Polymer Bulletin 21, 5–12 (1989)

Polymer Bulletin

Electron donors in carbocationic polymerization

IV. Preparation of narrow-dispersity *tert.*-chlorine-capped polyisobutylene by the *trans*-2,5-diacetoxy-2,5-dimethyl-3-hexene/BCl_3/dimethyl sulfoxide system*

Miklos Zsuga and J.P. Kennedy**

Institute of Polymer Science, University of Akron, Akron, OH 44325-3909, USA

SUMMARY

Low molecular weight ($\overline{M}_n$ ∿900-5000) narrow molecular weight distribution (MWD; $\overline{M}_w/\overline{M}_n$ = 1.1-1.2) tert.-chlorine telechelic polyisobutylenes (PIBs) have been synthesized by the use of the trans-2,5-dimethyl-2,5-diacetoxy-3-hexene ($DiOAcDMeH_6$)/BCl_3 initiating system in the presence of the electron donor (ED) dimethyl sulfoxide (DMSO) in methyl chloride diluent at -30°C. The living character of the polymerization was demonstrated by linear $\overline{M}_n$ versus W_p (weight of polymer) plots starting at the origin with the slope of $1/[I_o]$ (where $[I_o]$ = initiator concentration). DMSO reduces the overall rate of polymerization, however, it increases the initiator efficiency (I_{eff}) to ∿100%. The number average tert.-chlorine end functionality is $\overline{F}_n = 1.97 \pm 0.04$, by ^1H NMR spectroscopy. Polymerization mechanistic details are discussed. This is the first time narrow MWD tert.-chlorine telechelic PIB has been prepared close to the reflux temperature of methyl chloride.

INTRODUCTION

An important objective of our studies on living carbocationic polymerization is the preparation of liquid narrow-dispersity tert.-chlorine-capped PIBs by a simple low-cost process. The synthesis of these products by cumyl-type initiators is often cumbersome on account of the formation of undesirable indanyl end-structures whose suppression requires the use of low temperatures (e.g., -78°C) and polar-nonpolar solvent mixtures (e.g., CH_3Cl/n-C_6H_{14}) (1). Earlier research has also shown that the aliphatic initiating system $DiOAcDMeH_6/BCl_3$ gives tert.-chlorine-telechelic PIB by living polymerization, however, due to relatively slow initiation (2) the lower limit of molecular weight was about $\overline{M}_n$ ∿2500. This research concerns the synthesis of very low molecular weight (liquid) narrow MWD tert.-chlorine-telechelic PIBs by a new living carbocationic polymerization method (3,4) using the $DiOAcDMeH_6/BCl_3$ system in the presence of DMSO in a single solvent at relatively high temperatures.

EXPERIMENTAL

Materials. The synthesis of $DiOAcDMeH_6$ (2) and the source of the other materials used have been published (5). DMSO (Fisher Scientific) was used as received.

---

*Paper XXVII in the series on Living Carbocationic Polymerization. For paper XXVI see Kaszas et al., J. Macromol. Sci. Chem. to appear (1989)

**Visiting scientist, permanent address: Department of Applied Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary

Polymerizations. Polymerizations were carried out in a dry box under a dry N_2 atmosphere. Procedural details have been described (5).

Characterization. Molecular weights and molecular weight distributions were determined by GPC (5). ^1H NMR spectra were recorded by a Varian 60 instrument. Details concerning instrumentation and procedures have been described (5).

RESULTS AND DISCUSSION

A. Kinetic and MWD Studies

In view of its high donicity (6) DMSO was selected as the ED used in these investigations. Figure 1 shows the results of a duplicate series of IB polymerizations and demonstrates that the $DiOAcDMeH_6/BCl_3/DMSO$ system yields living polymerization and that the PIBs exhibit close to Poisson MWD even at $\overline{M}_n$s below ∿1000. Specifically, the linear $\overline{M}_n$ versus W_p plot obtained by the IMA technique (5) starting from the origin and having a slope of $1/[DiOAcDMeH_6]$, together with the narrow MWD products rigorously prove living polymerizations. While in the presence of DMSO average conversions are ∿20% and I_{eff} ∿100%, in the absence of DMSO the same system rapidly yields ∿100% conversions but I_{eff}'s are much lower than ∿100% (2). A mechanistic interpretation is given in Section C.

