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A. Fehérvári[a]; J. P. Kennedy[b]; F. Tüdös[c]
[a] (A. Fehérvári) Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary [b] Institute of Polymer Science The University of Akron, Akron, Ohio [c] Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

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New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers). VI. Chain Transfer, Molecular Weight Distribution, and NMR Study of Telechelic α,ω-Di(tert-chloro)-polyisobutylene

A. FEHÉRVÁRI* and J. P. KENNEDY

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

and

F. TÜDŐS

Central Research Institute for Chemistry of the
Hungarian Academy of Sciences
H-1525 Budapest, Hungary

ABSTRACT

This paper concerns an investigation of kinetic aspects of the synthesis and structure of α,ω-di(tert-chloro)-polyisobutylene (Cl–PIB–Cl). The molecular weight distribution function and dispersion ratio $\overline{M}_w/\overline{M}_n$ characteristic for Cl–PIB–Cl have

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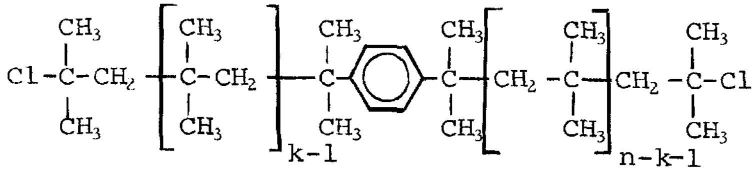
*Visiting scientist. Permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, Hungary.

been derived. In agreement with theory, $\overline{M}_w/\overline{M}_n = 1.5$ by experiment. An expression for the number-average degree of polymerization, $\overline{DP}_n$, has been deduced from the distribution function. Chain transfer studies based on this equation and its integrated form are presented. Chain transfer to monomer has been found to be negligible, and chain transfer to inifer was found to be a major process ($C_I = 0.3$) determining molecular weight and terminal functionality of the polymer. Temperature and solvent polarity (within a modest range) do not affect chain transfer to inifer. NMR spectroscopy of low molecular weight Cl–PIB–Cl confirms the structure of the chain ends to be $\sim CH_2–C(CH_3)_2Cl$. Number-average molecular weights ($\overline{M}_n$'s) determined by ^1H NMR spectroscopy and GPC were compared. The accuracy of $\overline{M}_n$'s calculated from GPC traces were confirmed by the more accurate and direct NMR method.

INTRODUCTION

In the course of our continued studies on the mechanism of carbocationic polymerization, we have developed a new method, termed the inifer method, for the synthesis of new telechelic (α,ω diterminally functional) polymer [1, 2]. The principle of this method is the use of bifunctional initiator-transfer agents (inifers) in conjunction with suitable coinitiators. For example, p-di(2-chloro-2-propyl)benzene, commonly called p-dicumyl chloride (DCC), in the presence of BCl_3 readily converts isobutylene into the new telechelic prepolymer [1, 2]:



This paper concerns a continued investigation of mechanistic-kinetic aspects of the synthesis leading to this prepolymer with special regard to molecular weight distribution and chain transfer processes. In addition, structural details of Cl–PIB–Cl, particularly its endgroups, have been defined by ^1H NMR spectroscopy.

EXPERIMENTAL

The synthesis of p-di(2-chloro-2-propyl)benzene (inifer) has been described [2]. Isobutylene was dried by passing the gas through a column packed with BaO and condensing it under dry nitrogen atmosphere. Methylcyclohexane was refluxed with sulfuric acid, washed neutral, dried with molecular sieves and calcium hydride, and distilled under nitrogen atmosphere. Methylene chloride was dried over molecular sieves, refluxed with triethylaluminum under a nitrogen atmosphere overnight, and distilled on the day of the experiment. Boron trichloride and trimethylaluminum were used as received.

Polymerization and alkylation experiments were carried out between -40 and -70° C using culture tubes with Teflon screw caps under a dry nitrogen atmosphere. Overall procedures followed in polymerization experiments [2] and alkylation by trimethylaluminum [3] have been described. Care was exercised to maintain quasi-homogeneous polymerization conditions, i.e., the charge became slightly hazy upon BCl_3 addition but precipitation of polymer did not occur. Polymerizations were terminated by the addition of prechilled methanol. Low monomer conversions were achieved by short polymerization times using a solvent mixture of low polarity.

