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Living carbocationic polymerization

XXIX. The synthesis of telechelic polyisobutylenes by the *trans*-2,5-diacetoxy-2,5-dimethyl-3-hexene/BCl_3 initiating system in 1,2-dichloroethane in the –30 to 21°C range*

M. Zsuga[1,**], **R. Faust**[2], **and J.P. Kennedy**[1]

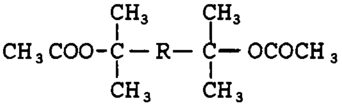
[1] Institute of Polymer Science, University of Akron, Akron, OH 44325-3909, USA
[2] Chemistry Department, University of Lowell, Lowell, MA 01854, USA

ABSTRACT

The living polymerization of isobutylene (IB) by the trans-2,5-diacetoxy-2,5-dimethyl-3-hexene (DiOAcDMH$^{=}_{6}$)/BCl_3 initiating system in 1,2-dichloroethane (DCE) in the -30 to +21°C range has been investigated. Well-defined tert-chlorine terminated polyisobutylenes (^{t}Cl-PIB-Cl^{t}) have been obtained at suitably low IB and DiOAcDMH$^{=}_{6}$ concentrations in the -30° to 0°C range. Theoretical Cl^{t} end functionality $\overline{F}_n$ ∿2.0 ± 0.1 was demonstrated by dechlorination with sodium biphenyl coupled with titration using a chloride ion selective electrode, and by ^1H NMR spectroscopy. The ^{t}Cl-PIB-Cl^{t} was quantitatively dehydrochlorinated to $\sim CH_2C(CH_3)=CH_2$ capped PIBs which in turn were quantitatively converted by hydroboration/peroxidation to $\sim CH_2CH(CH_3)CH_2OH$ ended PIBs. The internal $\sim C(CH_3)_2CH{=}CHC(CH_3)_2\sim$ initiator fragment in the polymer remains unchanged during end group functionalizations due to steric protection by the gem-dimethyl groups and the polymer chain.

INTRODUCTION

The routine preparation of well-defined ^{t}Cl-PIB-Cl^{t} is of great interest in our laboratories and we have developed several methods for the synthesis of this intermediate (1,2,3). Aliphatic tert-acetates



$$CH_3COO{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}R{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OCOCH_3$$

where R = $-CH_2CH_2-$, $-C{\equiv}C-$, $-CH_2C(CH_3)_2CH_2-$ and $-pC_6H_4-$ gave well-defined products, however, with the first two substituents initiator efficiencies (I_{eff}) were less than 100% and the polymerizations were relatively slow, and with R = $-CH_2C(CH_3)_2CH_2-$ and $-pC_6H_4-$ relatively broad molecular weight distributions (MWD) and indanyl skeletons, respectively, have been obtained (4). In contrast, the DiOAcDMH$^{=}_{6}$/BCl_3/IB/CH_3Cl/-35° system, i.e., with R = trans-CH=CH-, gave satisfactory product and very rapid overall polymerizations (100% conversion in 1 min) but I_{eff} was ∿70% due to relatively slow initiation (5). Thus the lowest molecular weight telechelics that could be prepared by this system were in excess of $\overline{M}_n$ ∿2500. Another limitation of this system is that at [IB]/[DiOAcDMH$^{=}_{6}$] ratios higher than ∿155 PIB due to the formation of relatively high molecular

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

weight product precipitation occurs which may induce chain transfer to monomer (6). Recent research showed that by the use of an electron donor, such as dimethyl sulfoxide, the I_{eff} could be raised to ∿100%, however, the overall rate of polymerization necessarily declined (7).

This report concerns the discovery that the same system in DCE diluent rapidly yields well-defined $^{\underline{t}}$Cl-PIB-Cl$^{\underline{t}}$ with theoretical $\bar{M}_n$ (I_{eff} = 100%) and narrow MWD even in the -30 to 0°C range.

