Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Electron-Pair Donors in Carbocationic Polymerization. III. Carbocation Stabilization by External Electron-Pair Donors in Isobutylene Polymerization

Gabor Kaszas[a]; Judit E. Puskas[a]; Joseph P. Kennedy[a]; C. Charles Chen[a]
[a] Institute of Polymer Research The University of Akron, Akron, Ohio

To cite this Article Kaszas, Gabor , Puskas, Judit E. , Kennedy, Joseph P. and Chen, C. Charles(1989) 'Electron-Pair Donors in Carbocationic Polymerization. III. Carbocation Stabilization by External Electron-Pair Donors in Isobutylene Polymerization', Journal of Macromolecular Science, Part A, 26: 8, 1099 — 1114

To link to this Article: DOI: 10.1080/00222338908052037

URL: http://dx.doi.org/10.1080/00222338908052037

J. MACROMOL. SCI.–CHEM., A26(8), pp. 1099-1114 (1989)

ELECTRON-PAIR DONORS IN CARBOCATIONIC POLYMERIZATION. III. CARBOCATION STABILIZATION BY EXTERNAL ELECTRON-PAIR DONORS IN ISOBUTYLENE POLYMERIZATION

GABOR KASZAS, JUDIT E. PUSKAS, JOSEPH P. KENNEDY,*
and C. CHARLES CHEN

Institute of Polymer Research
The University of Akron
Akron, Ohio 44325-3909

ABSTRACT

The polymerization of isobutylene (IB) initiated by a variety of tertiary chloride/$TiCl_4$ or BCl_3 systems can be very beneficially influenced by deliberately added electron-pair donors (ED's). ED's whose Gutmann's donor number is larger than ~26, e.g., dimethylsulfoxide (DMSO) and dimethylacetamide (DMA), are most suitable to mediate numerous most desirable effects. Thus, in the presence of DMSO or DMA: (1) quasi-living polymerizations initiated by cumyl chloride (CumCl)/$TiCl_4$ or 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ give rise to very narrow molecular weight distribution (MWD) polyisobutylene (PIB) ($\bar{M}_w/\bar{M}_n$ = 1.1-1.2); (2) the CumCl/BCl_3/IB inifer system becomes living and yields PIB with very narrow MWD; (3) the polymerization-inactive TMPCl/BCl_3 system becomes active and induces living IB polymerization to narrow-MWD product; (4) indanyl end-group formation, which may occur in the CumCl/BCl_3 or *p*-dicumyl chloride/BCl_3, inifer systems, is eliminated. The effect of reaction conditions, e.g., polarity and $[TiCl_4]/([CumCl] + [DMSO])$ ratio, on these polymerizations has been investigated. All the observations and effects can be explained by a reduction of cationicity of the polymerization-active species by ED's.

INTRODUCTION

Parts I and II of this series [1, 2] concerned the discovery that *in situ* electron-pair donors (ED's) arising in tertiary ester /$TiCl_4$ and tertiary ether/$TiCl_4$-initiated IB polymerizations mediate living polymerizations and give rise to narrow-MWD polyisobutylene (PIB). A preliminary series of experiments [2] has shown that not only *in situ* ED's but also certain external ED's added to a quasiliving CumCl/$TiCl_4$/IB system elicit a profound MWD-narrowing effect. This effect was attributed to carbocation stabilization by ED complexes. Prompted by these observations and conclusions, we decided to further investigate the effect of deliberately added ED's on cationic polymerization in general and on IB polymerizations in particular. An objective of the present report is to introduce Gutmann's donor scale [3] as a guide for the selection of carbocation-stabilizing ED's and, specifically, to show that, by the use of properly chosen strong Gutmann donors, highly efficient living polymerizations and products of very narrow MWD can be obtained not only with tertiary chloride/$TiCl_4$ systems but even with the tertiary chloride/BCl_3 system. This report also demonstrates that, in the presence of suitable ED's, undesirable side reactions, such as uncontrolled initiation by protic impurities and intramolecular alkylation leading to indanyl structures, can be suppressed or totally eliminated.

EXPERIMENTAL

Materials

The syntheses of 2-chloro-2-phenylpropane (cumyl chloride, CumCl), 1,4-(2-chloro-2-propyl)benzene (dicumyl chloride, DiCumCl), 2,4,4-trimethyl-2-acetyl-pentane (TMPOAc), and 2-chloro-2,4,4-trimethylpentane (TMPCl) have been described previously [4-7]. The source and purity of IB, CH_3Cl, n-C_6H_{14}, $TiCl_4$, and BCl_3 have also been described previously [7, 8]. Ethyl acetate (EtOAc) was freshly distilled over phosphorus pentoxide under dry nitrogen. Anhydrous dimethylsulfoxide (DMSO), dimethylacetamide (DMA), and methanol (Aldrich) were used as received.

Procedures

Polymerizations were carried out in a dry box under dry nitrogen in large test tubes by the IMA technique or in round-bottom flasks as reported [7, 8].