Molecular weights ($\overline{M}_n$ and $\overline{M}_w$) have been determined using a Waters high-pressure GPC instrument, Model 6000A pump, a series of 5 Styragel columns (500, 10^3, 10^4, 10^5, 10^6 A). Differential Refractometer R401 and UV Absorbance Detector Model 440. Samples were injected in 0.1% by weight THF solutions.

NMR spectra were taken by a Varian T-60 NMR spectrometer using concentrated (10 to 20% by weight) carbon tetrachloride solutions and TMS standard.

RESULTS AND DISCUSSION

Theory

According to the earlier kinetic scheme [2], the growing carbocation may undergo:

Propagation

$$M_n^{\oplus} + M \xrightarrow{k_p} M_{n+1}^{\oplus} \qquad (1)$$

Chain transfer to inifer:

$$M_n^{\oplus} + I \xrightarrow{k_{tr,I}} M_n + I^{\oplus} \qquad (2)$$

Chain transfer to monomer:

$$M_n^{\oplus} + M \xrightarrow{k_{tr,M}} M_n + M^{\oplus} \tag{3}$$

Termination:

$$M_n^{\oplus}G^{\ominus} \xrightarrow{k_t} M_n + G \tag{4}$$

where M, I, $M_n^{\oplus}$, and $G^{\ominus}$ stand for monomer, inifer, growing polymer, and counteranion, respectively; k_p, $k_{tr,I}$, $k_{tr,M}$, and k_t are the rate constants of the corresponding reactions.

The probability p that the growing cation adds another monomer molecule is

$$p = \frac{k_p[M]}{k_p[M] + k_{tr,I}[I] + k_{tr,M}[M] + k_t}$$

$$= \frac{1}{1 + C_I[I]/[M] + C_M + k_t/k_p[M]} \tag{5}$$

where $C_I = k_{tr,I}/k_p$ and $C_M = k_{tr,M}/k_p$ are chain transfer constants. The probability of polymer formation (i.e., chain breaking) is, in turn, equal to 1 - p. Since the inifer is difunctional, a polymer consisting of n monomer units plus an inifer residue can be constructed in (n + 1)/2 ways depending on the manner of monomer incorporation at the two functional groups of the inifer. Hence the probability that a polymer will consist of n monomer units [1] is

$$F_{n+1} = \frac{(n+1)}{2}(1-p)^2 p^{n-k} p^k = \frac{(n+1)}{2}(1-p)^2 p^n \tag{6}$$

where F is the frequency factor, $0 \leq k \leq n$ is the number of monomers on one functional group of inifer, and the inifer is considered to be an additional unit in the polymer chain, hence n + 1.

The number- and weight-average degrees of polymerization are, by definition, e.g., Refs. 4 and 5:

$$DP_n = \frac{\Sigma(n+1)F_{n+1}}{\Sigma F_{n+1}} = \frac{\Sigma\frac{1}{2}(n+1)^2(1-p)^2p^n}{\Sigma\frac{1}{2}(n+1)(1-p)^2p^n} = \frac{1+p}{1-p} \tag{7}$$

$$DP_w = \frac{\Sigma(n + 1)^2 F_{n+1}}{\Sigma(n + 1) F_{n+1}} = \frac{\Sigma \frac{1}{2}(n + 1)^3(1 - p)^2 p^n}{\Sigma \frac{1}{2}(n + 1)^2(1 - p)^2 p^n} = \frac{p^2 + 4p + 1}{(1 + p)(1 - p)} \tag{8}$$

Hence the dispersion ratio is

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{DP_w}{DP_n} = 1 + \frac{2p}{(1 + p)^2} \tag{9}$$

Equations (7)-(9) are similar to expressions obtained for polymerizations initiated by biradicals and terminated by disproportionation [6].

