAB, EDAB, and quinoline, which was attributed to onium salts which are known to be insoluble in the polymerization medium. However, while colored polymerizations were obtained using DMMT, a significant amount of precipitate was observed, suggesting that its complex is not fully soluble. First-order kinetic plots for each of the EDs under representative polymerization conditions are shown in Fig. 5. It may be observed that all four EDs produced linear plots that passed through the origin, thereby demonstrating the absence of termination within the lifetimes of the polymerizations. It is also apparent that essentially the same rate was obtained for the polymerizations utilizing ODAB and EDAB, while different rates were obtained for the polymerizations utilizing DMMT and quinoline. The observation of different rates must reflect differences in the position of the equilibrium between the free Lewis acid and ED and the complex formed between them.

It is predictable that ODAB and EDAB, whose structures differ only by the alkoxy group of their ester functionalities, would act essentially identically as observed. Furthermore, since both of these EDs contain two potential sites for complexation with $TiCl_4$, it is not surprising that they were the most efficient depressors of the polymerization rate, although stoichiometries of the various complexes were not measured. DMMT and quinoline, by comparison, have only one site for complexation, and the observed polymerization rates were higher. It is risky to speculate as to the cause for a slightly higher rate with DMMT compared to quinoline, since the former does not produce a fully soluble complex.

Figure 6 shows $\overline{M}_n$ vs conversion plots which resulted from the same polymerizations whose kinetic runs were plotted in Fig. 5 (all EDs in the colored concentra-

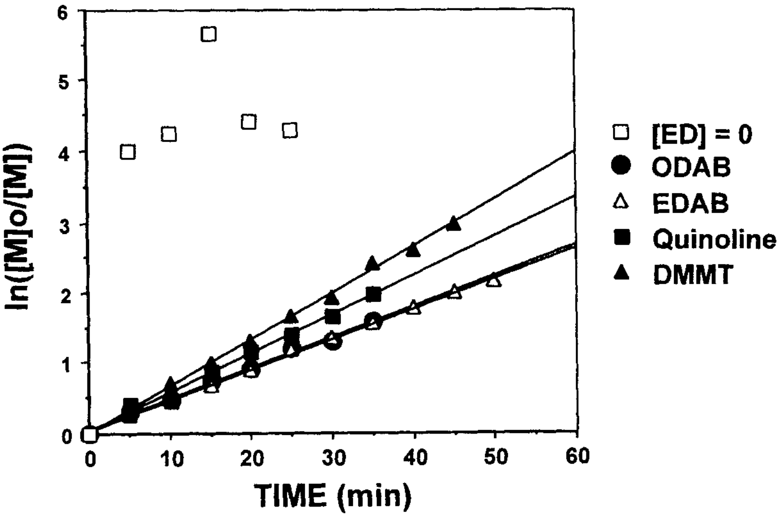


FIG. 5. Effect of various EDs on the rate of IB polymerization at −70°C. $[IB]_0$ = 1 M; $[t\text{-bu-}m\text{-DCC}]_0 = 2.5 \times 10^{-3}$ M; $[ED] = 2.5 \times 10^{-3}$ M; $[TiCl_4]_0 = 5 \times 10^{-2}$ M; hexane/MeCl = 60/40 (v/v).

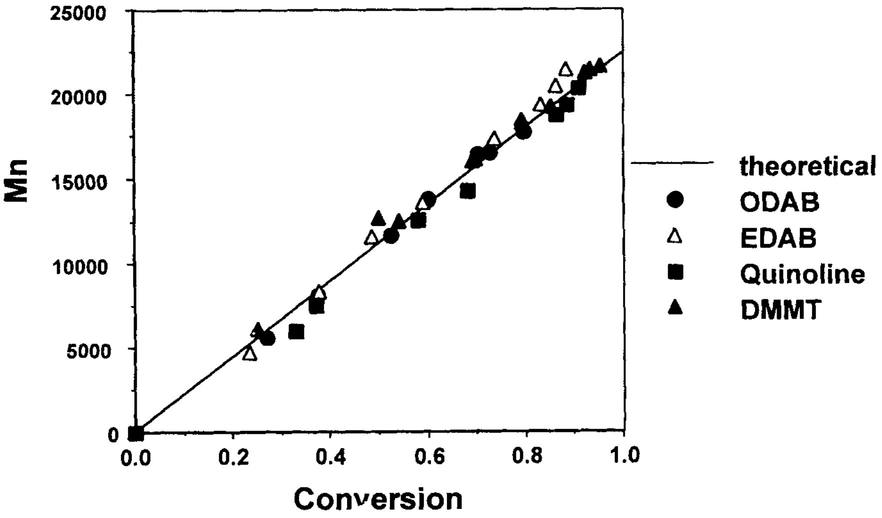


FIG. 6. $\overline{M}_n$ vs conversion plots for IB polymerizations at −70°C. Line is theoretical. $[IB]_0$ = 1 M; $[t\text{-bu-}m\text{-DCC}]_0 = 2.5 \times 10^{-3}$ M; $[ED] = 2.5 \times 10^{-3}$ M; $[TiCl_4]_0 = 5 \times 10^{-2}$ M; hexane/MeCl = 60/40 (v/v).

tion regime). All of the plots were observed to be linear and to fall on the theoretical line, demonstrating the absence of chain transfer in the polymerizations. Representative GPC traces for the formed PIBs are shown in Fig. 7 (solid lines). Also shown is a representative GPC curve for a colorless polymerization (ODAB = ED) (dashed line), which clearly shows high molecular weight PIB produced by protic initiation. It is apparent that all four EDs, when used at concentrations > [HA], yielded living polymerizations which produced narrow MWD PIBs without detectable fractions due to protic initiation.

