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LIVING CARBOCATIONIC POLYMERIZATION. V. LINEAR TELECHELIC POLYISOBUTYLENES BY BIFUNCTIONAL INITIATORS

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ABSTRACT

The synthesis of α,ω-di-*t*-chloropolyisobutylene has been accomplished by living polymerization using aliphatic and aromatic *tert*-diacetate initiators in conjunction with BCl_3 coinitiator in various solvents in the -20 to -70°C range. The living nature of the polymerizations was demonstrated with the instantaneous initiators 2,4,4,6-tetramethylheptane-2,6-diacetate and 1,4-di(2-propyl-2-acetate)benzene by linear $\bar{M}_n$ versus amount of PIB formed (W_{PIB}) plots starting at the origin. The formation of undesirable indanyl structures that arise with the aromatic initiator can be suppressed by decreasing the temperature and the polarity of the polymerization medium (i.e., by using $CH_3Cl/n\text{-}C_6H_{14}$ mixtures). Living polymerization of isobutylene can also be obtained with noninstantaneous initiators, e.g., 2,5-dimethylhexane-2,5-diacetate, 2,5-dimethylhexyne-2,5-diacetate. However, with these systems the initiator efficiency is less than 100%.

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I. INTRODUCTION

Since the introduction of the "inifer" technique [1], a number of telechelic polyisobutylenes (PIBs) carrying a variety of end groups have been prepared by converting *t*-chloro telechelic PIBs to the corresponding polymers ending in olefin [2], alcohol [3], phenol [4], etc. Recently semicontinuous [5] and continuous [6] inifer methods have been described that yielded quantities of well-defined linear and three-arm star telechelic products with essentially theoretical end-functionalities ($\bar{F}_n = 2$ or 3.0 ± 0.1) and close to theoretical molecular weight dispersities.

We recently discovered [7] truly living polymerization of isobutylene (IB) induced by new initiating systems comprising organic acetate-BCl_3 complexes under mild conditions in the temperature range of -10 to -50°C.

The living nature of the polymerizations has been demonstrated by linear $\bar{M}_n$ vs weight of PIB (W_{PIB}) formed plots starting from the origin. Independent studies have shown that forced termination can be effected in living polymerizations, and that these processes usually yield tertiary chloro-terminated prepolymers. These investigations have opened unexpected avenues toward the convenient synthesis of telechelic PIBs, macromers, copolymers, and products that will be the subject of forthcoming publications.

This paper, the fifth in the series on living carbocationic polymerization [7-10], describes the living polymerization of IB initiated by bifunctional tertiary diacetates in conjunction with BCl_3 coinitiator and the synthesis of linear *t*-chloro telechelic isobutylene prepolymers.

II. EXPERIMENTAL

A. Materials

Dicumyl acetate (p-$AcOC(CH_3)_2C_6H_4C(CH_3)_2OAc$, DiCumOAc) was prepared by adding acetyl chloride (46.6 g, 0.59 mol) dropwise to a solution of 48.5 g (0.25 mol) dicumyl alcohol and 73 g (0.6 mol) dimethylaniline in 200 mL dioxane at 0°C. After stirring at room temperature for 2 days, ether was added and the solution was washed successively with distilled water, 10% aqueous H_2SO_4, distilled water, 10% aqueous $NaHCO_3$, and finally with distilled water until neutral. The ether solution was dried over $CaCl_2$ and the solvent evaporated. DiCumOAc was purified by repeated recrystallization from *n*-hexane, in which the unreacted alcohol is insoluble. Yield: 16.0 g, 23%.

2,5-Dimethyl-3-hexyne-2,5-diacetate (DMHyDiOAc) was prepared by slowly adding acetyl chloride (55 g, 0.7 mol), to a solution of 2,5-dimethyl-3-hexyne-2,5-diol (DMHyDiOH) (42.6 g, 0.3 mol) and dimethylaniline (86 g, 0.72 mol) in 200 mL ether at such a rate as to maintain a gentle reflux. After 24 h of refluxing, the alcohol was converted and the mixture was cooled to room temperature, treated with water, and the organic layer was separated. The ether solution was washed with 10% aqueous H_2SO_4, water, and dried over anhydrous Na_2SO_4. The solvent was removed by Rotovap, and the product was distilled at reduced pressure. bp 73°C at 1.5 torr. Yield: 27.1 g, 40%.