Detailed concentrations and conditions are given in the text, and in table or figure captions. Initiator/Lewis acid ratios (I/LA) were 1/16, unless noted otherwise.

Molecular weights of PIB's were determined by GPC as reported previously [8]. ^{1}H-NMR spectra were obtained with a Varian T-60 spectrometer using carbon tetrachloride solutions and TMS standards.

RESULTS AND DISCUSSION

Use of Gutmann's Donor Scale for the Selection of ED's

A thorough search through the scientific and patent literature has shown that a variety of nucleophiles, such as acetone [9] and nitrogen or oxygen containing compounds [10-12], have been claimed to produce PIB of higher molecular weight and/or relatively narrow MWD; however, the selection of these chemicals was purely intuitive, and the effects have not been discussed. Recently, Higashimura et al. [13] used various oxygen-containing compounds (i.e., ethyl acetate, dioxane, tetrahydrofuran, diethyl ether) to effect living polymerization of vinyl ethers and related monomers and concluded that the function of these nucleophiles was to stabilize the carbocations. We have found recently that CumCl/$TiCl_4$-initiated quasiliving IB polymerizations in the presence of EtOAc lead to products of very narrow MWD and, similarly to Higashimura et al., have concluded that carbocation stabilization was responsible for this effect (see Parts I and II of this series [1, 2]).

After a thorough literature search into carbocation/ED interactions and some scouting experiments, we decided to select the ED's for our polymerization systems by Gutmann's donor scale [3]. Gutmann expressed the electron donating ability of chemicals by empirical donor numbers (DN = the molar enthalpy of the reaction between a donor and a 1-mmol/L $SbCl_5$ reference acceptor solution in dichloroethane). The higher the DN, the stronger the electron-pair donating tendency ("donicity") of the chemical. Gutmann's DN's have previously been used to interpret ion-solvent interactions in carbocationic polymerizations [14].

According to the data in Table 1, the DN's of ED's used to date in cationic polymerizations [9-13] are in the range 12-20. In line with Gutmann's views [3], we have speculated that ED's whose donicity is close to or larger than that of Cl^- will be able to compete for the polymerization-active carbocation and to modulate its cationicity. Thus, we have selected the strong Gutmann ED's DMA and DMSO for further investigations.

Figure 1 shows representative GPC traces of PIB's obtained by the TMPCl/

TABLE 1. Donor Numbers of Electron-Pair Donors [3]

Solvent	DN
Dioxane	11.8
Acetone	17.0
Ethyl acetate	17.1
Diethyl ether	19.2
Tetrahydrofuran	20.0
Cl^- (estimated)	26.0
Dimethylformamide	26.6
Dimethylacetamide	27.8
Dimethylsulfoxide	29.8

$TiCl_4$ initiating system in the absence of ED, and in the presence of a moderate (EtOAc) and a strong ED (DMSO). In the absence of an ED and in the presence of EtOAc, bimodal GPC traces were obtained. The broad peaks at higher molecular weights represent polymer formed by uncontrolled protic initiation. The extent of protic initiation, however, is suppressed in the presence of EtOAc. The MWD's obtained by controlled initiation (the sharp peaks in Fig. 1) in the absence and in the presence of EtOAc had $\bar{M}_w/\bar{M}_n$ 1.21 and 1.06, respectively (determined by peak deconvolution). Importantly, in the presence of DMSO, protic initiation was virtually absent and a product of very narrow MWD ($\bar{M}_w/\bar{M}_n$ 1.05) was obtained. Initiating efficiencies (I_{eff}) were ~100% throughout. Conversions were ~100% in the absence of ED, 44% in the presence of EtOAc, and 27% in the presence of DMSO. Obviously, increasing the DN decreases the polymerization rate and reduces the MWD close to a Poisson distribution.

The exact nature of the carbocation modulating entity is obscure. Since the charges contain an excess of Friedel-Crafts acid and the nucleophilicity of the ED is certainly larger than that of isobutylene, the Friedel-Crafts acid is most likely complexed with the ED; however, the stoichiometry of this interaction is unknown (see also below). Evidently the empirical Gutmann donicity scale provides a satisfactory first approximation for the selection of carbocation-stabilizing ED's.