Thus, from (5) and (7):

$$DP_n = \frac{1}{1/2(C_I[I]/[M] + (k_t/k_p)(1/[M]) + C_M)} + 1 \tag{10}$$

and since $DP_n \gg 1$, the reciprocal degree of polymerization is

$$DP_n^{-1} = 1/2(C_I[I]/[M] + C_M + k_t/k_p[M]) \tag{11}$$

Equation (11) has been used to determine chain transfer constants at low monomer conversion (< 10%). When monomer conversion is significantly higher than 10%, Eq. (11), assuming constant monomer and inifer concentrations throughout the polymerization, does not apply. Thus when conversions were higher than ~15% the integrated form of Eq. (11) has been used.

The number-average degree of polymerization is by definition [7]:

$$\overline{DP}_n = \frac{\int_0^t R_p\, dt}{\int_0^t (R_t + \Sigma R_{tr})\, dt} \tag{12}$$

where R_p, R_t, and R_{tr} are the rates of propagation, termination, and various transfer reactions, respectively. Introducing [M] as the independent variable instead of time:

$$\overline{DP}_n = \frac{\int_{[M]_0}^{[M]} d[M]}{\int_{[M]_0}^{[M]} (R_t/R_p + \Sigma R_{tr}/R_p)\, d[M]} \quad (13)$$

or its reciprocal

$$\overline{DP}_n^{-1} = \frac{\int_{[M]_0}^{[M]} (R_t/R_p + \Sigma R_{tr}/R_p)\, d[M]}{\int_{[M]_0}^{[M]} d[M]} = \frac{\int_{[M]_0}^{[M]} DP_n^{-1}\, d[M]}{\int_{[M]_0}^{[M]} d[M]} \quad (14)$$

It is apparent from Eqs. (12) through (14) that in general $\overline{DP}_n^{-1}$ is the average of the instantaneous $\overline{DP}_n^{-1}$'s over the change in monomer concentration during polymerization. Hence

$$\overline{DP}_n^{-1} = \frac{\int_{[M]_0}^{[M]} 1/2(C_I[I]/[M] + C_M + k_t/k_p[M])\, d[M]}{\int_{[M]_0}^{[M]} d[M]} \quad (15)$$

All terms in Eq. (15) are readily integrable except the first term in the numerator

$$\int_{[M]_0}^{[M]} 1/2(C_I[I]/[M])\, d[M] \quad (16)$$

containing two variables [I] and [M]. The exact solution of Integral (16) could be obtained provided the complete mechanisms of polymerization were known. Since the kinetics of initiation is as yet unexplored, the exact relationship between [I] and [M] could not be established. Our experimental findings indicate, however, that at higher $\overline{DP}_n$'s ($\overline{DP}_n \geq 10^2$), $d[I]/d[M] \leq 10^{-2}$, i.e., the decrease in

[I] is relatively slow. Therefore, instead of the actual inifer concentration, in first approximation an average $[\bar{I}]$ can be used. Hence Eq. (16) becomes

$$\int_{[M]_0}^{[M]} 1/2(C_I[I]/[M])\,d[M] = 1/2C_I[\bar{I}] \int_{[M]_0}^{[M]} (1/[M])\,d[M]$$

$$= 1/2C_I[\bar{I}] \ln\frac{[M]}{[M]_0} \qquad (17)$$

Thus at high conversions (from Eqs. 15 through 17):

$$\overline{DP}_n^{\,-1} = 1/2(C_I[\bar{I}]\frac{1}{[M]_0 - [M]} \ln\frac{[M]_0}{[M]}$$

$$+ \frac{k_t}{k_p}\,\frac{1}{[M]_0 - [M]} \ln\frac{[M]_0}{[M]} + C_M) \qquad (18)$$

Equation (18), the integrated inifer equation, is a correct relation derived for the study of chain transfer processes in experiments carried to high conversions with cationic inifer systems.