2,5-Dimethylhexane-2,5-diacetate ($AcOC(CH_3)_2CH_2CH_2C(CH_3)_2OAc$, DMHDiOAc) was synthesized by the procedure used for the preparation of DMHyDiOAc (see above).

2,4,4,6-Tetramethylheptane-2,6-diacetate ($AcOC(CH_3)_2CH_2C(CH_3)_2$-$CH_2C(CH_3)_2OAc$, TMH_7DiOAc) was prepared as follows: 3,3-Dimethylglutaric acid (Aldrich) was esterified by refluxing a CH_3OH solution containing catalytic amounts of concentrated H_2SO_4. 2,4,4,6-Tetramethylheptane-2,6-diol was prepared from 3,3-dimethylglutaric acid dimethylester by Grignard reaction: 32 g (0.18 mol) glutaric acid dimethylester in 50 mL ether was slowly added to 250 mL (3 *M*) methyl magnesium bromide (Aldrich) in ether between 0 and 5°C. After refluxing for 3 to 5 h, the charge was cooled to ambient temperature and slowly added to a stirred NH_4Cl-ice mixture. The organic layer was separated, washed with ice water, and dried over $CaCl_2$. The solvent was evaporated, and the product was purified by recrystallization from *n*-hexane. Yield: 20 g, 40%.

The esterification of the 2,4,4,6-tetramethylheptane-2,6-diol was carried out by essentially the same procedure as that for DMHyDiOH, described above. The acetyl chloride was in fivefold excess, and unreacted alcohol could not be detected by ^1H NMR spectroscopy after 24 h. Yield: 80%. The other materials and procedures used in this research have been described previously [10].

B. Polymerization and Characterization Methods

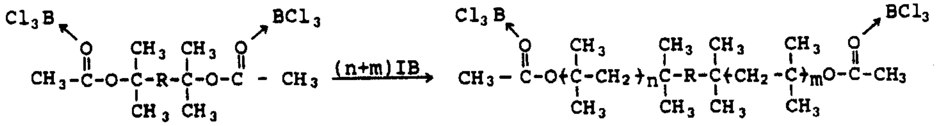
Polymerization and characterization methods have been described [10]. The functionalities of α,ω-chloro telechelic PIBs were determined by titration according to Ref. 11.

III. RESULTS AND DISCUSSION

A. Living Isobutylene Polymerization by Bifunctional Initiators

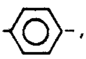
In our earlier publication [10] we described that complexes of BCl_3 with tertiary acetates, e.g., cumyl acetate ($C_6H_5C(CH_3)_2-OCOCH_3$, CumOAc) or 2,4,4-trimethyl-2-pentyl acetate ($(CH_3)_3CCH_2C(CH_2-OCOCH_3$, TMPOAc), are efficient initiators for the living polymerization of isobutylene in a variety of solvents at moderately low temperatures, i.e., in the range from -10 to -50°C. Polymerization was visualized to occur by a mechanism akin to group transfer [12] and to involve polyisobutylene chains carrying living mono-acetate growing centers [10].

In line with these investigations, we postulated that similar complexes of BCl_3 with ditertiary acetates will give rise to α,ω-telechelic living chains, i.e., chains propagating at both extremities in the absence of chain transfer to monomer and termination:

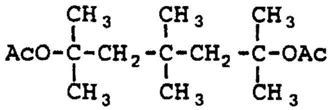


$$CH_3-\overset{\overset{Cl_3B\nwarrow}{O}}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{CH_3}{C}}-R-\underset{CH_3}{\overset{CH_3}{C}}-O-\overset{\overset{\nearrow BCl_3}{O}}{\overset{\|}{C}}-CH_3 \xrightarrow{(n+m)IB} CH_3-\overset{\overset{Cl_3B\nwarrow}{O}}{\overset{\|}{C}}-O(\underset{CH_3}{\overset{CH_3}{C}}-CH_2)_n\underset{CH_3}{\overset{CH_3}{C}}-R-\underset{CH_3}{\overset{CH_3}{C}}(CH_2-\underset{CH_3}{\overset{CH_3}{C}})_mO-\overset{\overset{\nearrow BCl_3}{O}}{\overset{\|}{C}}-CH_3$$

(1)

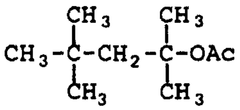
where R = $-CH_2CH_2-$, $-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-$, $-C\equiv C-$, , etc.