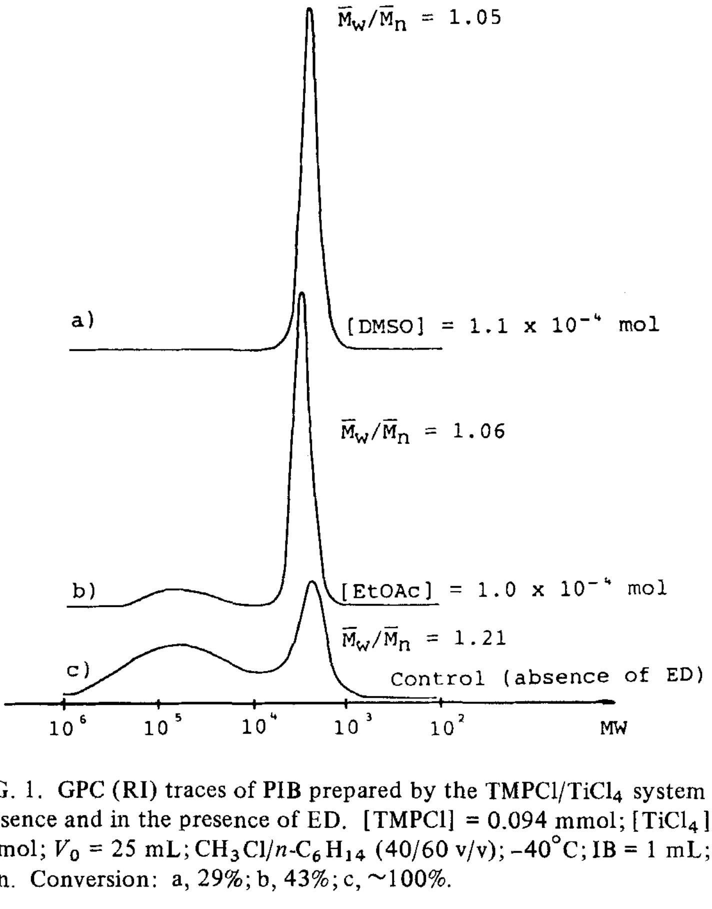


FIG. 1. GPC (RI) traces of PIB prepared by the TMPCl/$TiCl_4$ system in the absence and in the presence of ED. [TMPCl] = 0.094 mmol; [$TiCl_4$] = 1.5 mmol; V_0 = 25 mL; $CH_3Cl/n\text{-}C_6H_{14}$ (40/60 v/v); -40°C; IB = 1 mL; 30 min. Conversion: a, 29%; b, 43%; c, ~100%.

The Effect of Electron-Pair Donors on IB Polymerization Initiated by tertiary Chloride/$TiCl_4$ Systems

Narrow MWD by Living Polymerization in the Presence of Strong ED

Although IB polymerizations initiated by CumCl/$TiCl_4$ and TMPCl/$TiCl_4$ are quasiliving [5], the MWD's of the products are not narrow, and uncontrolled protic initiation is present at -40°C. Thus, it was of interest to investigate the effect of ED's on these systems. IB polymerizations were initiated by the quasiliving CumCl/$TiCl_4$ and TMPCl/$TiCl_4$ systems in the presence of the

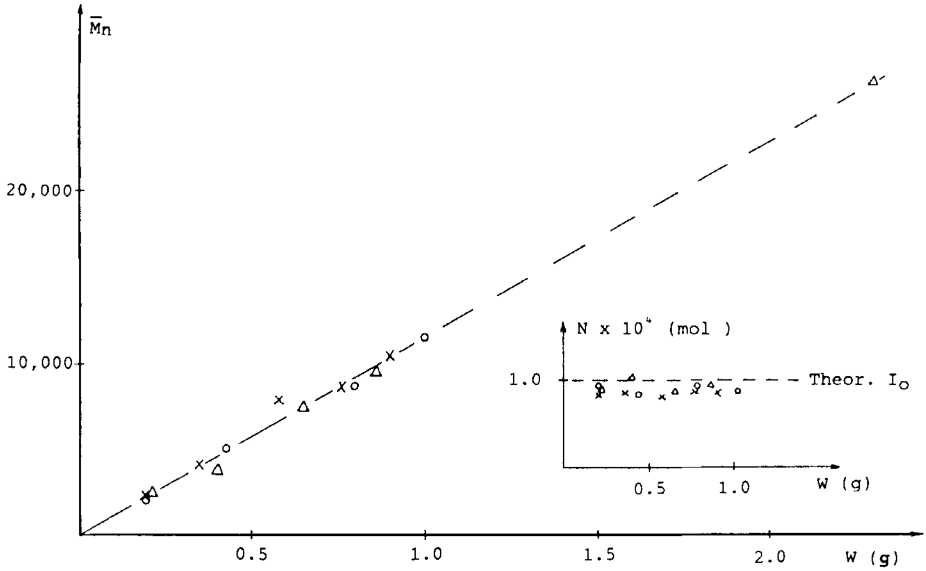


FIG. 2. Living IB polymerization by tertiary chloride/ED/$TiCl_4$ systems. (X) [TMPCl] = 0.094 mmol, [DMSO] = 0.1 mmol; (○) [CumCl] = 0.109 mmol, [DMSO] = 0.1 mmol; (△) [CumCl] = 0.109 mmol, [DMA] = 0.1 mmol; [$TiCl_4$] = 1.5 mmol; V_0 = 25 mL; CH_3Cl/n-C_6H_{14} (40/60 v/v); -40°C; IMA technique, 5 X (1 mL IB/30 min).