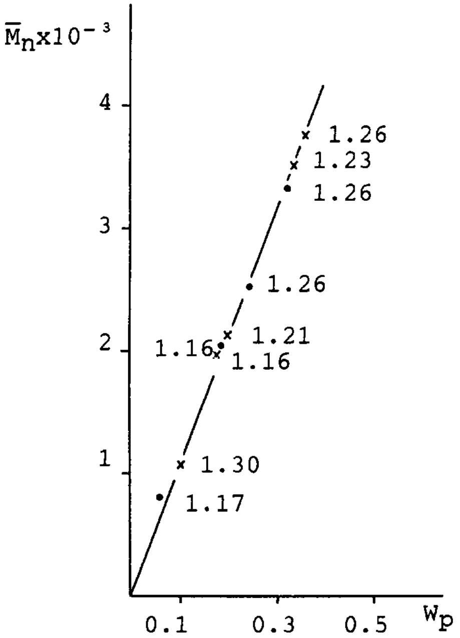


Figure 1. The $\overline{M}_n$ versus W_p plot for $DiOAcDMeH_6/BCl_3/IB/DMSO$ systems. (Duplicate series of experiments, IMA technique, 5x[IB] = 0.24 mole/L per 30 mins., $[DiOAcDMeH_6] = 3.8 \times 10^{-3}$ mole/L, $[BCl_3 = 2.7 \cdot 10^{-2}$ mole/L, $[DMSO] = 5.6 \cdot 10^{-3}$ mole/L, MeCl, -35°C, total initial vol. 25 mL. The solid line shows theoretical $\overline{M}_n$ values for I_{eff} = 100%. The numbers are $\overline{M}_w/\overline{M}_n$ values.)

A further series of experiments have been carried out to determine the rate of living polymerization obtained by the $DiOAcDMeH_6/BCl_3/IB/DMSO$ system. Table I and Figures 2 and 3 show the data. The living nature of the system has again been proven by the usual linear $\overline{M}_n$ versus W_p plot and associated horizontal N versus W_p plot (with the intercept at $[DiOAcDMeH_6]$).

TABLE I

The Time Dependence of Living Isobutylene Polymerization by the $DiOAcDMeH_6/BCl_3/IB/DMSO$ System ($[IB] = 0.478$ mole/L, $[BCl_3] = 2.710^{-2}$ mole/L, $[DMSO] = 5.610^{-3}$ mole/L, CH_3Cl, -35°C, total vol. 25 mL)

t min	Conv. %	$[DiOAcDMeH_6]\cdot 10^3$ mole/L	$\overline{M}_n\cdot 10^{-3}$ g/mole	$\overline{M}_w/\overline{M}_n$	I_{eff} %
45	35.8	3.16	3.15	1.18	97
60	47.5	3.10	4.62	1.21	88
90	53.2	3.05	4.56	1.18	96
120	62.6	3.62	4.85	1.22	96
180	74.6	3.38	5.60	1.23	> 96
1*	100	3.69	5.60	1.26	65

*Control, in the absence of DMSO; $[IB] = 0.239$ mole/L

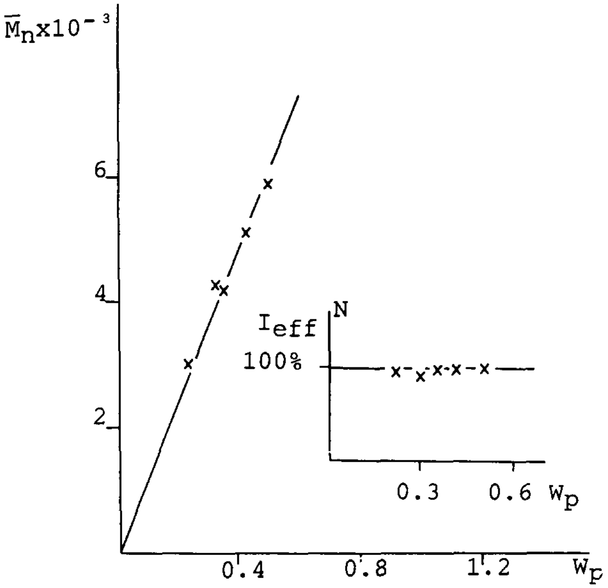


Figure 2. The $\overline{M}_n$ versus W_p plot constructed from the data of Table I. (The $\overline{M}_n$ values are normalized to the average initiator concentration).

