

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Living Carbocationic Polymerization. XXIII. Analysis of Slow Initiation in Living Isobutylene Polymerization

M. Zsuga^{ab}; J. P. Kennedy^a; T. Kelen^c

^a Institute of Polymer Science The University of Akron, Akron, Ohio ^b Institute of Applied Chemistry, Kossuth Lajos University, Debrecen, Hungary ^c Institute of Applied Chemistry Kossuth Lajos University, Debrecen, Hungary

To cite this Article Zsuga, M. , Kennedy, J. P. and Kelen, T.(1989) 'Living Carbocationic Polymerization. XXIII. Analysis of Slow Initiation in Living Isobutylene Polymerization', Journal of Macromolecular Science, Part A, 26: 9, 1305 — 1319

To link to this Article: DOI: 10.1080/00222338908052050

URL: <http://dx.doi.org/10.1080/00222338908052050>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIVING CARBOCATIONIC POLYMERIZATION. XXIII. ANALYSIS OF SLOW INITIATION IN LIVING ISOBUTYLENE POLYMERIZATION

M. ZSUGA[†] and J. P. KENNEDY*

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

T. KELEN

Institute of Applied Chemistry
Kossuth Lajos University
4010 Debrecen, Hungary

ABSTRACT

The aim of this research was to develop a quantitative treatment of the consequences of relatively slow initiation on \bar{M}_n and N (the number of molecules formed, W_p/\bar{M}_n , where W_p = weight of polymer formed) in living carbocationic polymerizations, particularly for the case of the incremental monomer addition (IMA) technique. This has been achieved by analysis of the effect of initiator efficiency ($I_{eff}(\%) = 100N/[I_0]$, where $[I_0]$ = initiator input) on \bar{M}_n versus W_p , and N versus W_p plots. Three types of systems have been discerned: 1) I_{eff} equal to 100%; 2) I_{eff} constant but less than 100%; and 3) I_{eff} less than 100% but increasing with increasing number of monomer increments j by the IMA technique. Thus conditions can be found under which slowly initiating systems yield close to "ideal" product, i.e., one with $\bar{DP}_n = [M_0]/[I_0]$

[†]Visiting scientist. Permanent address: Institute of Applied Chemistry, Kossuth Lajos University, 4010 Debrecen, Hungary.

(60.3%) (2); mp 96-98°C (Ref. 6: 97°C), $^1\text{H-NMR}$: 1.26 ppm (s, 12H), 5.67 ppm (s, 2H) in CCl_4 solution. According to $^1\text{H-NMR}$ spectroscopy, the product contained 17% unconverted starting material.

***trans*-2,5-Diacetoxy-2,5-dimethyl-3-hexene (DiOAcDMH₆) (3)**

The acetylation of (2) was carried out according to Paulson et al. [7]. Thus, 4.0 g crude (2) gave 3.2 g (50.9%) (3); mp = 71-73°C (Ref. 7: 71°C), $^1\text{H-NMR}$: 1.52 ppm (s, 12H), 1.95 ppm (s, 6H), 5.85 ppm (s, 2H) in CCl_4 (Ref. 7: 1.48 ppm (s, 12H), 1.92 ppm (s, 6H), 5.84 ppm (s, 2H)).

The source and purification of isobutylene, BCl_3 , and solvents, and details of polymerization and polymer purification have been described previously [3, 8]. Specific further information is given in figure and table captions. $^1\text{H-NMR}$ spectra were recorded on a Varian T-60 spectrometer with TMS as internal standard. Molecular weights were determined by a Waters high-pressure GPC instrument (Model 6000A pump, a series of five μ -Styragel columns (10^5 , 10^4 , 10^3 , 500, 100 Å), a differential refractometer Model 2401, and a UV absorbance detector Model 440. The calibration was made with well-fractionated polyisobutylene standards [2].