EXPERIMENTAL

Materials. DCE (Aldrich Chemical Co., water content <0.005%) was used as received. The synthesis, purity and/or source of the other materials used have been published (2,5).
Polymerizations. Polymerizations were carried out in a dry box under a dry N_2 atmosphere. Details have been described (2).
Dechlorination by sodium biphenyl. The tert-chlorine end-functionality was determined by dechlorination with sodium biphenyl (Aldrich Chemical Co.) followed by chloride ion concentration quantitation by a chloride selective electrode (8).
Dehydrochlorination by t-BuOK. The $^{\underline{t}}$Cl-PIB-Cl$^{\underline{t}}$ was quantitatively dehydrochlorinated by tert-BuOK in THF solutions at reflux temperature (9).
Hydroboration/peroxydation. The hydroboration of isopropylidene capped PIBs was carried out by BH_3 in THF at 0°C (10). A tenfold excess of BH_3 per chain end was used.
Characterizations. Molecular weights and distributions were determined by GPC using well-fractionated PIB-standards (2). A Waters Model 6000A solvent delivery system equipped with a differential refractometer, Model 410, and a UV detector, Model 440, were used. The details of the GPC technique have been published (2).

RESULTS AND DISCUSSION

The DiOAcDMH$^{=}_{6}$/BCl_3/IB/CH_3Cl/-35° system yields well-defined $^{\underline{t}}$Cl-PIB-Cl$^{\underline{t}}$, however, on account of relatively slow initiation the $\bar{M}_n$ cannot be decreased below $\bar{M}_n$ ∿2500 without some MWD broadening (5). Many applications, however, demand narrow MWDs and lower than ∿2500 M_ns. It has also been shown that I_{eff} is affected by the [IB]/[DiOAcDMH$^{=}_{6}$] ratio and that at [IB]/DiOAcDMH$^{=}_{6}$ ∿155 close to 100% I_{eff}, i.e. close to theorectical $\bar{M}_n$, and reasonably narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.4) can readily be obtained. The onset of precipitation and subsequent proton elimination (chain transfer to monomer) (6) at [IB]/[DiOAcDMH$^{=}_{6}$] >155 sets the upper $\bar{M}_n$ limit of attainable $^{\underline{t}}$Cl-PIB-Cl$^{\underline{t}}$.

In the course of our continuing investigations to broaden the synthesis window of well-defined $^{\underline{t}}$Cl-PIB-Cl$^{\underline{t}}$, it became apparent that the nature of the solvent was of paramount importance in controlling the rates and MWDs. A reasonably high polarity solvent (e.g., CH_3Cl, CH_2Cl_2) was needed to insure a satisfactory rate of initiation (ionization), however, these polar liquids are bad solvents for PIB and cause precipitation if the $\bar{M}_n$ is in excess of ∿5000. The solubility range can be extended by the use of polar/nonpolar (e.g., CH_3Cl/n-C_6H_{14}) solvent mixtures (e.g., PIB of $\bar{M}_n$ ∿150,000 is soluble in 50/50 v/v $CH_3Cl/n-C_6H_{14}$), however in this case the rate of polymerization (initiation) is drastically reduced and di- and multimodal MWDs may arise. Some illustrative data relative to this point are shown in Table I.

TABLE I

The Effect of the Solvent Composition on the Polymerization of Isobutylene Initiated by the DiOAcDMH$_6^=$/BCl_3 Initiating System ([DiOAcDMH$_6^=$] = $3.88 \cdot 10^{-3}$ mole/L, [BCl_3] = 0.11 mole/L, [IB] = 0.23 mole/L, -35°C,10 min, 25 mL)

MeCl/nC_6H_{14} v/v		Conv. %	$\overline{M}_n \cdot 10^{-3}$ g/mole	$\overline{M}_w/\overline{M}_n$
25	-	∿100	5.56	1.20
20	5	∿100	5.14	1.28
15	10	70		bm*
10	15	65		mm**
5	20	38		mm**
-	25	4	-	-

* bimodal GPC traces
**multimodal GPC traces

The dielectric constant is of little predictive value for the selection of solvents: In spite of the great similarity of the dielectric constants of CH_3Cl, CH_2Cl_2 and C_2H_5Cl (11) these solvents yield quite different rates of polymerizations and MWDs; the discussion of these matters is beyond the scope of this brief report. Extensive research with a great number of solvents (see above plus CS_2, CCl_4, $CHCl_3$, SO_2) and their mixtures failed to yield a workable solvent selection guide-line in terms of rates and MWDs; evidently every system has to be examined and optimized independently.