strong ED's DMSO and DMA. In this system the initiating TMP^+ mimicks the structure of the growing PIB^+ chains. Figure 2 shows representative data. The polymerizations were homogeneous on account of the mixed solvent employed. The linear $\bar{M}_n$ versus W plots starting at the origin, together with the horizontal N versus W plots, indicate living polymerizations for all three systems, i.e., TMPCl/$TiCl_4$/DMSO, CumCl/$TiCl_4$/DMSO, and CumCl/$TiCl_4$/DMA. The overall rates of polymerizations were slow by cationic standards (note the $\bar{M}_n$ of 26 200 and $\bar{M}_w/\bar{M}_n$ of 1.07 reached after 300 min with the latter system). According to routine ^{1}H-NMR analysis, the end structures were the anticipated and often characterized [4, 15-17] cumyl- and t-butyl head groups due to controlled living initiation by CumCl and TMPCl, respectively, and the tertiary chlorine tail group. Uncontrolled initiation by moisture was absent (monomodal GPC traces), initiator efficiencies were invariably ~100%, and the MWD's were very narrow ($\bar{M}_w/\bar{M}_n \approx 1.1$). The MWD-narrowing effect of ED's, i.e., leveling of reactivities and selective reduction of R_i in preference to R_p, has been discussed in Part II [2].

As usual, the polymerizations were started by adding the coinitiator ($TiCl_4$) solution to solvent-monomer-initiator-ED systems. Upon the addition of $TiCl_4$, a characteristic yellow precipitate (more so with DMSO than with DMA) formed. The formation of a similar yellow precipitate was also observed when ED and $TiCl_4$ were mixed in the absence of monomer and initiator. Evidently the $DMSO \cdot TiCl_4$ or $DMA \cdot TiCl_4$ complexes are only partially soluble in the relatively nonpolar medium used, so that the amount of ED remaining in the polymerization solution is less than charged ($[I]/[ED] = 1$). This means that a less than equimolar ED relative to the growing chains suffices for stabilizing the carbocations or that only a fraction of the propagating chains is active. A similar conclusion has been reached in regard to *in situ* ED systems as well (Part II [2]).

The Effect of the $[TiCl_4]/([I] + [ED])$ Ratio on the Rate

The effect of $TiCl_4$ concentration relative to that of the sum of the initiator and ED concentrations, $[TiCl_4]/([I] + [ED])$, on the rate of living IB polymerization has been investigated (I = CumCl, ED = DMSO). The $[TiCl_4]$ was varied while the sum of [CumCl] + [DMSO] was kept constant. Figure 3 shows the results and defines reaction conditions. Polymerization was absent up to $[TiCl_4]/([CumCl] + [DMSO]) = 2/(1 + 1)$ mole ratio. Increasing this ratio further increases the rate almost linearly with increasing $[TiCl_4]/([CumCl] + [DMSO])$, and the polymerizations consistently yield narrow-MWD PIB. The absence of polymerization at $[TiCl_4]/([CumCl] + [DMSO]) = 2/(1 + 1)$ indicates that 1 mol of DMSO is able to complex 2 mol of $TiCl_4$. Hence, under these conditions, excess $TiCl_4$ is not available to ionize CumCl and thus to initiate the polymerization (see Scheme I in Part II [2]). Consequently, the system most likely contains $DMSO \cdot 2TiCl_4$ together with some $DMSO \cdot TiCl_4$ and perhaps even some uncomplexed DMSO. The available data are insufficient to pinpoint which of these entities is responsible for carbocation stabilization. We speculate that uncomplexed DMSO, if present at all, would be too strongly nucleophilic and would inhibit carbocationic polymerization. Perhaps the reduced nucleophilicity of the complexes such as $DMSO \cdot 2TiCl_4$ and/or $DMSO \cdot TiCl_4$ may be just right for stabilizing the active species without completely suppressing its propagating ability. Research is continuing to clarify these matters.

The Effect of Medium Polarity on the Rate

It was of interest to investigate the effect of medium polarity, i.e., polar/nonpolar solvent composition, on the rate of living IB polymerization. The