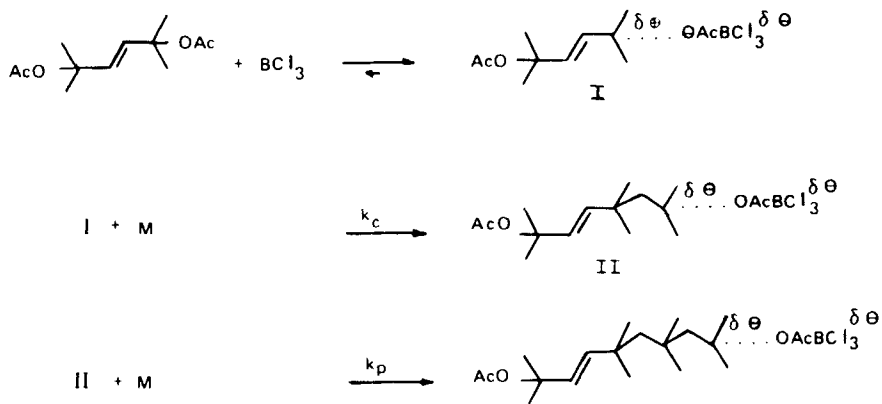
III. RESULTS AND DISCUSSION

Polymerization of Isobutylene by the DiOAcDMH₆/BCl₃ System

One of our continuing objectives is the convenient synthesis of telechelic polyisobutylenes by aliphatic initiators to prevent unacceptable indanyl head-group formation [8, 9]. Research with the aliphatic "binifer" system $\text{Cl}(\text{CH}_3)_2\text{CCH}=\text{CHC}(\text{CH}_3)_2\text{Cl}/\text{BCl}_3$ [10] and aliphatic bifunctional living initiating system $\text{AcO}(\text{CH}_3)_2\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OAc}/\text{BCl}_3$ [8] has demonstrated the validity of this approach. In line with this background, research has recently been focusing on the DiOAcDMH₆/BCl₃ combination, readily obtainable from commercially available starting materials. Encouraging orientation experiments were followed up by quantitative kinetic investigations.

The elementary steps involved in initiation and propagation of living isobutylene polymerization by the DiOAcDMH₆/BCl₃ initiating system may be illustrated by Scheme 2. The process may be visualized to start with the formation of polarized Species I (ion generation). The latter adds monomer to yield II (cationation), which then continues the chain (propagation).

Figures 1 and 2 and Table 1 show representative results obtained with the



SCHEME 2.

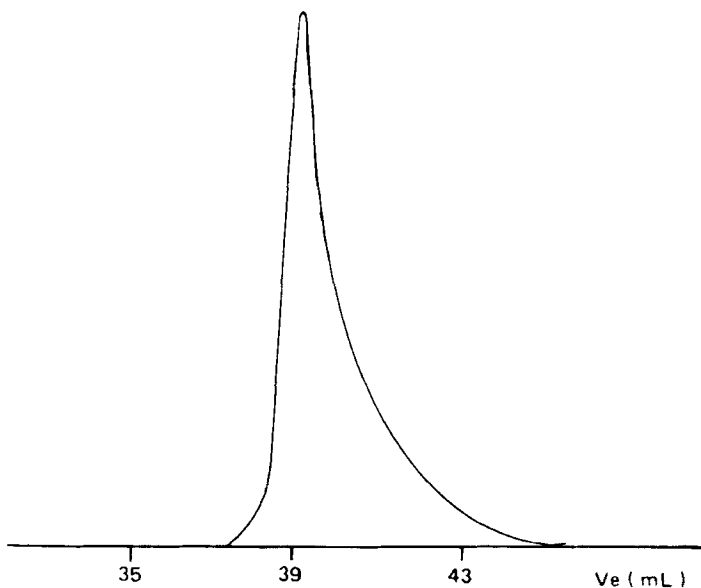


FIG. 1. A representative GPC trace of a PIB sample ($\bar{M}_n = 4590$; the first sample by the IMA technique; MeCl ; $[\text{BCl}_3] 0.11 \text{ mol/L}$, $[\text{I}_0] 3.7 \text{ mmol/L}$, $[\text{M}_0] = 0.19 \text{ mol/L}$, $V_0 = 25 \text{ mL}$, 10 min , -35°C).