According to the rate data shown in Figure 3 conversions increase with time in a characteristic manner. After a brief period the polymerization becomes apparently first order in monomer. The linear ln(1-C) versus time plot (C = conversion) indicates that the concentration of living species is constant over a wide time-range. (Inset in Figure 3). The apparent discrepancy between these rate data and those obtained by the

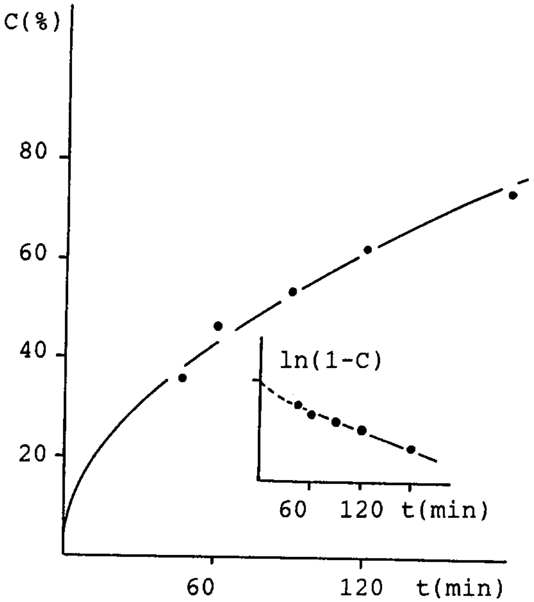


Figure 3. Time dependence of conversion and ln(1-C) (Experimental Details in Table I).

IMA technique in this work (see first paragraph in this section) and by Kaszas et al. (3,7) has been noted. While Figure 3 suggests polymerization apparently first order in monomer the data generated by the conventional (IMA) technique suggest an apparently zero order process. The reason for this apparent contradiction may be due to the different experimental techniques used. The accuracy of the data is insufficient to resolve this dilemma at the present time.

B. Structure Characterization

The structure of PIBs obtained in the presence of DMSO has been analyzed by ^1H NMR spectroscopy. Figure 4 shows a representative spectrum together with assignments. On account of the low $\overline{M}_n$ all the resonances can be readily identified. Integration relative to the internal standard (=C$\underline{H}$-) yields $\overline{M}_n$ = 1000 which is in good agreement with the datum obtained by GPC ($\overline{M}_n$ = 1070).

The number average tert.-chlorine end functionality $\overline{F}_n$ was obtained by integrating the resonances associated with the tert.-chlorine end groups (δ = 1.60 and 1.83 ppm) relative to the sum of aliphatic protons in the repeat units and the initiator fragment, and using the equation:

$$\overline{F}_n = \frac{\overline{DP}_n \cdot N_1 + N_3}{N_2} \cdot \frac{I_1}{I_2}$$

where N_1, N_2 and N_3 are, respectively, the number of protons in a repeat unit, end group, and initiator fragment; I_1 is the intensity of end group protons and I_2 that of all other aliphatic protons. According to this analysis $\overline{F}_n$ = 1.97 ± 0.04, indicating the formation of perfectly tert.-chlorine telechelic PIBs within what is considered to be experimental error.

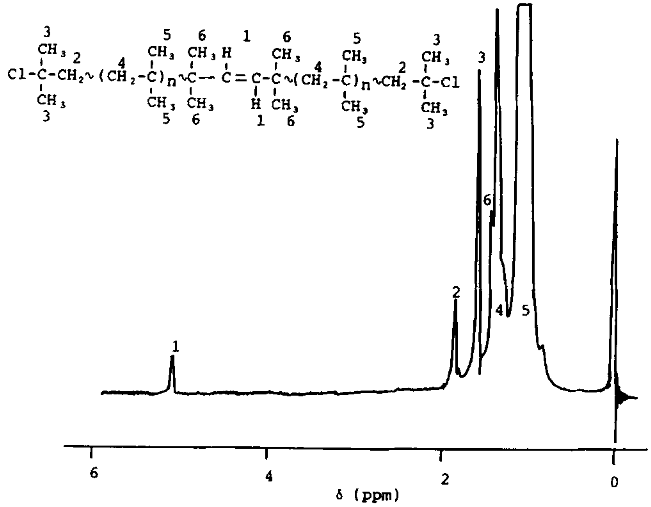


Figure 4. ^{1}H NMR spectrum of a low molecular weight ($\overline{M}_{n,GPC}$ = 1070).