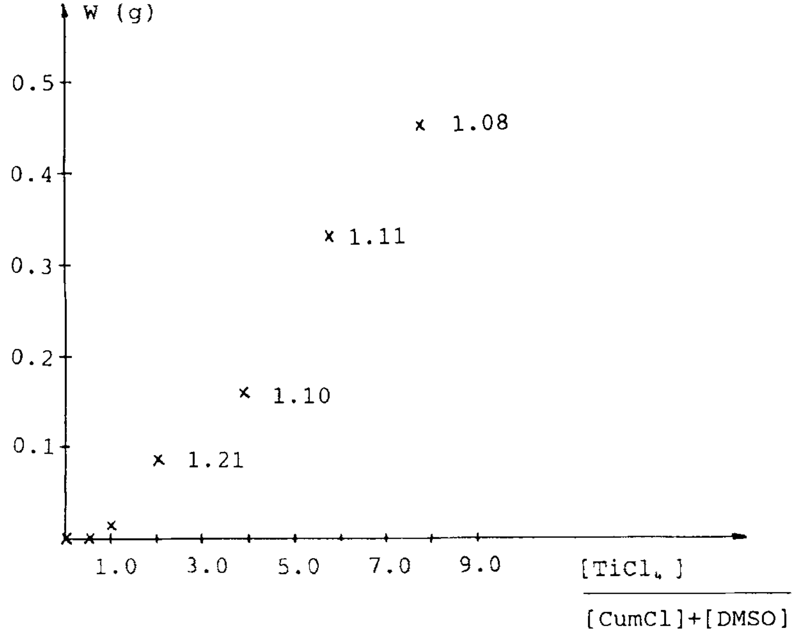


FIG. 3. Effect of the ratio $\frac{[\mathrm{TiCl_4}]}{[\mathrm{CumCl}] + [\mathrm{DMSO}]}$ on IB polymerization. Numbers indicate $\bar{M}_w/\bar{M}_n$ values. [CumCl] = 0.11 mmol; [DMSO] = 0.13 mmol; V_0 = 25 mL; $CH_3Cl/n\text{-}C_6H_{14}$ (40/60 v/v); -40°C; IB = 1 mL; 60 min.

results of a representative series of experiments are shown in Table 2. The rate increased with increasing medium polarity, which is characteristic of ionic reactions. The MWD's are only slightly broader in more polar medium, which suggests strong cation stabilization by $DMA\cdot nTiCl_4$ even in pure CH_3Cl.

Importantly, uncontrolled protic initiation was absent (narrow MWD) even in 100% CH_3Cl. In contrast, in the presence of relatively weak *in situ* ED's [2], i.e., with the tertiary ester/$TiCl_4$ or tertiary ether/$TiCl_4$ systems at higher than 60% CH_3Cl, uncontrolled (moisture) initiation is dominant, and PIB with broad MWD is obtained [8]. It is of import that, in the presence of strong ED's, narrow-MWD products with theoretical $\bar{M}_n$ (i.e., $\bar{M}_n = W(\mathrm{g})/I(\mathrm{mol})$) can be harvested even by using the relatively polar diluent CH_3Cl.

TABLE 2. Effect of Polarity on IB Polymerization by the CumCl/DMA/$TiCl_4$ System[a]

CH_3Cl vol%	n-C_6H_{14} vol%	W, g	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	I_{eff}, %
40	60	0.106	1 200	1.11	81
60	40	0.546	5 900	1.19	85
80	20	1.405	15 400	1.13	83
100	0	1.433	14 400	1.21	91

[a] [CumCl] = 0.109 mmol; [DMA] = 0.1 mmol; V_0 = 25 mL; [$TiCl_4$]/([CumCl] + [DMA]) = 8; IB = 2 mL; -40°C; 10 min.

The Effect of ED on IB Polymerizations Initiated by tertiary Chloride/BCl_3 Systems

After having demonstrated the effect of ED's on IB polymerizations initiated by tertiary chloride/$TiCl_4$ systems, we have extended our studies to those initiated by tertiary chloride/BCl_3. There are some significant differences in the polymerization characteristics between these two types of systems; for example, the latter is much less sensitive to initiation by protic impurities [7, 8]. The tertiary chloride/BCl_3/IB system has been the subject of extensive investigations. It was shown that aliphatic tertiary chlorides are *not* polymerization initiators in conjunction with BCl_3 in CH_3Cl diluent [18], while under the same conditions tertiary aralkyl chlorides, such as CumCl or DiCumCl [4, 15, 18-21], are most efficient, albeit nonliving, initiators. With the cumyl-type initiators ("inifers"), chain transfer to monomer was shown to be absent [4]. However, extensive chain transfer to inifer and some termination did occur, both of which gave initiation-inactive aliphatic tertiary chlorine end groups. The unusual effects observed with tertiary chloride/BCl_3 systems are due to the high acidity of BCl_3 combined with the low stability of the BCl_4^- counteranion [22].

A series of important observations and conclusions has been made in the course of the present investigations: (1) In the presence of DMSO, the typical inifer system CumCl/BCl_3 is modified to exhibit living character (i.e., to yield theoretical molecular weights) *and* narrow MWD product; (2) in the CumCl/BCl_3/IB/DMSO system, termination to tertiary chlorine becomes reversible so that (3) in the presence of strong ED's, even aliphatic tertiary

TABLE 3. Polymerization of IB by the CumCl/BCl_3/DMSO Initiating System[a]

W, g	$\bar{M}_n$ By GPC	$\bar{M}_n$ By ^{1}H NMR	$\bar{M}_w/\bar{M}_n$	I_{eff}, %
0.0506	350	420	1.43	99
0.0653	450	500	1.43	99
0.0815	590	610	1.42	97
0.1009	710	740	1.40	98
0.1191	820	810	1.38	99

[a] Control (BCl_3 + DMSO; absence of CumCl): no polymer. [CumCl] = 0.146 mmol; BCl_3/CumCl = 35; [DMSO] = 0.1 mmol; V_0 = 25 mL CH_3Cl; IMA technique, 5 × (0.5 mL IB/10 min); -40°C.

chloride/BCl_3 induces living polymerization; and (4) in the presence of DMSO or DMA, indanyl ring formation in the CumCl/BCl_3 and DiCumCl/BCl_3 systems is suppressed or completely eliminated. The experiments below serve to substantiate these statements.