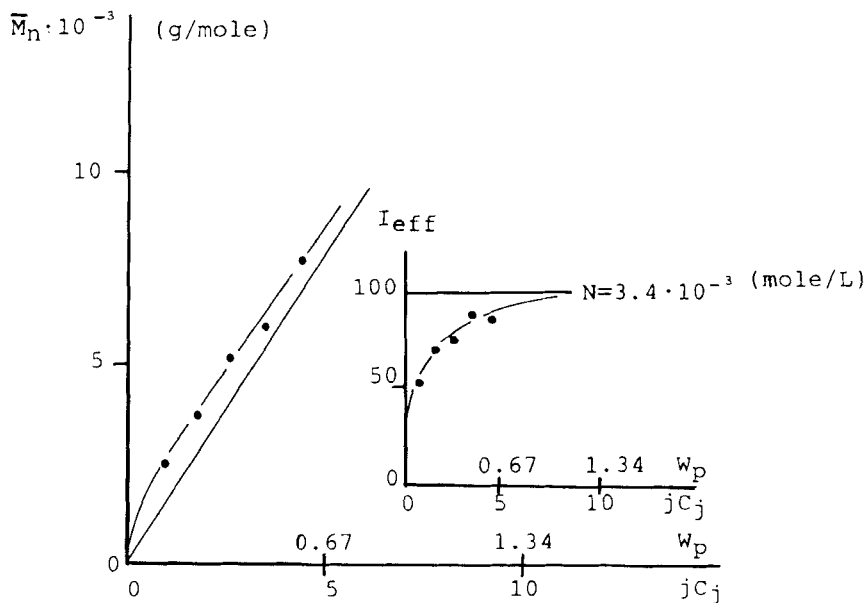


FIG. 2. \bar{M}_n vs W_p and N vs W_p plots. (IMA method, MeCl, $[\text{BCl}_3]$ 0.11 mol/L, $\Delta M = 0.096$ mol/L, $[I_0]$ 3.4 mmol/L, $V_0 = 25$ mL, 10 min, -35°C). The curve was calculated by Eq. (10), and the straight line gives the "ideal" case, i.e., $I_{eff} = 100\%$.

TABLE 1. Polymerization of Isobutylene by the *trans*-2,5-Diacetoxy-2,5-dimethyl-3-hexene/ BCl_3 Initiating System^a

j	Yield, %	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n	I_{eff}
1	96	2.5	1.19	58
2	88	3.7	1.30	70
3	87	5.3	1.37	73
4	88	6.1	1.44	87
5	90	7.8	1.42	85

^aConditions: IMA Method, MeCl, $[\text{BCl}_3] = 0.11$ mol/L, $[I_0] = 3.4$ mol/L, $\Delta M = 0.096$ mol/L, $V_0 = 25$ mL, 10 min, -35°C .

DiOAcDMH₆/BCl₃/isobutylene system under the conditions specified in the captions. Polymerizations were homogeneous even after the addition of the last 0.096 mol/L monomer increment by the IMA technique, and the system remained precipitation-free up to $\bar{M}_n \approx 8000$. By the use of larger monomer increments (e.g., 0.192 mol/L), precipitation started as early as at $\bar{M}_n \approx 6000$. As shown by Fig. 1, the GPC traces of the products obtained by the AMI (i.e., by the first step of IMA) technique showed a persistent low molecular weight tail, and consequently the molecular weight distributions were somewhat broader than anticipated for a fast-initiating living polymerization. In contrast, the molecular weight distributions obtained by the IMA technique become broader after adding the second, third, etc., monomer increments.

While the \bar{M}_n values grew monotonically, the I_{eff} values were initially low but increased with j , the number of incremental monomer additions. The data are collected in Table 1 and illustrated in the inset of Fig. 2. The yields are $\sim 100\%$ within what is considered to be unavoidable losses during polymer work-up. Figure 2 shows further consequences of slow initiation, i.e., higher than ideal \bar{M}_n and a lower than ideal N . Similar features have been observed in other slowly initiating polymerization systems as well [2, 5].