During these investigations we have discovered that the DiOAcDMH$_6^=$/BCl_3 system in DCE, an inexpensive relatively polar (ε = 12.7 at -10°C (11))widely used solvent, gives high IB polymerization rates, close to theoretical $\overline{M}_n$s, and narrow MWDs over the desirable low $\overline{M}_n$ (liquid) range. Under suitable conditions (see below) the polymerizations start instantaneously upon BCl_3 addition in the -30 to 0°C range and although ^{t}Cl-PIB-Cl^t precipitation occurs in a few seconds produce close to theoretical $\overline{M}_n$s and narrow MWDs. Precipitation is sudden and essentially complete, and the addition of the precipitant CH_3OH to the clear solution does not produce additional product. Table II shows representative results. As indicated by the I_{eff} = 100 (±5)% data essentially theoretical $\overline{M}_n$ and narrow MWDs can be obtained with [IB] = 0.23 mole/L in the -30 to 0°C range. Detailed end group characterization (see later) did not show evidence for chain transfer. While the living nature of the system could not be rigorously proven because premature precipitation precluded a diagnostic IMA series (2), the above data and accumulated related evidence (5,6) suggest that the DiOAcDMH$_6^=$/BCl_3/IB/DEC/ -30 to 0°C system is most likely also a living one.

The monomer concentration, or rather the [IB]/ [DiOAcDMH$_6^=$] ratio, significantly affects the results. Efforts to increase this ratio and thus to prepare higher $\bar{M}_n$ product failed, i.e., the conversions decreased below 100% and I_{eff} rose to above 100%. The I_{eff} >100% cannot be due to additional polymer by chain transfer to monomer because the absence of olefinic end groups in the product indicates the absence of this reaction (even after quenching with pyridine so as to exclude HCl addition to possibly available terminal unsaturation). The additional product (i.e., I_{eff} >100%) may be due to relatively slow polymerization by adventitious protic impurities.

TABLE II

Polymerization of Isobutylene by the DiOAcDMH$_6^=$/BCl_3 Initiating system at Various Temperatures ([DiOAcDMH$_6^=$] = $3.98 \cdot 10^{-3}$ mole/L, [BCl_3] = 0.049 mole/L, DCE, 10 mins., 25 mL)

T °C	[IB] mole/L	Conv. %	$\bar{M}_n \cdot 10^{-3}$ g/mole	$\bar{M}_w/\bar{M}_n$	I_{eff} %
-30	0.46*	52	10.00	2.02	-
	0.23	∿100	3.30	1.10	95
	1.14	66	5.04	1.20	234
-15	0.46*	74	8.80	1.61	-
	0.18**	93	2.10	1.30	88
	0.23	∿100	3.60	1.15	104
	0.46	71	4.30	1.15	123
	0.69	75	4.80	1.22	176
	0.92	67	5.00	1.28	200
	1.15	60	5.00	1.37	227
0	0.46*	58	8.50	1.52	-
	0.23***	80	2.60	1.25	∿100
	0.46	40	2.40	1.47	107
	0.69	62	4.33	1.27	138
	0.92	53	4.71	1.27	147
	1.15	54	4.80	1.32	187

* Control, [DiOAcDMH$_6^=$] = 0;
** [DiOAcDMH$_6^=$] = $5.5 \cdot 10^3$ mole/L;
***Average of five experiments

In an effort to prevent premature precipitation a series of experiments have also been carried out at a higher temperature, i.e., at 21°C. Figure 1 shows the conversion-time profile together with $\bar{M}_n$, MWD and I_{eff} data and Figure 2 the ^1H NMR spectrum of the $\bar{M}_n$ = 820 product. Evidently, the product exhibited ^1H NMR resonances characteristic of $-CH_2C(CH_3)=\underline{CH_2}$ (δ = 4.62 and 4.85 ppm) and $-\underline{CH}=C(CH_3)_2$ (δ = 5.25 ppm) groups. According to the data in Figures 1 and 2, at 21°C substantial chain transfer to monomer occurs and the system is no longer living.