C. Mechanistic Speculations

In a previous publication of this series (8) it was postulated that initiation of living carbocationic polymerizations of isobutylene induced by tert.-ester/BCl$_3$ systems may under certain conditions involve the formation of tert.-chlorides. According to this view the DiOAcDMeH$_6$/BCl$_3$ system may yield the trans-2,5-dichloro-2,5-dimethyl-3-hexene (DiClDMeH$_6$) initiator and upon polymerization tert.-chloride terminated PIBs. This question was addressed by comparing the results of polymerizations obtained with DiOAcDMeH$_6$/BCl$_3$ and DiClDMeH$_5$/BCl$_3$ systems butotherwise under virtually identical conditions. Table II shows the conditions employed and the data. Evidently the polymerization induced by the diacetate/BCl$_3$ is much faster than that by the dichloride/BCl$_3$ system; also the $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ data are quite different. Therefore in the DiOAcDMeH$_6$/BCl$_3$ system the diacetate is the true initiator and it is not rapidly converted to the corresponding dichloride.

Aging (premixing) of DiOAcDMeH$_6$ plus BCl$_3$ yielded multimodal polymer indicating the presence of a multiplicity of active centers arising from the diacetate, although the aging time ($\sim$5 min) was much longer than necessary to produce $\sim$100% conversion in the absence of aging. Figure 5 shows GPC traces of products obtained in the absence and presence of aged initiating systems.

In the absence of DMSO polymerizations rapidly yield 100% conversions, however, I_{eff} is significantly lower than 100% (2); see also "control" in Table I. Evidently, the rate of initiation (most likely cationation (2)) is low relative to propagation and the monomer is depleted before all the initiator is consumed. In the presence of DMSO and an excess of BCl$_3$ rapid complexation will occur giving rise to DMSO•BCl$_3$ or similar species (DMSO·2BCl_3, etc.). As discussed in the previous paper of this series (8), the DMSO·BCl_3 complex is probably sufficiently nucleophilic to modulate (stabilize) the polymerization-active carbocations but not to deactivate them completely. As demonstrated by detailed studies (3,8) DMSO·BCl_3 complexes very beneficially affect carbocationic polymerizations, i.e., they suppress or eliminate undesirable side reactions, allow living polymerizations to arise in otherwise nonliving systems, give rise to very narrow MWD.

TABLE II

Polymerization of Isobutylene by DiOAcDMeH_6 and DiClDMeH_6/BCl_3 Initiating Systems
(MeCl, -30°C, [BCl_3] = 0.11 mole/L, [DiOAcDMeH_6]=[DiClDMeH_6]= 4.10^{-3} mole/L, 10 min., 25 mL)

System	iC_4H_8 mole/L	Conv. %	$\bar{M}_n \cdot 10^{-3}$ g/mole	$\bar{M}_w/\bar{M}_n$	I_{eff} %	Observation
Control*	0.191	2.5	-	-	-	homog.
DiOAcDMeH_6	0.191	∿100	4.57	1.35	57	homog.
	0.382	∿100	7.78	1.34	75	homog.
	0.574	∿100	9.06	1.42	95	milky
	0.766	∿100	10.70	1.34	104	milky
	0.957	∿100	10.10	1.47	143	ppt on wall
DiClDMeH_6**	0.957	32	4.34	2.90	91	homog.