On analyzing the results, we became aware of the absence of a general quantitative analysis of the consequences of a relatively low rate of initiation (R_i) and a high rate of propagation (R_p) in cationic systems. In carbocationic polymerization the overall rate of the polymerization is high, i.e., the final yield is reached within the shortest time. Therefore, the living nature of polymerization has to be investigated by the IMA technique [2] and by plotting the directly obtainable final \bar{M}_n values as a function of W_p . Thus, one of the purposes of this paper is to examine the consequences of the IMA technique on $\bar{M}_n = W_p/N$ and I_{eff} .

A survey of numerous published [2-5, 8, 9, 12-14] and unpublished living carbocationic systems showed essentially three types of systems in terms of I_{eff} : I) The ideal case in which $I_{eff} = 100\%$; II) systems in which I_{eff} is less than 100% but constant; III) systems in which I_{eff} increases with j , the number of incremental monomer additions (i.e., slow IMA systems). As shown schematically in Fig. 3, these systems (I-III) can be readily diagnosed by \bar{M}_n versus W_p plots, and corresponding N or I_{eff} versus W_p plots.

In Case I, $I_{eff} = 100\%$, the \bar{M}_n versus W_p plot is linear, passing through the origin with a slope of $1/[I_0]$ [3, 8, 9, 12, 14] and the corresponding N versus W_p plot is a horizontal line with $N = [I_0] = \text{constant}$. In these systems $R_t = 0$ and $R_{tr} = 0$, and $R_i > R_p$, as reflected by the relatively narrow, close-to-Poisson, molecular weight distributions.

In Case II, $I_{eff} < 100\%$ but constant [4, 5, 12], the \bar{M}_n versus W_p plot is

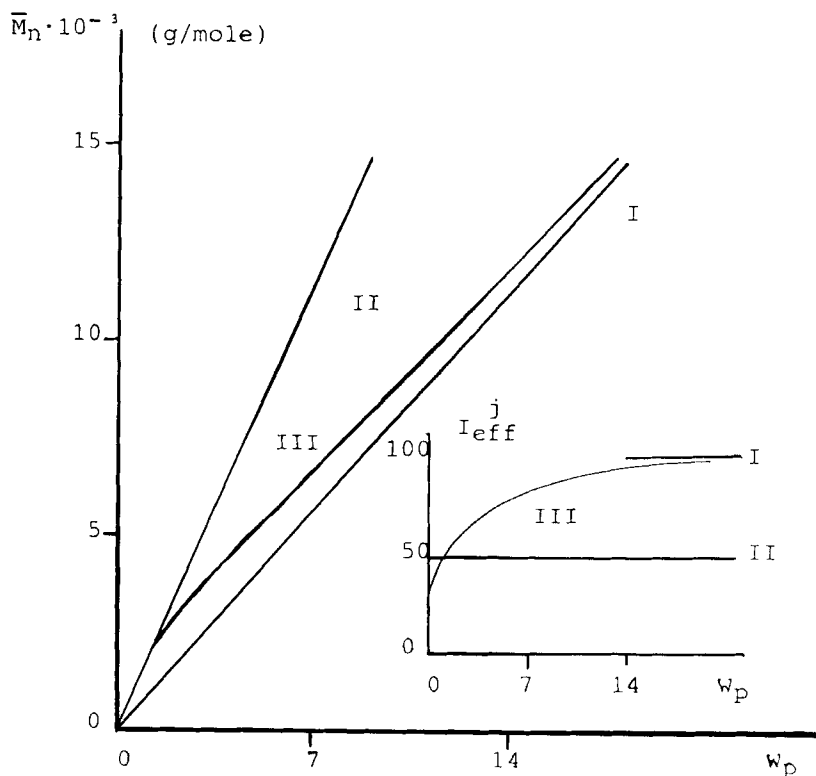


FIG. 3. \bar{M}_n vs W_p and N vs W_p plots for $I_{eff} = 100\%$ (I), $I_{eff} = 50\%$ (II), and for I_{eff} calculated according to Eq. (10) with $Q = 0.1$ (III) ($\Delta M = 0.5$ mol/L, $[I_0] = 0.05$ mol/L, $V_0 = 25$ mL).

also linear and passes through the origin; however, the slope is $1/([I_0]I_{eff}/100)$. The corresponding N versus W_p plot is also horizontal, but $N = [I_0]I_{eff}/100 = \text{constant}$. These correlations also indicate that $R_t = 0$ and $R_{tr} = 0$. However, in these systems $[I_0]_{exp} < [I_0]_{theor}$ for a variety of possible reasons, e.g., presence of impurities, etc. For the IMA technique, this scenario may also arise if the lifetime of the initiating system is shorter than the time interval preceding the next monomer addition.