Chain Transfer Studies

Equation (11) has been used to determine chain transfer constants at low monomer conversions, where [M] and [I] are assumed to be constant throughout the polymerization. Chain transfer to monomer has been studied at constant inifer and moderate monomer concentrations (up to 2 M) in solvent mixtures of low polarity. Results are summarized in Table 1, and Fig. 1 is a plot of $\overline{DP}_n^{\,-1}$ versus $1/[M]_0$. The line fitted to the experimental points by linear regression gives a negligible intercept which indicates negligible chain transfer to monomer i.e., $C_M \sim 0$.

Chain transfer to inifer has been investigated at both low and high monomer conversions using Eqs. (11) and (18), respectively, to determine C_I. Low conversions were achieved by stopping the polymerizations 1/2 to 1 min after BCl_3 addition, while high monomer conversions were obtained by quenching after 30 min. The data obtained at low monomer conversion are summarized in Table 2, and Fig. 2 shows the

TABLE 1. Chain Transfer to Monomer Study at Constant Inifer Concentration $[I]_0 = 5.34 \times 10^{-3}$ $\underline{M}$ at -50°C[a]

$[M]_0^{-1}$	Conversion (%)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
2.376	8.1	45	69	1.54
2.079	10.5	50	85	1.70
1.848	12.8	59	91	1.54
1.663	10.5	70	101	1.45
1.386	13.7	65	105	1.61
1.188	10.7	83	133	1.59
1.040	8.6	89	133	1.50
0.924	5.8	111	159	1.43
0.520	9.0	141	200	1.43

[a] Monomer concentration changed by replacing aliquots of monomer with methylcyclohexane compensating diluent. Linear regression coefficient r = 0.986.

DP_n^{-1} versus $[I]_0$ plot. The slope of the line fitted to the experimental points by linear regression gives $C_I = 0.206$ and from the intercept $k_p/k_t = 5.06 \times 10^{-4}$.

At high monomer conversions the rearranged form of Eq. (18) has been used:

$$([M]_0 - [M])(\ln [M]_0/[M])^{-1}\overline{DP}_n^{-1} = 1/2(C_I[\bar{I}] + k_t/k_p) \qquad (19)$$

Since C_M was shown to be zero, both sides of Eq. (18) were divided by

$$\frac{1}{[M]_0 - [M]} \ln [M]_0/[M]$$

and in Fig. 3 the left-hand side of Eq. (19) was plotted against $[\bar{I}]$ to give a straight line whose slope is $1/2C_I$ and where intercept is $1/2(k_t/k_p)$. The arithmetic mean of the initial and final inifer concentration was used for the average inifer concentration. The final inifer concentration was assumed to be zero even if initiation efficiency (i.e.,