The data collected in Table 3 substantiate the first point. In the absence of DMSO the nonliving CumCl/BCl_3 inifer system yields tertiary chlorine tail groups mainly by chain transfer to CumCl [21]. In the presence of DMSO, the same system yields living polymerization, i.e., essentially theoretical molecular weights with high efficiencies *and* narrow MWD's. In view of the very low $\bar{M}_n$ produced (in the 400-800 range), the narrowness of the MWD's is quite remarkable ($\bar{M}_w/\bar{M}_n \approx 1.4$). The ^{1}H-NMR spectrum of a representative sample is shown in Fig. 4. Due to the low $\bar{M}_n$, essentially all the protons can be assigned. The spectrum shows the Cum- head group and tertiary chlorine tail group expected to arise by controlled initiation followed by living propagation and reversible termination to tertiary chlorine. These facts in turn indicate reinitiation of dormant tertiary chlorines by BCl_3 in the presence of DMSO, i.e., bear out Point (2) above.

The latter conclusion leads to the important prediction that polymerization-inactive aliphatic tertiary chlorine/BCl_3 systems become active in the presence of ED's. To corroborate this prediction (see Point 3 above), experiments were carried out in which BCl_3 was added to various TMPCl/IB/ED combinations. TMPCl mimicks the tertiary chlorine terminus of PIB. Con-

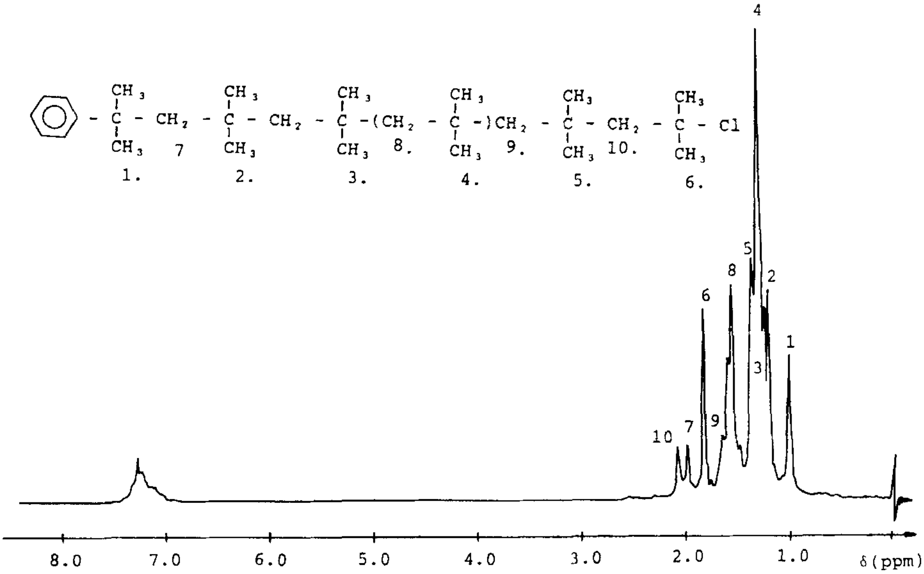


FIG. 4. ^{1}H-NMR spectrum of PIB prepared by the CumCl/DMSO/BCl_3 system ($\bar{M}_n$ = 500, see Table 3 for experimental details).

sequently, these experiments are model experiments for reversible termination. Table 4 shows experimental details and the results. Evidently living polymerization to narrow-MWD PIB occurred readily in the presence of the strong ED's DMSO and DMA.

^{1}H-NMR analysis of representative samples showed the expected structure, i.e., the *t*-butyl head group (from TMP) and the tertiary Cl tail group (see Fig. 5). In the control experiments (i.e., in the absence of TMPCl initiator) in the absence of ED, polymerization by protogenic impurities occurred, producing PIB of high MW and broad MWD, while polymerization was absent in the presence of DMSO. The weaker ED's, EtOAc and dioxane, were found to be inactive, i.e., in their presence only polymerization due to uncontrolled initiation was observed (see Table 4).