CONCLUSIONS

The polymerization of isobutylene initiated by the *t*-Bu-*m*-DCC/$TiCl_4$ system in hexane/methyl chloride (60/40 v/v) cosolvents and in the presence of a tertiary amine-type ED selected from the group ODAB, EDAB, DMMT, and quinoline, was investigated. It was found that the ED caused a retardation of the rate of polymerization, and if used in sufficient concentration, provided living polymerizations yielding narrow molecular weight polymers with theoretical molecular weights. Furthermore, polymerizations changed from colorless to brightly colored when the concentration of the ED exceeded about 1×10^{-3} M, which is believed to be the approximate concentration of protic impurities (i.e., water) in the system. It was proposed that the color is due to a $TiCl_4$:tertiary amine complex that can persist only after all protic impurities have been trapped as ammonium salts. GPC chromatograms demonstrated that elimination of PIB chains initiated by protic impurities coincided with the color change. These results support a mechanism in which the major role of the tertiary amine-type ED in $TiCl_4$-coinitiated systems is to remove

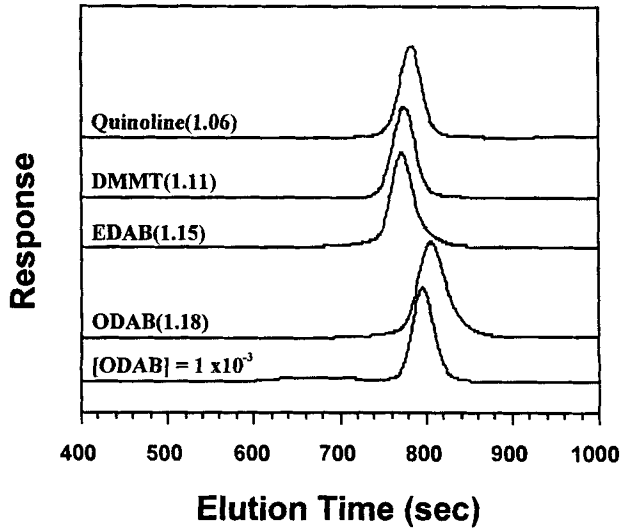


FIG. 7. GPC traces demonstrating effect of [ED] on MWD at −70°C. Dashed lines = UV, solid lines = RI. $[IB]_0$ = 1 M; [*t*-bu-*m*-DCC]$_0$ = 2.5×10^{-3} M; [ED] = 2.5×10^{-3} M; $[TiCl_4]_0$ = 5×10^{-2} M; hexane/MeCl = 60/40 (v/v).

protic impurities from the system; no evidence was observed that tended to support a mechanism involving carbocation stabilization by the formed complexes. The colored complexes described herein represent a useful technological tool for prediction and confirmation of the attainment of conditions conducive to living cationic polymerization.

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REFERENCES

[1] M. Szwarc, *Ionic Polymerization Fundamentals*, Hanser/Gardner Publications, Cincinnati, OH, 1996.

[2] R. Faust and J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem., A25*, 1847 (1987).

[3] G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Macromol. Chem., Macromol. Symp., 13/14*, 473 (1988).

[4] G. Kaszas, J. E. Puskas, and J. P. Kennedy, *Polym. Bull., 18*, 123 (1988).

[5] M. K. Mishra and J. P. Kennedy, *J. Macromol. Sci.—Chem., A24*(8), 933 (1987).

[6] G. Kaszas, J. Puskas, C. C. Chen, and J. P. Kennedy, *Polym. Bull., 20*, 413 (1988).

[7] G. Kaszas, J. E. Puskas, C. C. Chen, and J. P. Kennedy, *Macromolecules, 33*, 3909 (1990).

[8] M. Gyor, H. C. Wang, and R. Faust, *J. Macromol. Sci.—Pure Appl. Chem., A29*, 639 (1992).

[9] R. F. Storey and Y. Lee, *Ibid., A29*(11), 1017 (1992).

[10] R. F. Storey, B. J. Chisholm, and L. B. Brister, *Macromolecules, 28*(12), 4055 (1995).

[11] R. F. Storey and K. R. Choate Jr., *ACS Div. Polym. Chem., Polym. Prepr., 35*(2), 506, (1994).

[12] R. F. Storey and K. R. Choate Jr., "Kinetic Investigation of the Living Cationic Polymerization of Isobutylene using a *t*-Bu-*m*-DCC/$TiCl_4$/2,4-DMP Initiating System," *Macromolecules*, Submitted for Publication.

[13] R. F. Storey, B. J. Chisholm, and Y. Lee, *Polymer, 34*(20), 4330 (1993).

[14] R. F. Storey, B. J. Chisholm, and K. R. Choate, *J. Macromol. Sci.—Pure Appl Chem., A31*(8), 969 (1994).

[15] R. F. Storey, B. J. Chisholm, and M. A. Masse, *Polymer, 37*, 2925 (1996).

[16] R. F. Storey, K. A. Shoemake, and B. J. Chisholm, *J. Polym. Sci., Part A: Polym. Chem., 34*, 2003 (1996).

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