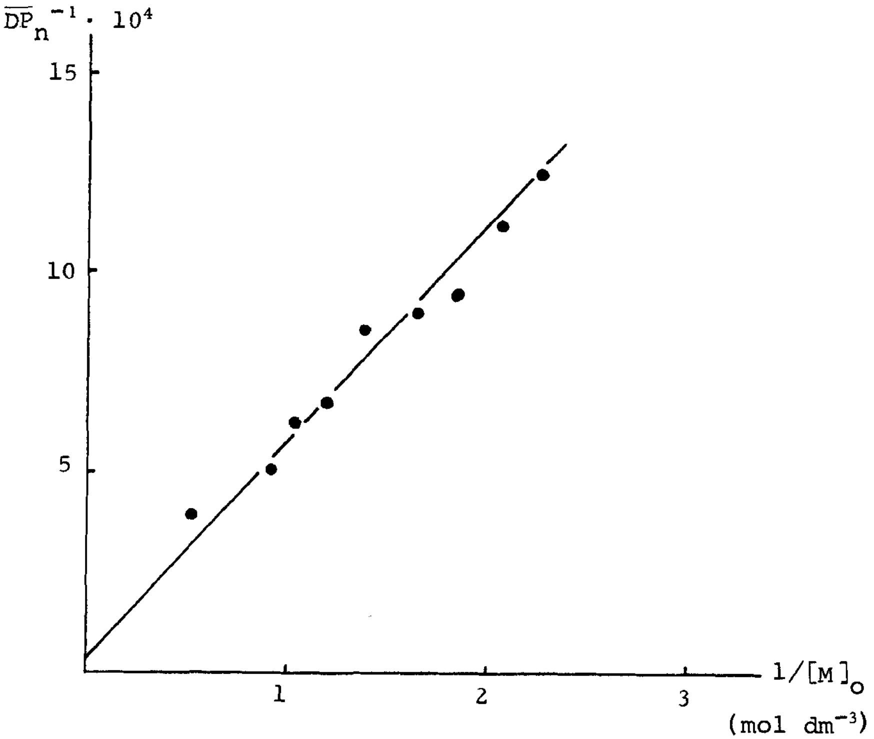


FIG. 1. Chain transfer to monomer in the inifer system at -50°C.

$$\frac{([M]_0 - [M])}{\overline{DP}_n [I]_0} 100)$$

was not 100% and monomer conversion was incomplete. (Separate experiments showed that a certain fraction of the inifer may be consumed in some unknown manner. Thus a representative polymerization experiment was performed, and after reaching a final monomer conversion (~30% within 1/2 hr), the same initial amount of inifer was added, which doubled the monomer conversion (~60%). Repeated additions of the initial amount of inifer increased the monomer conversion (to ~90%). This experiment indicates that a possible byproduct does not interfere with the polymerization.)

The numerical values of C_I and k_t/k_p are summarized in Table 3. They show good agreement between C_I values determined at low conversion by Eq. (11) and at high conversion by Eq. (19) at the same

TABLE 2. Chain Transfer to Inifer Study at Constant Monomer Concentration $[M]_0$ = 1.00 M at -50°C. Low Conversion Data[a]

$[I]_0 \times 10^3$ M	Conversion (%)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
3.874	4.5	96	152	1.59
3.874	10.8	80	136	1.70
2.543	6.1	114	165	1.46
2.543	9.5	102	158	1.54
0.9583	5.4	171	256	1.50
0.9583	6.0	151	246	1.59

[a] Linear regression coefficient r = 0.951.

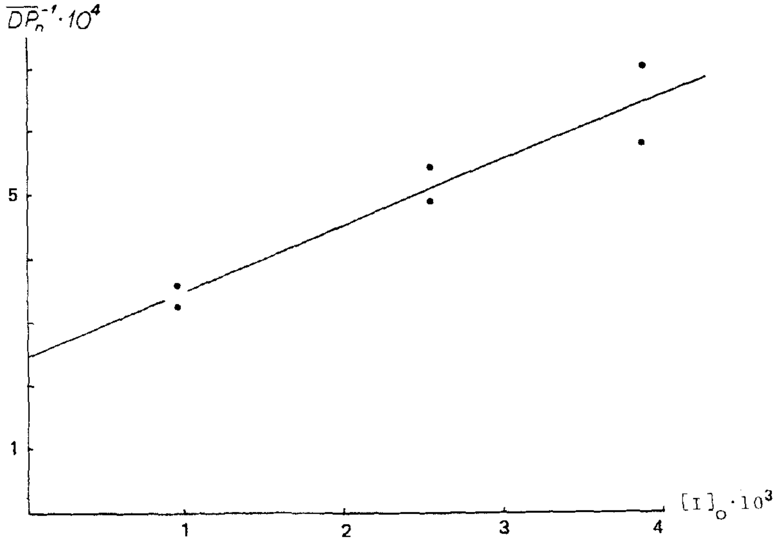


FIG. 2. Determination of C_I at low conversion at -50°C.