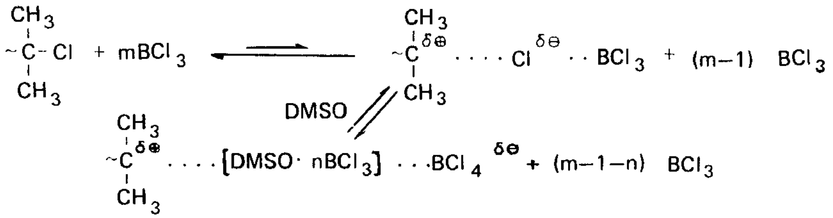
The polymerization-inducing or ionization-enhancing effect of strong ED's may be visualized by the following symbolism:

TABLE 4. Polymerization of IB by the TMPCl/ED/BCl_3/CH_3Cl System[a]

ED	Time, min	[TMPCl], mmol	Conversion, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	I_{eff}, %
DMA	30	0.29	8.0	380	1.66	100
DMSO	30	0.29	7.0	370	1.36	90
"	60	0.29	15.1	600	1.47	117
"	90	0.29	27.2	1270	1.35	102
"	120	0.29	38.7	1780	1.26	103
"	150	0.29	41.3	2080	1.26	93
EtOAc	30	0.29	2.3[b]	9700[b]	2.17	–
Dioxane	30	0.29	3.4[b]	9650[b]	2.26	–
Controls:						
–	30	0	5.0[b]	9900[b]	3.26	–
DMSO	30	0	0.0	No polymer		

[a] $[BCl_3]$ = 6.3 mmol; [DMSO] = 0.29 mmol; [DMA] = 0.3 mmol; [EtOAc] = 0.28 mmol; [dioxane] = 0.3 mmol; IB = 2 mL; V_0 = 25 mL; -40°C.

[b] Due to uncontrolled (moisture) initiation.



The aliphatic tertiary chloride is polymerization-inactive under conventional conditions because the equilibrium is strongly shifted to the left. However, in the presence of DMSO (rather than the DMSO·$nBCl_3$ complex), the cation may be stabilized by a species akin to that shown above. Strong ED's help to stabilize incipient carbocations arising from aliphatic tertiary chlorides, thus rendering them polymerization-active. Weak ED's may not be able to fulfill this function.

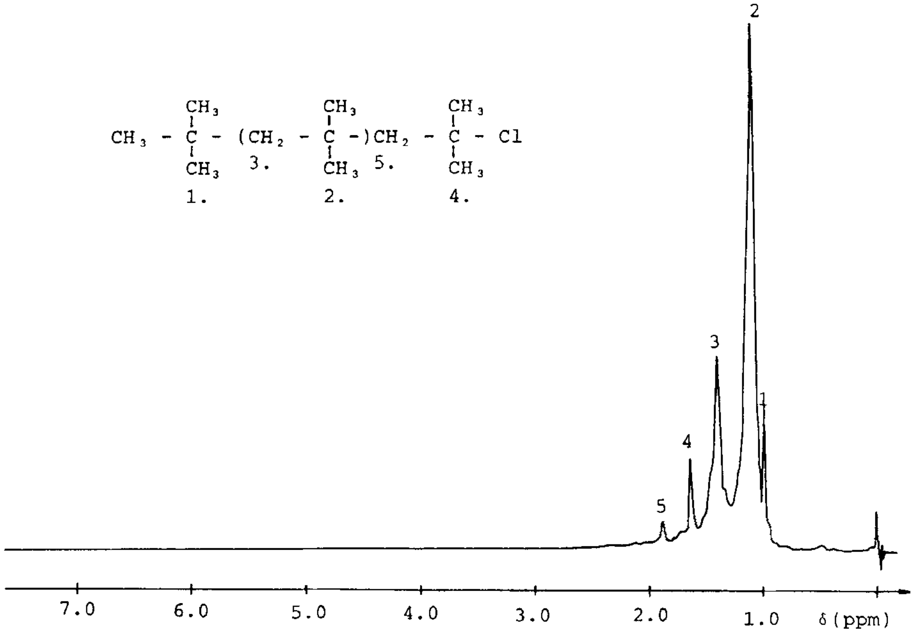
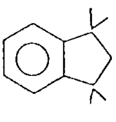
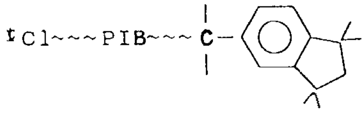


FIG. 5. ^{1}H-NMR spectrum of PIB prepared by the TMPCl/DMSO/BCl_3 system ($\bar{M}_n$ = 1270, see Table 4 for experimental details).

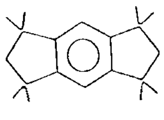
Cumyl-type initiators are prone to give indanyl Structures I (with CumCl) and II and III (with DiCumCl) by intramolecular self-alkylation [15] :



I



II



III

Structures I and III, which may arise in the CumCl/BCl_3 and DiCumCl/BCl_3 systems, respectively, reduce initiator efficiency but can be removed by washing the polymer. Structure II, however, cannot be removed just by washing and thus may prevent the production of telechelic ^{t}Cl-PIB-Cl^t with the theoretical end functionality of 2. To avoid this undesirable side reaction, the polymerization temperature and/or medium polarity must be lowered [15].