To insure rapid polymerizations, initial experiments have been carried out with DiCumOAc (R= ) and TMH_7DiOAc ($R = -CH_2C(CH_3)_2-CH_2-$), the monofunctional equivalents of which, CumOAc and TMPOAc, have been shown to be efficient instantaneous initiators [10]:



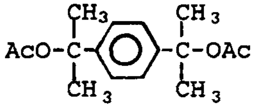
$$AcO-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OAc$$

TMH_7DiOAc

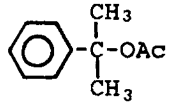


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OAc$$

TMPOAc



DiCumOAc



CumOAc

Orienting experiments showed that these ditertiary acetates are indeed efficient, very rapid initiators in the presence of BCl_3 for isobutylene polymerizations in both CH_3Cl and CH_2Cl_2 diluents. Representative data are shown in Table 1.

Since the polymerizations were usually complete a few seconds after mixing the ingredients, subsequent systematic experimentation, whose aim was to demonstrate living polymerizations, was carried out by the incremental monomer addition technique [10].

Figure 1 shows a representative $\overline{M}_n$ vs W_{PIB} plot obtained in experiments with TMH_7DiOAc and CH_3Cl diluent at -30°C. Similarly, Fig. 2 shows the $\overline{M}_n$ vs W_{PIB} plot for experiments with DiCumOAc under essentially identical conditions. The inserts in Figs. 1 and 2 show the number of molecules N as a function of W_{PIB}. The treatment of the data is identical to that developed earlier [10]. The living nature of the polymerizations is indicated by the linearity of the $\overline{M}_n$ vs W_{PIB} plots starting from the origin and by the horizon-

TABLE 1. Representative Data of Preliminary Experiments using the TMH_7DiOAc/BCl_3 Initiating System[a]

[M], mol/L	[I], mmol/L	Conversion, %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	I_{eff}[b]
0.92	5.88	100	8 900	1.8	101
0.92	8.82	100	6 800	2.3	89
0.92	11.8	100	4 260	2.6	105
0.92	14.7	100	3 800	2.6	98
0.92	29.4	100	2 040	3.1	97

[a] -20°C, CH_2Cl_2, time 1 min, $[BCl_3]$ = 0.26 mol/L.

[b] I_{eff} = (number of polymer chains) X 100/I.

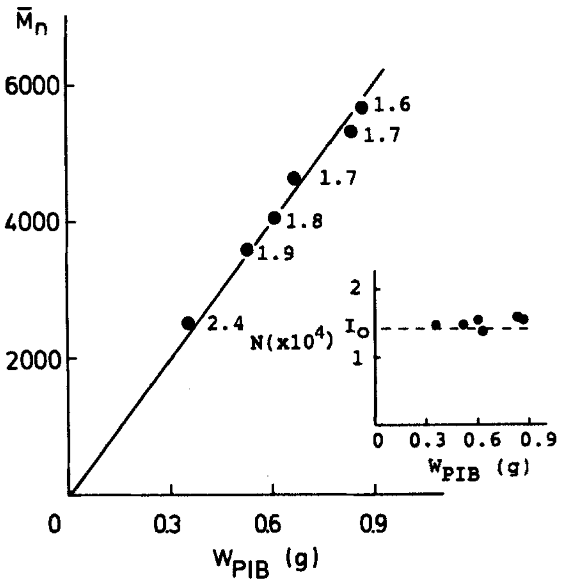


FIG. 1. Living polymerization of isobutylene by the TMH$_7$DiOAc/BCl$_3$ system (CH$_3$Cl, -30°C). The numbers are $\bar{M}_w/\bar{M}_n$.