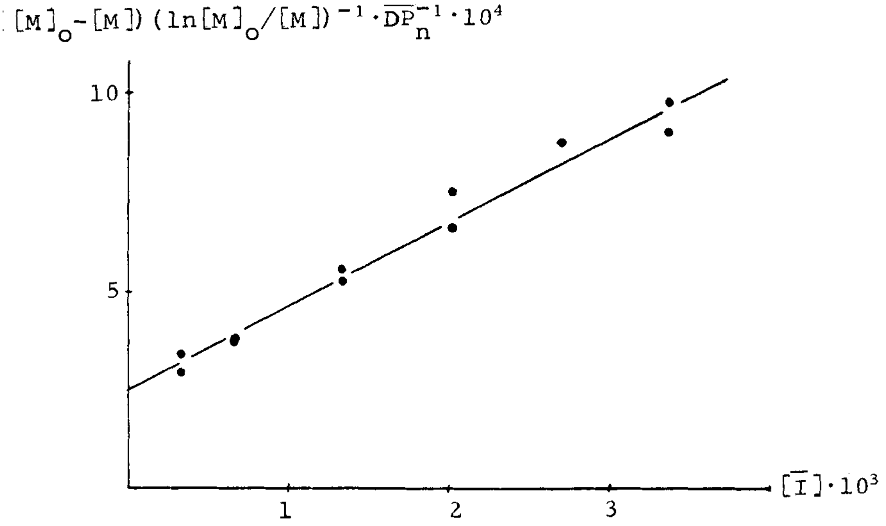


FIG. 3. Determination of C_I at high conversion at -50°C.

TABLE 3. Chain Transfer Constants (C_I) and k_t/k_p Ratios for the iC_4H_8/DCC/BCl_3/CH_2Cl_2 + Methylcyclohexane System. High Conversion Data

T (°C)	CH_2Cl_2 (%)	Conversion (%)	$k_t/k_p \times 10^4$ (M)	$C_I = k_{tr,I}/k_p$	r
-40	60	~50	7.68	0.556	0.989
-50	57	<10	5.0	0.206	0.951
	57	30-40	8.6	0.338	0.966
	64	50-70	5.0	0.423	0.988
	69	85-95	6.7	0.225	0.982
-60	60	60-70	7.2	0.320	0.994
-70	60	75-80	4.5	0.322	0.961

initial charge composition. This agreement supports the approximation used in the derivation of the integrated Eq. (18).

A modest change in solvent polarity does not significantly affect the chain transfer constant. The data obtained at -50°C in experiments

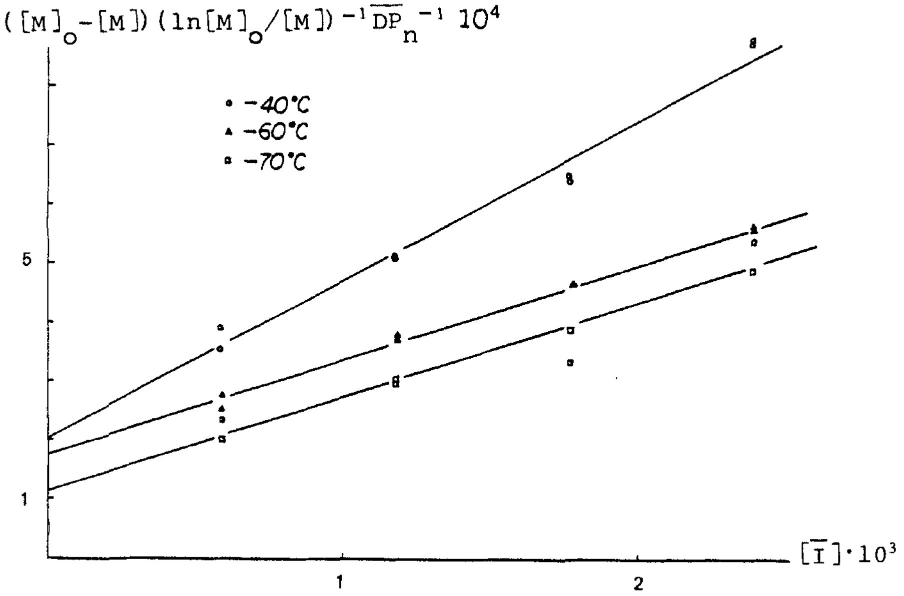


FIG. 4. Determination of C_I at high conversion at -40, -60, and -70°C.