In Case III, I_{eff} increases with j , as in numerous IMA systems [2, 5], the \bar{M}_n versus W_p plot exhibits a characteristic curved shape above the ideal

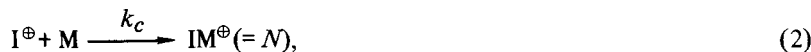
($I_{eff} = 100\%$) straight line, and converges toward it at higher j values. The corresponding N versus W_p plot starts below the ideal ($N = [I_0]$) horizontal line and approaches it exponentially with increasing j . This situation arises for the IMA technique only when $R_i < R_p$ and the initiating system is stable. In these instances the initiator is not consumed entirely during the first, second, etc., monomer increments but continues slowly to initiate throughout the IMA experiment. The concentration of active species is not constant in such systems, which seems to violate the rigorous definition of living polymerization [11]. Can such a polymerization be regarded as living, and how should one treat the experimental data, in particular \bar{M}_n and N ? The answer may be provided by the following analysis.

By definition, living polymerizations involve only initiation and propagation, but initiation occurs in two steps in carbocationic polymerization: ion generation and cationation [15], and either step may become rate determining. Schematically:

Ion generation:



Cationation:



Propagation:



where I is initiator and M is monomer, while k_c and k_p are the rate constants of the steps indicated. The positive charge does not necessarily indicate a free cationic species, rather it stands for any cationically active chain end including undissociated polarized complexes.

In our case cationation is expected to be the rate-determining step due to the highly stable, less reactive allyl cation formed by ion generation (see Scheme 2). Thus, the rates of initiation and propagation are

$$R_i = \frac{dN}{dt} = k_c [I] [M] = k_c ([I_0] - N) [M], \quad (4)$$

$$R_p = \frac{dP}{dt} = k_p N[M], \quad (5)$$

where $[I]$ and $[I_0]$ are the actual and initial initiator concentrations, respectively, and P denotes the moles of monomer M built into the polymer. The differential equation system of Eqs. (4) and (5) has been studied by Litt [16] and others (see Ref. 17) for anionic systems.

If k_p/k_c is large,

$$\frac{[M_0]}{[I_0]} \approx -(k_p/k_c)[I_{eff}/100 + \ln(1 - I_{eff}/100)], \quad (6)$$

where $[M_0]$ is the total amount of monomer added. Szwarc et al. [18] recently showed that in this case $[I_0] - N$ is independent of the actual concentration of monomer, and the final I_{eff} does not depend on the manner of monomer addition. Thus, Eq. (6) can be recast:

$$j \frac{k_c \Delta M C_j}{k_p [I_0]} = -\ln(1 - I_{eff}^j/100) - I_{eff}^j/100, \quad (7)$$

where ΔM is the monomer increment, C_j is the apparent conversion, and I_{eff}^j is the apparent initiator efficiency after the addition of the j th monomer increment. According to Eq. (7),

$$I_{eff}^j/100 = 1 - \exp(-Qj - I_{eff}^j/100), \quad (8)$$

where

$$Q = \frac{k_c \Delta M C_j}{k_p [I_0]} \quad (9)$$

The extent by which I_{eff}^j is less than 100% is a quantitative measure of R_i/R_p .

Equation (8) cannot be solved in explicit form, but I_{eff}^j s can be obtained graphically, as illustrated in Fig. 4. Table 2 gives representative calculated I_{eff}^j values as a function of the number of incremental monomer additions. For $Q = 1.0$, I_{eff}^j reaches nearly 100 with the third or fourth increment. Obviously, the AMI and IMA techniques are identical at $j = 1$, i.e., the AMI technique is a limiting case of the IMA process.