TABLE 5. The Effect of ED's on Indanyl Skeleton Formation in Select IB Polymerization Systems

DiCumCl, mmol	ED, mmol	BCl_3, mmol	IB, mmol	Solvent, mL	Temperature, °C	Conversion, % (time)	$\bar{M}_n$	I_{eff}, %	$\bar{M}_w/\bar{M}_n$	Undesirable structures, % II	Undesirable structures, % III	Ref.
5.0	DMSO, 10	100	200	CH_3Cl, 200	-40	~100 (120 min)	2570	97	1.14	5	0	This work
8.5	DMSO, 0.43	3.25	37	CH_3Cl, 25	-50	~100 (180 min)	2860	93	1.32	2	0	“
0.85	DMA, 0.43	3.25	37	CH_3Cl, 25	-50	79 (180 min)	2100	91	1.18	0	0	“
5.0	DMSO, 10	100	210	CH_3Cl, 200	-60	~100 (120 min)	2490	92	1.15	0	0	“
0.65	None	3.25	2.6	CH_3Cl_2, 50	-40	NA	NA	NA	NA	22.9	51.4	15
“	None	“	“	“ “	-60	NA	NA	NA	NA	22.2	20.1	15
“	None	“	“	“ “	-80	NA	NA	NA	NA	14.0	10.5	15

Against this background, a series of experiments was designed to study the effect of ED's on indanyl end-group formation in IB polymerization initiated by the CumCl/BCl_3 and DiCumCl/BCl_3 system (see Point 4 above). Table 5 shows the results obtained and conditions with the DiCumCl/BCl_3 system, together with some earlier data obtained in the absence of ED's. It is quite evident that considerable indanyl group formation has taken place in the absence of ED's. In contrast, in the presence of DMSO or DMA, this unacceptable side reaction is suppressed or eliminated, even at higher temperatures. Similarly, Table 3 also indicates the absence of the undesirable Structure I in PIB's prepared by the CumCl/BCl_3 combination. According to these data, I_{eff} was ~100% in every instance; had Structure I been present, I_{eff} would have been less. Conceivably, ED-stabilized carbocations hava a lower tendency of intramolecular alkylation than unmodified carbocations.

It appears that all the observations made in these experiments carried out in the presence of ED's, i.e., reduced polymerization rates, narrower MWD, and diminished indanyl-skeleton formation, may be due to one fundamental effect, namely, carbocation stabilization by a suitable ED. Steric hindrance may also be partially responsible; strong ED's in the proximity of carbocations may reduce the rate of propagation and self-alkylation.

ACKNOWLEDGMENT

This material is based on research supported by the NSF under Grant DMR-84-18617.

REFERENCES

[1] G. Kaszás, J. Puskás, C. C. Chen, and J. P. Kennedy, *Polym. Bull., 20,* 413 (1988).

[2] G. Kaszás, J. Puskás, J. P. Kennedy, and C. C. Chen, *Macromolecules,* In Press.

[3] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions,* Plenum, New York, 1978.

[4] J. P. Kennedy and R. A. Smith, *J. Polym. Sci., Polym. Chem. Ed., 18*(5), 1523 (1980).

[5] J. Puskás, G. Kaszás, J. P. Kennedy, T. Kelen, and F. Tüdös, *J. Macromol. Sci.–Chem., A18*(9), 1229 (1982-83).

[6] G. Kaszás, M. Györ, and J. P. Kennedy, *Ibid., A18*(9), 1367 (1982).

[7] R. Faust and J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed., 25,* 1847 (1987).

[8] G. Kaszás, J. Puskás, and J. P. Kennedy, *Makromol. Chem., Macromol. Symp., 13/14,* 473 (1988).

[9] Polish Patent 93,855 (1977).

[10] British Patent 1,056,730 (1967), Nippon Oil Co.

[11] German Patent 2,163,956 (1972), Sumimoto Chem. Co.

[12] German Patent 2,163,957 (1972), Sumimoto Chem. Co.

[13] T. Higashimura, S. Aoshima, and M. Sawamoto, *Makromol. Chem., Macromol. Symp., 13/14,* 457 (1988).

[14] J. Puskás, G. Kaszás, J. P. Kennedy, T. Kelen, and F. Tüdös, *J. Macromol. Sci.-Chem., A18*(9), 1353 (1982-83).

[15] V. S. Chang, J. P. Kennedy, and B. Iván, *Polym. Bull., 3,* 339 (1980).

[16] L. Tomán, S. Pokorny, G. Spevacek, and J. Danhelka, *Polymer, 27,* 1121 (1986).

[17] M. Tessier and E. Maréchal, *Eur. Polym. J., 19,* 889 (1986).

[18] J. P. Kennedy, S. Y. Huang, and S. C. Feinberg, *J. Polym. Sci., Polym. Chem. Ed., 15,* 2801 (1977).

[19] J. P. Kennedy, *J. Macromol. Sci.-Chem., A13,* 695 (1979); *A14,* 1 (1980).

[20] A. Fehérvári, J. P. Kennedy, and F. Tüdös, *Ibid., A15,* 215 (1980).

[21] J. P. Kennedy and M. Hiza, *Polym. Bull., 8,* 557 (1982).

[22] R. Wondraczek, J. P. Kennedy, and R. F. Storey, *J. Polym. Sci., Polym. Chem. Ed., 20*(1), 43 (1982).

Received November 14, 1988