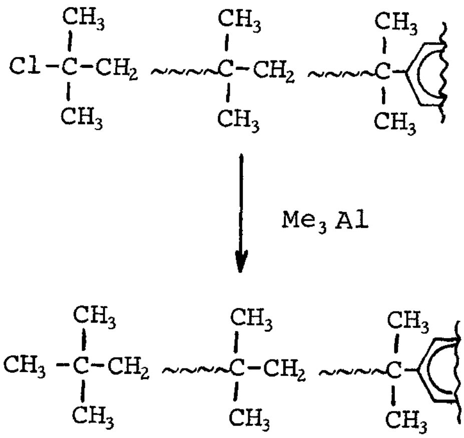
in which the CH_2Cl_2 concentration was increased from 57 to 69%, shown in Table 3, bear out this statement. The composition of the solvent mixture could not be changed over a wider composition range, because below 50% CH_2Cl_2 polymerization did not occur, and at high CH_2Cl_2 content the polymerization became heterogeneous due to PIB precipitation.

The effect of temperature has been studied in the range from -40 to -70°C. Chain transfer constants and k_t/k_p ratios are summarized in Table 3, and Fig. 4 shows inifer plots for -40, -60, and -70°C. The ratios k_t/k_p and C_I obtained at different temperatures yield $E_t - E_p = 1.5$ kcal/mole and $E_{tr,I} - E_p = 1.5$ kcal/mole where E_t, $E_{tr,I}$, and E_p are, respectively, activation energies of termination, chain transfer to inifer, and propagation. In line with these low activation energy differences, the molecular weight of polymers governed by these ratios are only slightly affected by temperature.

Evidently chain transfer to inifer determines both molecular weights and endgroups.

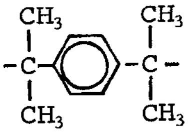
Structure

Earlier NMR studies [2] concerning the detailed structure of Cl–PIB–Cl have been extended by analyzing structural elements of a low molecular weight Cl–PIB–Cl sample and its methylated derivative CH_3–PIB–CH_3. A low molecular weight Cl–PIB–Cl sample (M_n = 2000, prepared by using DCC/BCl_3, i-C_4H_8 = 1 M, CH_3Cl solvent at -40°C) was treated with $(CH_3)_3Al$ to convert the chlorine endgroups to CH_3 termini [3]:



Figures 5(a) through 5(c) show ^1H NMR spectra of the original Cl–PIB–Cl and the product. The spectra of Cl–PIB–Cl (5a) and CH_3–PIB–CH_3 (5c) both exhibit strong signals at 1.1 and 1.4 ppm, corresponding to methyl (1) and methylene (2) protons of polyisobutylene. The relatively weak signal at 7.1 ppm in the region of aromatic protons is associated with the four aromatic protons of the inifer residue (3). The signal at 1.3 ppm evident in both spectra was attributed to the 12 methyl protons of the inifer residue (4) [2]. The two resonances at 1.65 and 1.9 ppm in the spectrum of Cl–PIB–Cl (5a) disappear on methylation and are absent in the spectrum of CH_3–PIB–CH_3 (5c). These signals are due to the methyl (5) and methylene (6) protons in the vicinity of the chlorine chain end, and their intensity ratio is 3:1 by integration.

The intensity of aromatic protons (3) relative to terminal methyl protons (5) and terminal methylene protons (6) is 1:3 and 1:1, respectively. According to this finding, Cl–PIB–Cl contains one residue