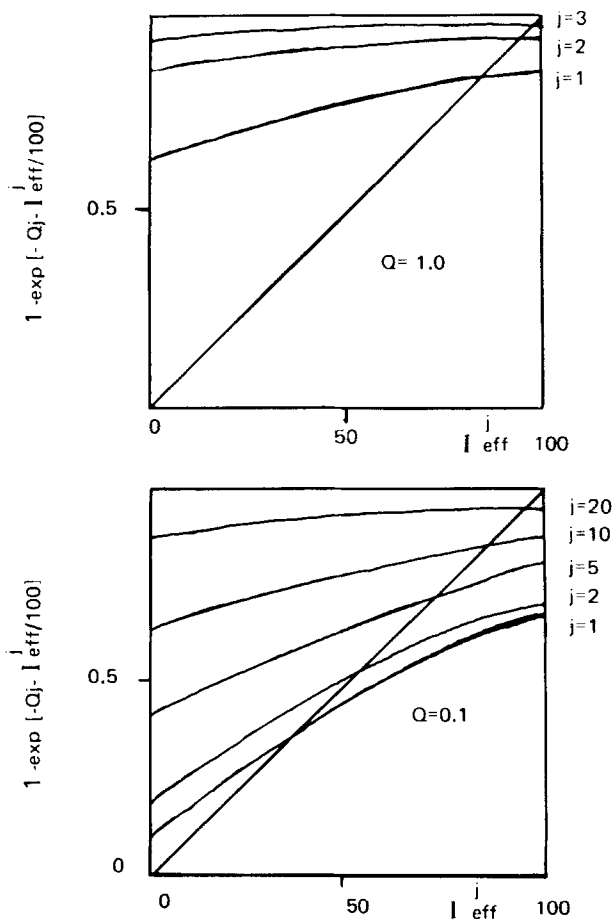


FIG. 4. Graphical solution of Eq. (8) (from $k_p/k_c = 10^3$, $\Delta M = 0.5$ mol/L, $[I_0] = 0.5$ mmol/L). Intersections with the diagonal give I_{eff}^j at a given Q and j .

We are now ready to calculate the \bar{M}_n obtained in an IMA series after the j th monomer addition:

$$\bar{M}_n^j = \frac{j(\Delta M)\mu C_j}{[I_0]I_{eff}^j/100} = \frac{W_p^j}{[I_0]I_{eff}^j/100}, \quad (10)$$

TABLE 2. Graphically Determined Initiator Efficiencies for Different Numbers of Monomer Additions^a

Q	j	$I_{eff}^j, \%$	Q	j	$I_{eff}^j, \%$
1.0	1	85	0.1	1	36
1.0	2	94	0.1	2	51
1.0	3	98	0.1	5	72
1.0	4	99.5	0.1	10	85
			0.1	20	94

^aFor parameters see caption to Fig. 4.

where μ is the molecular weight of the monomer and W_p^j is the weight of the polymer after the j th monomer increment. The lines III in Fig. 3 were calculated from the data in Table 2 for $Q = 0.1$. Evidently, by increasing the number of monomer increments j , an ideal (rapidly initiating) system ($I_{eff}^j = 100\%$) is approached. Since k_c and k_p are characteristic for a given system, the only way to increase the rate of convergence of a relatively slowly initiating system to the ideal is by increasing Q , that is, to increase $\Delta M/[I_0]$ (see Eq. 9).

Figure 5 shows the effect of Q on the rate of this converge of I_{eff}^j as a function of j . Evidently a *pro forma* nonliving system (i.e., one in which the number of living species is not constant [11]) rapidly approaches the character of a truly living system if the number of incremental monomer addition steps is increased. Thus, since

$$\lim_{j \rightarrow \infty} I_{eff}^j = 100,$$

an "ideal" polymer can be prepared even with slowly initiating systems by continuous slow monomer addition.