* Absence of initiator
** 30 min., [BCl_3] = 0.256 mole/L, data from ref. (9)

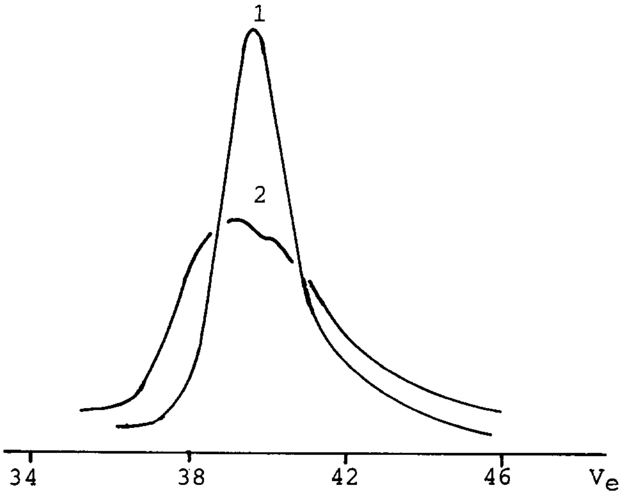
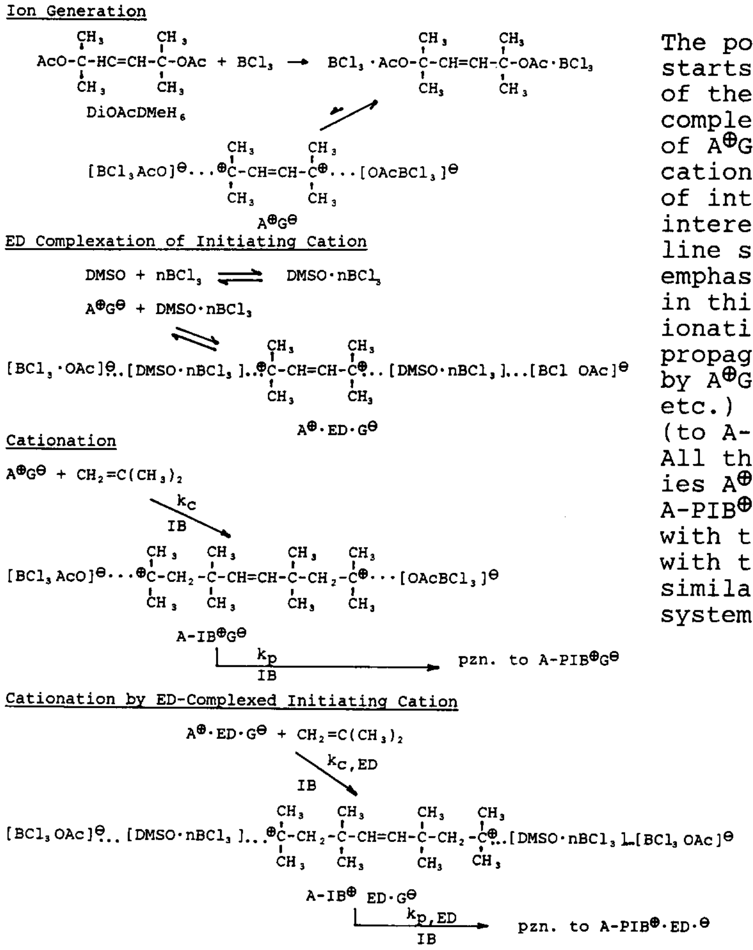


Figure 5. GPC traces of PIBs obtained with 1) No aging; 2) After 5 min. aging. (For exptl. conds. see "control" in Table II).

The following equations help to visualize the mechanism envisioned:



The polymerization starts by ionization of the DiOAcDMeH$_6$·BCl$_3$ complex. The ionicity of A$^{\oplus}$G$^{\ominus}$ (for allylic cation) is the subject of intense study and interest; the dotted line symbolism is to emphasize uncertainty in this regard. Cationation and subsequent propagation may occur by A$^{\oplus}$G$^{\ominus}$ (to A-IB$^{\oplus}$G$^{\ominus}$ etc.) or by A$^{\oplus}$·ED·G$^{\ominus}$ (to A-IB$^{\oplus}$·ED·G$^{\ominus}$, etc.). All the cationic species A$^{\oplus}$G$^{\ominus}$, A-IB$^{\oplus}$G$^{\ominus}$ and A-PIB$^{\oplus}$G$^{\ominus}$ may complex with the ED (in fact with the DMSO·BCl$_3$ or similar species in the system).