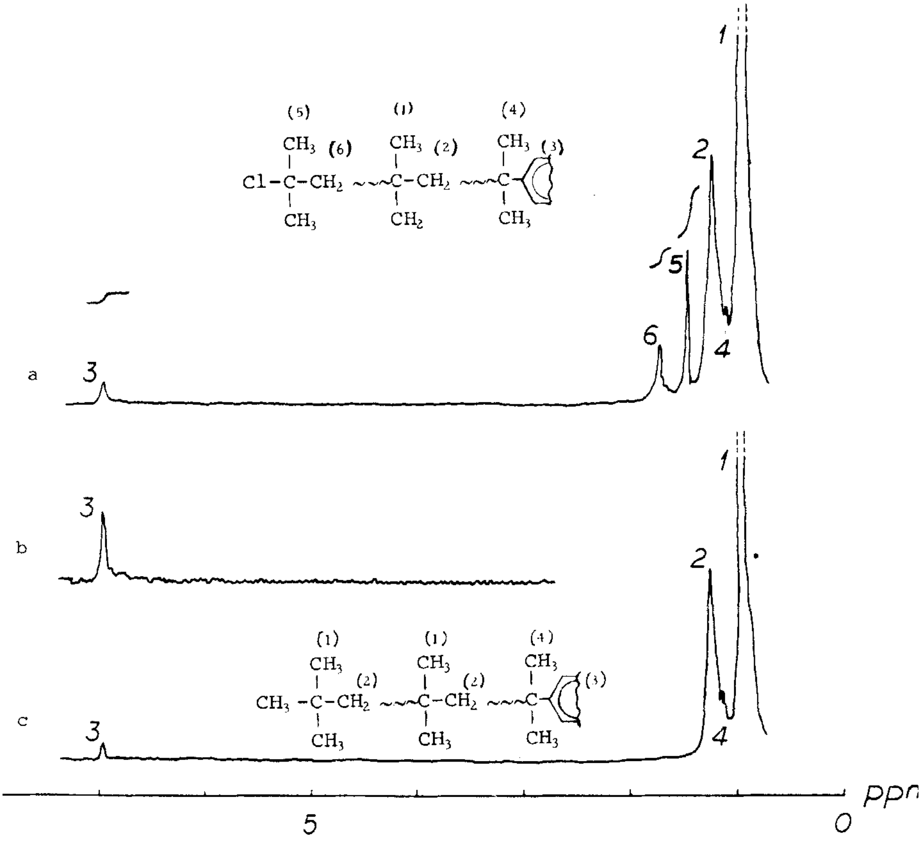
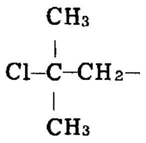


FIG. 5. NMR spectra. (a) Cl–PIB–Cl ($\overline{M}_n$ = 2000). (b) Cl–PIB–Cl; the region of aromatic and unsaturated protons at higher sensitivity. (c) CH_3–PIB–CH_3.

and two termini



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

The region of aromatic and unsaturated protons was examined at higher sensitivity (Fig. 5b); however, there was no evidence for the

TABLE 4. Comparison between Number-Average Molecular Weights Obtained by NMR and GPC Techniques

By NMR	By GPC
4000[a]	4300
3700	3600
3100	2900
2100	2200

[a] By vapor pressure osmometry $M_n = 3800$.

presence of unsaturated proton in the 3-6 ppm range. Chain transfer to monomer during the synthesis of Cl–PIB–Cl would give rise to terminal unsaturation. The spectra (particularly 5b) show no evidence for terminal double bonds although the molecular weight of the samples was sufficiently low for reliable analysis of aromatic protons introduced by the inifer. This indicates that chain transfer to monomer is negligible during the preparation of Cl–PIB–Cl.

In addition to structural insight, ^{1}H NMR spectroscopy also provided valuable molecular weight information of general significance. Thus by the use of sufficiently low molecular weight samples and integrated ^{1}H NMR spectra, the intensity ratio between aromatic ($-C_6H_4-$) and CH_3- and $-CH_2-$ protons has been determined. Since, akin to an internal standard, each Cl–PIB–Cl molecule contains one $-C_6H_4-$ group, ^{1}H NMR spectroscopy could be used for M_n determination. Simultaneously the M_n of the same set of samples have also been obtained by GPC and the data compared. Table 4 shows the results. Evidently, agreement between $\overline{M}_n$'s obtained by ^{1}H NMR spectroscopy and GPC are satisfactory. This agreement of the data obtained by the rather accurate (±5%) and direct spectroscopic and less accurate (±10%) and indirect GPC method lends credence to our GPC method routinely used with higher molecular weight samples ($M_n > 4000$) whose $\overline{M}_n$ cannot be obtained by ^{1}H NMR due to the weak and therefore inaccurate aromatic resonances.

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