In our case the increase of I_{eff}^j with j can be described by Eq. (7). Thus, in line with Eq. (7), the slope of the plots in Fig. 6 yields

$$Q = \frac{k_c}{k_p} \frac{\Delta M}{[I_0]},$$

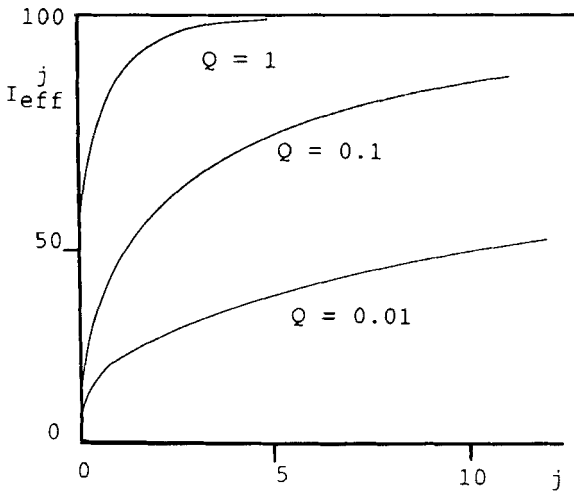


FIG. 5. The effect of Q on calculated I_{eff}^j versus j plots.

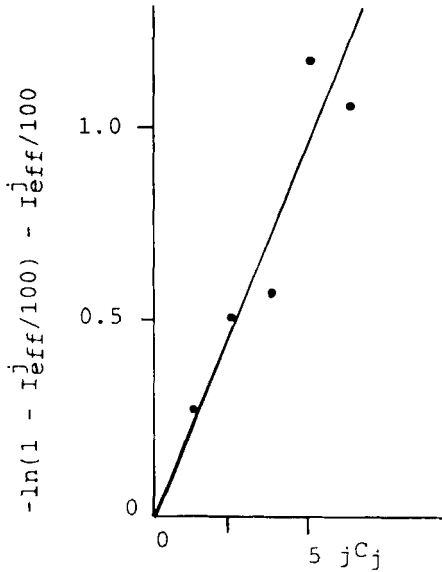


FIG. 6. Plot of $-\ln(1 - I_{eff}^j/100) - I_{eff}^j/100$ vs jC_j from data of Table 1.

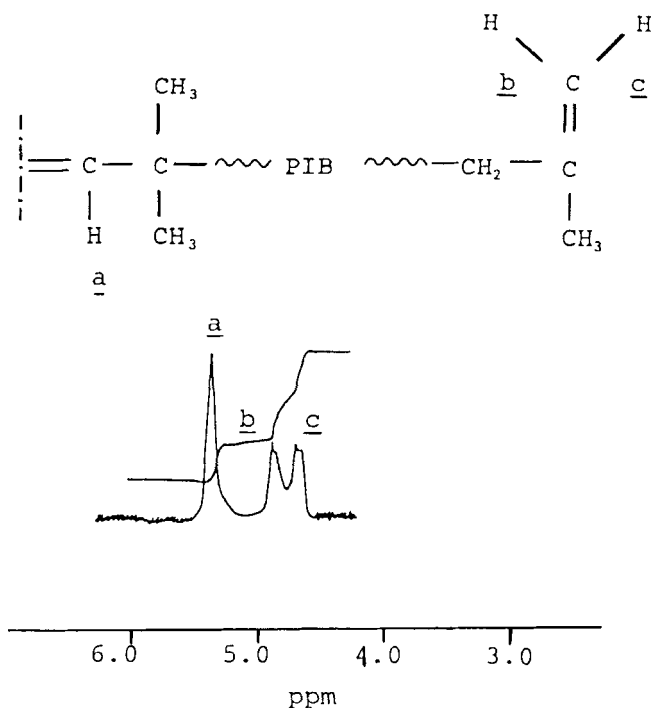


FIG. 7. Part of the $^1\text{H-NMR}$ spectrum of dehydrochlorinated PIB obtained by using the *trans*-2,5-diacetoxy-2,5-dimethyl-3-hexene/ BCl_3 system.

and by knowing ΔM and $[I_0]$, we can estimate k_c/k_p . According to the linear plot through the origin in Fig. 6, $Q = 0.26$ and $k_c/k_p = 0.009$. (The correlation coefficient is 0.973 and the intercept of the least-square plot is 0.01, which is considered to be within experimental error.) The linear nature of the plot passing through the origin in Fig. 6 supports the mechanism proposed, i.e., that cationation, a reaction first order in monomer, is rate determining. The k_c/k_p values obtained in this manner can be used to quantify slowly initiating systems in general. This powerful diagnostic tool is being explored further.