The Synthesis of Telechelic PIB-Diols

In line with previous experience with the DiOAcDMH$_6^=$/BCl_3 initiating system (5,6,7) the end groups of our products were expected to be $-CH_2C(CH_3)_2Cl$. This expectation has been corroborated by quantitating the Cl content of a representative

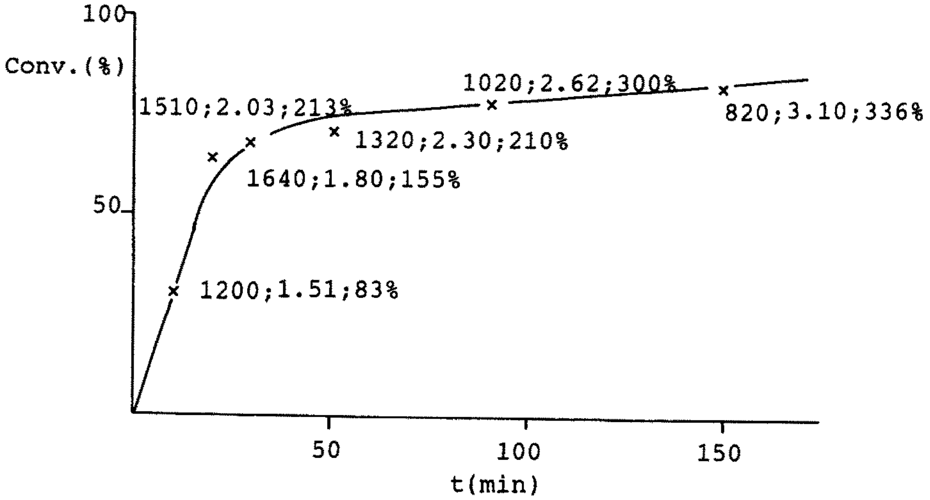

Figure 1. Conversion versus time plot of IB polymerization ([$\text{DiOAcDMH}^{=}_{6}$] = 6.77 mole/L, [BCl_3] = 0.22 mole/L, [IB] = 0.3 mole/L, DCE, 21°C, 150 mL, 20 mL aliquots withdrawn. The numbers indicate $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and I_{eff} values)

sample by sodium biphenyl dechlorination coupled with $Cl^{\ominus}$ determination by chloride selective electrode (8). According to this method the number average chlorine functionality is $\bar{F}_n$ = 2.13 ± 0.08. Subsequently, a sample was converted by the routine dehydrochlorination method (9) to the corresponding $-CH_2C(CH_3)=CH_2$ terminated telechelic. Figure 3 shows the olefinic proton resonance region of the ^1H NMR spectrum together with assignments. Integration of this spectrum i.e., the extent of the doublet at δ = 4.63 and 4.85 ppm, relative to the singlet at δ = 5.31 ppm (internal standard due to initiator fragment incorporation), gave $\bar{F}_n$ = 2.0 ± 0.1. According to these data the product was perfectly telechelic.

Finally the olefin-ended PIB was converted to the corresponding alcohol by routine hydroboration/peroxidation (10). To insure quantitative conversion a 10 fold excess of BH_3 per chain end was used. Figure 4 shows part of the ^1H NMR spectrum of the product together with assignments. The presence of the singlet at δ = 5.31 ppm indicates the absence of hydroboration/peroxidation at the internal double bond. Evidently the *gem*-dimethyl groups and/or the polymer chain shield the unsaturation from reaction. As expected, the resonances characteristic of the terminal olefins have completely disappeared and a complex multiplet at δ = 3.3-3.6 ppm characteristic of $C\underline{H}_2$ and $C\underline{H}$ protons adjacent to primary OH has appeared. Integration of the area of this multiplet relative to the sharp singlet (internal standard) gave the expected ratio: 3:1.