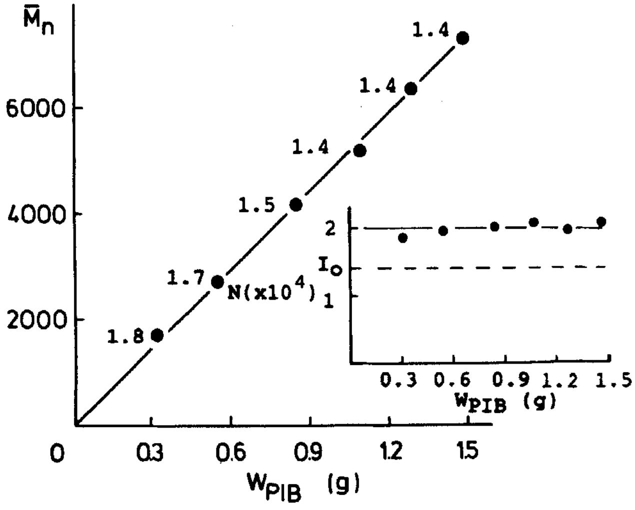
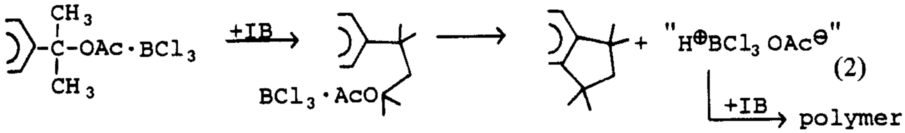


FIG. 2. Living polymerization of isobutylene by the CumOAc/BCl$_3$ system (CH$_3$Cl, -30°C). The numbers are $\bar{M}_w/\bar{M}_n$.

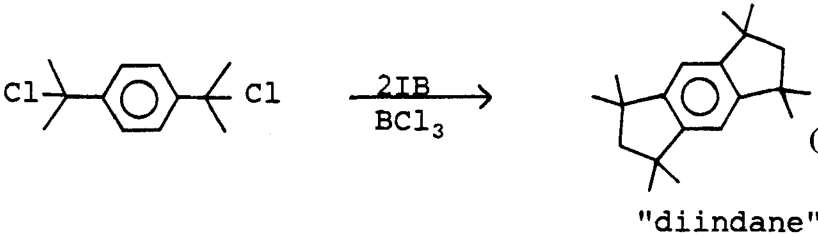
tal N vs W_{PIB} plots. Evidently the number of PIB chains remains constant during the experiment. Importantly, also, the $\overline{M}_w/\overline{M}_n$ values decrease, i.e., the molecular weight distributions show a narrowing tendency with incremental monomer addition (see data in Figs. 1 and 2). The living centers maintain their propagating ability throughout the run, with dormant species either absent or rapidly exchanging with the living centers.

In the case of TMH$_7$DiOAc, $N = [I_0]$ within experimental variation, which is self-explanatory; in the DiCumOAc system, N remains constant but is significantly larger than $[I_0]$. The latter facts are most likely due to indanyl ring formation during initiation:



(2)

The hypothetical acid "$H^{\oplus}BCl_3OAc^{\ominus}$" sustains the kinetic chain by protonating an incoming monomer. Intramolecular alkylation is quite favorable with aromatic inifers, and indeed, with the dicumyl chloride/BCl_3 system, the formation of even two condensed indanyl ring systems has been demonstrated [13]:



(3)

As a consequence of intramolecular alkylation (and assuming that each "$H^{\oplus}BCl_3OAc^{\ominus}$" species will protonate a monomer), two unconnected active chains will arise for every DiCumOAc molecule so that in the overall system $1 < N/I_0 < 2$. The number of active chains will always be two, irrespective of whether a monoindane or diindane is formed. Since the number of molecules increases due to intramolecular alkylation, i.e., due to a de facto chain transfer during initiation, the molecular weight of the PIB product must fall below the theoretical value (cf. Fig. 2). The discrepancy between the theoretical and experimental values suggests that, on the average, every third chain arose by the process outlined in Eq. (2).

Indanyl ring formation is an undesirable side reaction in inifer systems as well and has been examined in detail in conjunction with the dicumyl chloride (DCC)/BCl_3 system [13]. Indeed, the mechanism described by Eq. (2) is essentially identical to that proposed for the DCC/BCl_3 binifer system [13].

Ample direct evidence for indanyl ring formation has been found in the present investigations. Thus, ^1H NMR analysis of PIBs obtained with the DiCumOAc/BCl_3 system showed the presence of indanyl skeletons in the product, i.e., aromatic proton resonances at δ = 6.95 ppm [13], which indicates monoindanyl rings, and at δ = 6.6 ppm, which shows contamination by diindane [13].