The structure of the polymers obtained under homogeneous conditions have been determined. Figure 7 shows the critical part of a representative $^1\text{H-NMR}$ spectrum together with assignments. To facilitate $^1\text{H-NMR}$ spectroscopic investigations, the $-\text{C}(\text{CH}_3)_2\text{Cl}$ end groups of the starting polymers were quan-

titatively converted by our routine method [19] $-\text{C}(\text{CH}_3)=\text{CH}_2$ end groups. The two protons due to the $-\text{CH}=\text{CH}-$ initiator fragment (5.37 ppm) serve as internal standards for the four $-\text{CH}_2$ protons resonating at 4.62 and 4.83 ppm. Integration yields the number-average end functionality, $\bar{F}_n = 2.04 \pm 0.05$, which is strong evidence that the PIB's obtained in these investigations are indeed bifunctional *t*-chlorine telechelic materials and that chain transfer to monomer was absent during the synthesis.

ACKNOWLEDGMENTS

Support by NSF Grants DMR-84-18617 and INT-860-7993 are gratefully acknowledged. Helpful discussions with Drs. R. Faust, B. Iván, and G. Kaszás are also appreciated.

REFERENCES

- [1] For the previous paper in this series, XXII, see M. Zsuga, J. P. Kennedy, and T. Kelen, *Polym. Bull.*, **19**, 427 (1988).
- [2] R. Faust and J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1847 (1987).
- [3] B. Wang, M. K. Mishra, and J. P. Kennedy, *Polym. Bull.*, **17**, 205 (1987).
- [4] B. Wang, M. K. Mishra, and J. P. Kennedy, *Ibid.*, **17**, 213 (1987).
- [5] M. K. Mishra and J. P. Kennedy, *J. Macromol. Sci.—Chem.*, **A24**(8), 933 (1987).
- [6] K. Alder and H. von Brachel, *Ann. Chem.*, **608**, 195 (1957).
- [7] D. R. Paulson, L. S. Gilliam, V. O. Terry, S. M. Farr, E. J. Parker, Y. N. Tang, R. Ullman, and G. Ribar, *J. Org. Chem.*, **43**(9), 1783 (1978).
- [8] R. Faust, A. Nagy, and J. P. Kennedy, *J. Macromol. Sci.—Chem.*, **A24**, 595 (1987).
- [9] M. K. Mishra and J. P. Kennedy, *Polym. Bull.*, **17**, 7 (1987).
- [10] S. Mah, R. Faust, M. Zsuga, and J. P. Kennedy, *Ibid.*, **18**, 433 (1987).
- [11] J. P. Kennedy, T. Kelen, and F. Tüdös, *J. Macromol. Sci.—Chem.*, **A18**(9), 1189 (1982-83).
- [12] M. K. Mishra, B. Wang, and J. P. Kennedy, *Polym. Bull.*, **17**, 307 (1987).
- [13] R. Faust, A. Fehérvári, and J. P. Kennedy, *Br. Polym. J.*, **19**, 379 (1987).

- [14] G. Kaszás, J. Puskás, and J. P. Kennedy, *Polym. Bull.*, **18**, 123 (1987).
- [15] J. P. Kennedy and E. Maréchal, *Carbocationic Polymerization*, Wiley-Interscience, New York, 1982.
- [16] M. Litt, *J. Polym. Sci.*, **58**, 429 (1962).
- [17] M. Szwarc, *Carbanions, Living Polymers and Electron Transfer Processes*, Wiley-Interscience, New York, 1968.
- [18] M. Szwarc, M. van Beylen, and D. van Hayweghen, *Macromolecules*, **20**, 445 (1987).
- [19] J. P. Kennedy, V. S. C. Chang, R. A. Smith, and B. Iván, *Polym. Bull.*, **1**, 575 (1979).

Received August 2, 1988