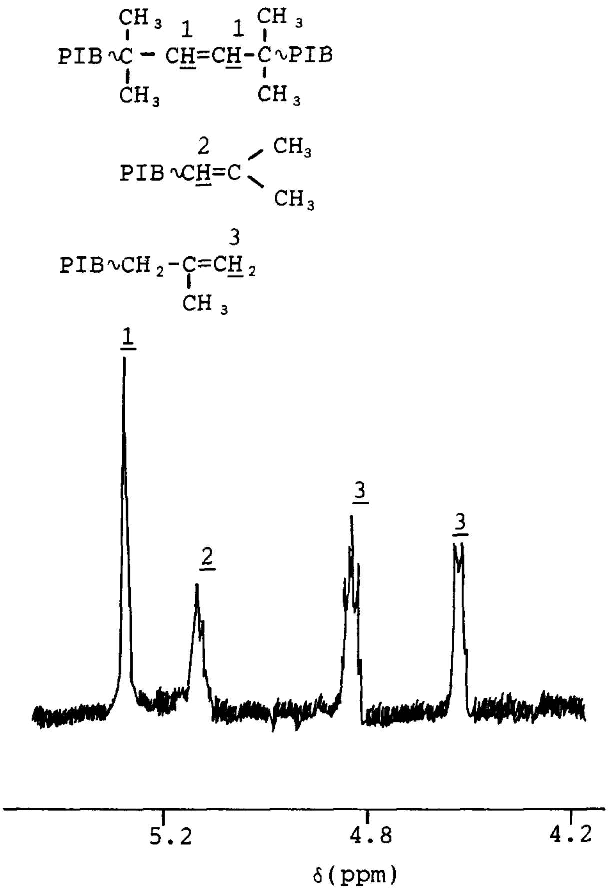

Figure 2. Partial ^{1}H NMR spectrum of a sample obtained at 21°C ($\bar{M}_n = 820$) (Synthesis conditions in Figure 1)

Independent quantitation of the $-CH_2OH$ function by the routine FTIR method (12) corroborated these data and yielded $F_n = 1.96 \pm 0.1$.

Evidently the formula given in Figure 4 correctly depicts the structure of the target PIB-diol.

ACKNOWLEDGEMENT

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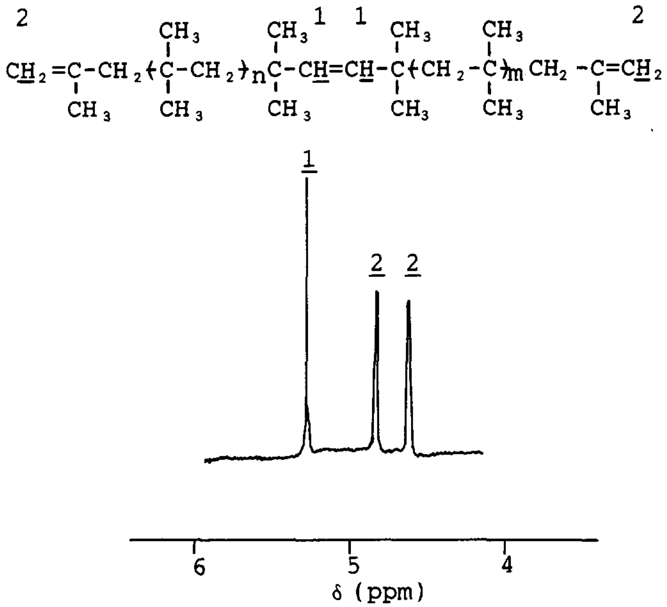

Figure 3. Partial ^{1}H NMR spectrum of a sample after dehydrochlorination ($\bar{M}_n$ = 3600)

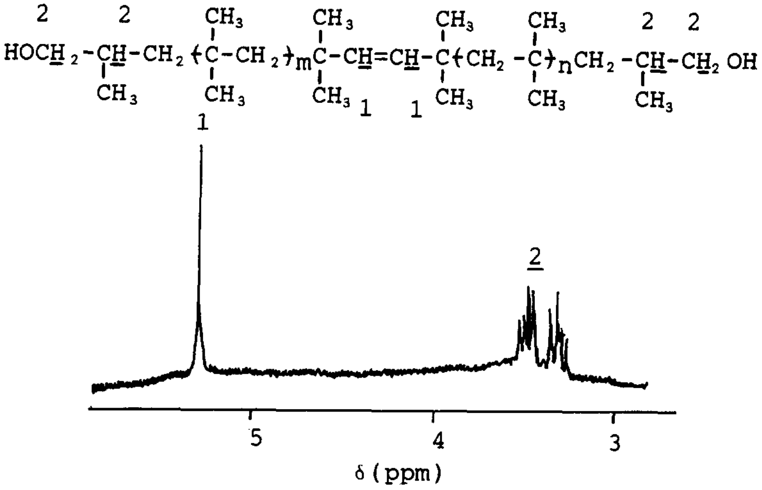

Figure 4. Partial ^{1}H NMR spectrum of a sample after hydroboration/peroxydation ($\bar{M}_n$ = 3700)

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