The fact that N remains constant throughout the run suggests extremely fast initiation by the DiCumOAc/BCl_3 system. Initiation involves not only the DiCumOAc•BCl_3 complex plus monomer but also the proton-elimination/monomer-protonation sequence shown by Eq. (2). The very high initiating activity of DiCumOAc is not surprising in light of the much higher inifer activity of dicumyl chloride compared to that of cumyl chloride ($C_{I_{DCC}} = 0.95$, $C_{I_{CC}} = 0.1$) [14].

It has been shown [13] that indanyl-ring-free product can be obtained in the closely related DCC/BCl_3 inifer system by reducing both the polarity of the system and the temperature. Thus efforts have been made to suppress intramolecular alkylation in the DiCumOAc/BCl_3 system by reducing the polarity of the medium, i.e., by using $CH_3Cl/n\text{-}C_6H_{14}$ mixtures (60/40 and 40/60 v/v), and lowering the temperature to -30, -50, and -70°C. Table 2 and Figure 3 show the experimental conditions employed and the results obtained. The composition of the products (amount of undesirable monoindane and di-indane structures present) was determined quantitatively by ^1H NMR spectroscopy [13]. The effect of reducing the polarity of the medium on product composition is quite strong between pure CH_3Cl and 60/40 $CH_3Cl/n\text{-}C_6H_{14}$, but becomes insignificant below this polarity level (Table 2). The effect of temperature seems to be linear at all three polarity levels investigated. According to these findings, indanyl-ring-free PIB can be obtained in relatively nonpolar media at low temperatures. Similar observations have been reported with the DCC/BCl_3 system [13].

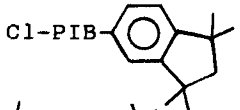
Closer examination of the data in Table 2 shows that not every "$H^{\oplus}BCl_3OAc^{\ominus}$" entity (see Eq. 2) will start a new PIB chain: much lower than expected N/I_0 values are obtained by assuming that two separate chains will arise from every DiCumOAc, leading to mono- or diindanes. For example, N/I_0 = 1.4 at -30° in line 1 of Table 2; however, if each "$H^{\oplus}BCl_3OAc^{\ominus}$" would have initiated one chain, the ratio N/I_0 should have been 1.72, i.e., 28 + (2 X 48) + (2 X 24). On lowering the temperature to -70°C, the "$H^{\oplus}BCl_3OAc^{\ominus}$" does not seem to initiate at all. It could be that, due to

TABLE 2. Effect of Medium Polarity and Temperature on the Formation of Indanyl Structures

Temperature, °C	Solvent composition		Product,[a] mol%		
	CH_3Cl/*n*-hexane, %	N/I_0	I	II	III
-30	100/0	1.4	28	48	24
-50	100/0	1.05	42	36	22
-70	100/0	0.7	46	32	21
-30	60/40	1.35	51	29	20
-50	60/40	1.15	71	18	11
-70	60/40	1.07	85	15	Traces
-30	40/60	1.15	50	30	19
-50	40/60	1.12	66	24	10
-70	40/60	1.1	>95	Traces	0

[a] I:

II:



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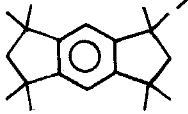
III:



(undesirable)

the presence of the ionized/dissociated growing centers ~PIB–$CH_2C^{\oplus}(CH_3)_2$·$BCl_3OAc^{\ominus}$, the ionization/dissociation of "$H^{\oplus}BCl_3OAc^{\ominus}$" is suppressed and, thus, the rate of initiation by the latter species is reduced.

By reducing the polarity of the medium, the overall rate of polymerization is also reduced as characterized by the amount of PIB formed (% conversion) after the rapid consumption of the first monomer increment by the incremental monomer addition technique [10]. For this reason we did not construct a $\bar{M}_n$ vs W_{PIB} plot. The possible reasons for the rate reduction, i.e., an increase in