The following scheme helps to simplify and generalize these relationships:

$$\begin{tikzcd}
\mathrm{DiOAcDMeH_6} \arrow[r, "\mathrm{BCl_3}"] & A^{\oplus}G^{\ominus} \arrow[r, shift left, "\mathrm{ED}"] \arrow[d, "\mathrm{IB}"', "k_c"] & A^{\oplus}\cdot\mathrm{ED}\cdot G^{\ominus} \arrow[l, shift left, "K_1"] \arrow[d, "\mathrm{IB}"', "k_{c,\mathrm{ED}}"] \\
& A\text{-}\mathrm{IB}^{\oplus}G^{\ominus} \arrow[r, shift left, "\mathrm{ED}"] \arrow[d, "\mathrm{IB}"', "k_p"] & A\text{-}\mathrm{IB}^{\oplus}\cdot\mathrm{ED}\cdot G^{\ominus} \arrow[l, shift left, "K_2"] \arrow[d, "\mathrm{IB}"', "k_{p,\mathrm{ED}}"] \\
& A\text{-}\mathrm{PIB}^{\oplus}G^{\ominus} \arrow[r, shift left, "\mathrm{ED}"] & A\text{-}\mathrm{PIB}^{\oplus}\cdot\mathrm{ED}\cdot G^{\ominus} \arrow[l, shift left, "K_n"]
\end{tikzcd}$$

The equilibrium constants K_1 and K_2 are not equal ($K_1 \neq K_2$) as they relate to different cations (allylic and tertiary). The equilibrium constants $K_2 \ldots K_n$, however, are very similar since they relate to essentially the same propagating structures. In regard to the rate constants, most likely $k_c \gg k_{c,ED}$ and $k_p \gg k_{p,ED}$, i.e., cationation and propagation by the uncomplexed cations are much faster than by the ED-complexed species. As a consequence of complexation the reactivity of the growing centers decreases and the overall rates of both cationation and propagation will diminish (8). Conceivably, the reactivity-reduction by ED (i.e., DMSO) complexation of the more reactive propagating tert.-cation will be larger than that of the more stable cationating allylic-cation, i.e., $R_p - R_{p,DMSO} > R_c - R_{c,DMSO}$ or $\Delta R_p > \Delta R_c$ where R_p and R_c are the rates of propagation and cationation, respectively. Due to the relatively larger reduction in the rate of propagation, the rate of initiation (i.e., rate of ion generation plus cationation) will correspondingly increase, $R_i > R_p$, so that the MWDs will become narrower. Thus in the presence of DMSO initiation will go to completion before propagation would consume the monomer so that I_{eff} will increase to $\sim$100%.

The present data also corroborates our earlier conclusion (2) that with the DiOAcDMeH$_6$/BCl$_3$ system in the absence of DMSO the rate determining step is cationation.

ACKNOWLEDGEMENT

This material is based on research supported by the NSF under DMR-84-18617 and INT-86-07993.

REFERENCES

1. R. Faust, A. Nagy and J. P. Kennedy, J. Macromol. Sci. Chem., A24(6), 595 (1987)
2. M. Zsuga, J. P. Kennedy, T. Kelen, J. Macromol. Sci. Chem., in press
3. G. Kaszas, J. Puskas, J. P. Kennedy, and C. C. Chen, Polym. Bull. 20, 413 (1988)
4. G. Kaszas, J. Puskas and J. P. Kennedy, U.S. Patent Application
5. R. Faust and J. P. Kennedy, J. Polym. Sci., Part A, Polym. Chem., 25, 1847 (1987)
6. V. Guttmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum Press, New York and London, 1978
7. G. Kaszas, J. Puskas and J. P. Kennedy, J. Macromol. Chem. 13/14, 475 (1988)
8. G. Kaszas, J. Puskas, J. P. Kennedy and C. C. Chen, J. Macromol. Sci., Chem., in press
9. S. Mah, R. Faust, M. Zsuga and J. P. Kennedy, Polym. Bull. 18, 433 (1987)

Accepted November 3, 1988 K