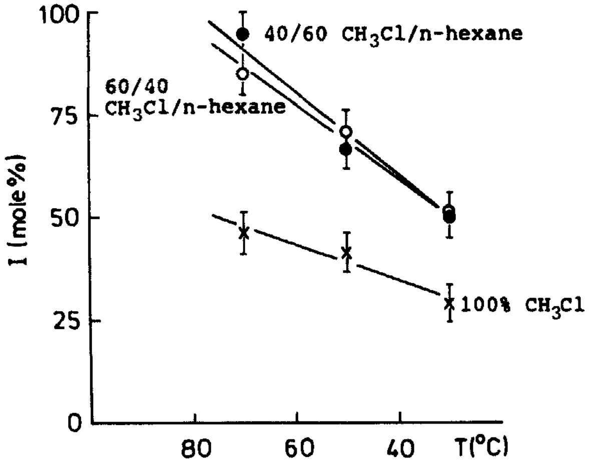


FIG. 3. Effect of medium polarity and temperature on the formation of relative amount of indanyl-free PIB.

the concentration of dormant species and/or a slow exchange between dormant and living centers leading to bimodal molecular weight distribution (also observed here), have been discussed for the CumOAc/IB system [10].

Instantaneous initiation, although not a criterion of living polymerization, greatly facilitates its diagnosis. In the systems investigated, the number of polymer molecules remains constant throughout the experiment (cf. Figs. 1 and 2). If initiation is noninstantaneous, the number of molecules increases during the run and the diagnosis of living polymerizations becomes difficult. It has been shown earlier that, under select conditions, CumOAc and TMPOAc give rise to virtually instantaneous living polymerizations [10], and in this paper that DiCumOAc and TMH_7DiOAc also yield instantaneous living polymerization of IB. In contrast, *t*-BuAc was found to be a less reactive ($I_{eff} \approx 40\%$) initiator, which albeit slower also gave complete conversion (particularly at higher temperatures) and also led to $\overline{DP}_n$ proportional to $[M_0]/[I_0]$. Evidently, simple aliphatic tertiary acetates and diacetates can be used for the synthesis of end-reactive PIBs.

Tables 3 and 4 illustrate the effect of temperature and the nature of the diluent on the conversion and molecular weights of isobutylene polymerizations initiated by DMHDiOAc and DMHyDiOAc ($R = -CH_2CH_2-$ and $-C{\equiv}C-$, respectively, in Eq. 1) in conjunction with BCl_3 coinitiator. These

TABLE 3. Polymerization of Isobutylene with the 2,5-Dimethylhexane-2,5-Diacetate/BCl_3 System[a]

[I], mmol/L	Diluent	Temperature, °C	Conversion, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	I_{eff}
5.6	CH_3Cl	-50	5.2	35 000	60 600	1.7	–
28	"	"	8.5	11 100	20 000	1.8	–
56	"	"	9.0	6 150	12 500	2.0	–
5.6	CH_3Cl	-30	16.8	–	–	–	–
28	"	"	10.1	–	–	–	–
56	"	"	17.5	–	–	–	–
5.6	CH_2Cl_2	-30	100	21 900	64 300	2.9	46
28	"	"	"	11 499	23 500	2.1	18
56	"	"	"	7 100	13 200	1.8	15
82.5	CH_2Cl_2	-20	"[b]	3 400	7 700	2.3	18
97	"	"	"	3 300	5 900	1.8	17
110	"	"	"	2 800	4 760	1.7	19
165	"	"	"[b]	2 000	5 800	2.9	16

[a] $[BCl_3]$ = 0.26 mol/L, [IB] = 1 mol/L, 30 min.

[b] After 1 min.

initiators have been selected because of their ready availability from the corresponding alcohols (see Experimental) and low cost.

Polymerizations were much faster in CH_2Cl_2 than in CH_3Cl under identical conditions. At -20°C, essentially complete conversions were obtained in less than 1 min in CH_2Cl_2. That isobutylene polymerizations proceed much faster in CH_2Cl_2 than in CH_3Cl has been observed and discussed in similar investigations [10]. The $\overline{M}_n$ values of the polymers were proportional to $[M_0]/[I_0]$ even when initiation was not instantaneous and conversions were less than 100%. That the molecular weight dispersities ($\overline{M}_w/\overline{M}_n$) are much greater than unity is mainly due to the relatively slow (noninstantaneous) initiation in these systems (also reflected by the low I_{eff}). The dependence of $\overline{M}_n$ on $[M_0]/[I_0]$ under noninstantaneous initiation conditions will be discussed in a forthcoming publication.

It appears that the aliphatic ditertiary acetates investigated readily lead to uniform α,ω-di-*t*-chloro PIBs, albeit the DMHDiOAc and DMHyDiOAc have less than 100% initiator efficiencies. Our next publication concerns continuous experiments with TMH_7DiOAc that readily gives telechelic product with $I_{eff} = 100\%$ [15].

B. Endgroup Determination

As discussed earlier [10], the end group of a TMPOAc-initiated isobutylene polymerization killed by methanol is $-CH_2C(CH_3)_2Cl$. Thus, it was not too surprising to find that the end groups of telechelic prepolymers prepared under similar conditions by the TMH_7DiOAc, DMHDiOAc, and DMHyDiOAc/BCl_3 systems were also *t*-chlorides, as indicated by ^1H NMR spectroscopy. Quantitative determination (titration and ^1H NMR spectroscopy, see Experimental) of representative, relatively low molecular weight ($\overline{M}_n$ 2000-3000) telechelic polyisobutylenes yielded $\overline{F}_n = 2.0 \pm 0.2$, i.e., the number-average endgroup functionality $\overline{F}_n$ was within experimental error of the theoretical value.

The products obtained by the DMHyDiOAc/BCl_3 system showed a weak but detectable UV absorption at 254 nm (the working wavelength of the UV detector), which was attributed to the triple bond in the initiator segment. Although acetylene absorbs in the far UV below the cutoff value of THF (the solvent used in GPC studies), alkyl substitution on the acetylenic carbon is expected to shift the absorption to higher wavelengths and to increase the molar absorption coefficient. While studies with acetylenic compounds are very limited [17], similar phenomena with olefinic compounds are well documented [18]. Figure 4 shows the modified Kennedy-Smith (KS) plot [16] of a representative sample. The KS plot provides quantitative insight into

TABLE 4. Polymerization of Isobutylene with the 2,5-Dimethylhexyne-2,5-Diacetate/BCl, System[a]

[I], mmol/L	Diluent	Temperature, °C	Time, min	Conversion, %	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	I_{eff}
5.6	CH_3Cl	-30	30	2.5	–	–	–	–
28	"	"	"	1.6	–	–	–	–
56	"	"	"	1.4	–	–	–	–
5.6	CH_2Cl_2	-30	30	49.0	5 500	10 700	1.9	–
28	"	"	"	45.8	3 200	5 150	1.6	–
56	"	"	"	49.5	2 400	3 700	1.5	–
28	CH_2Cl_2	-30	60	62.2	4 000	5 570	1.4	–
56	"	"	"	66.7	3 000	4 140	1.4	–
57	CH_2Cl_2	-20	30	100	2 600	5 720	2.2	36
114	"	"	"	"	2 000	5 000	2.5	24
171	"	"	"	"	1 400	3 780	2.7	22

[a] $[BCl_3]$ = 0.26 mol/L, [IB] = 1 mol/L, 30 min.

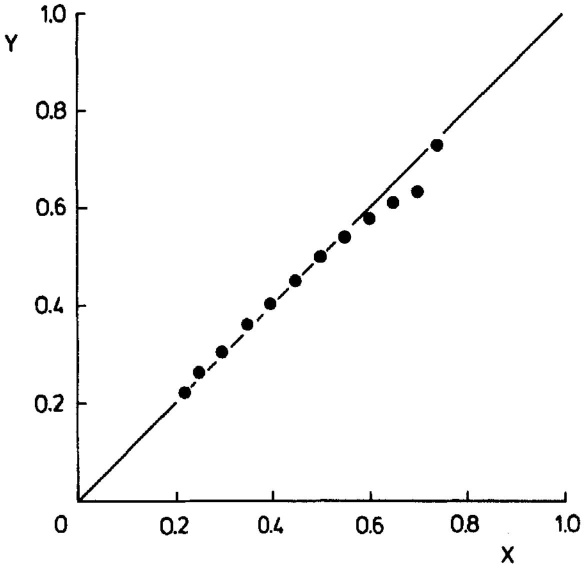


FIG. 4. Modified Kennedy-Smith plot for the PIBs obtained by the DMHyDiOAc/BCl_3 system.

$$Y = \frac{(UV/RI)_{peak}}{(UV/RI)_{peak} + (UV/RI)_x}, \qquad X = \frac{M_x}{M_{peak} + M_x}$$

the distribution of chromophores in a polymer. Evidently the RI and UV traces run parallel, leading to unit slope of the modified KS plot, which indicates that the distribution of C≡C groups in each fraction of the prepolymer is uniform.

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