Living Carbocationic Polymerization. 31. A Comprehensive View of the Inifer and Living Mechanisms in Isobutylene Polymerization

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ABSTRACT: The polymerization of isobutylene (IB) has been studied by use of a 1,4-bis(1-chloro-1-methylethyl)benzene (DiCumCl)/BCl_3 initiating system in CH_3Cl, CH_2Cl_2, and C_2H_5Cl solvents and a 90:10 v/v CH_3Cl/*n*-hexane mixture at −75 °C. It has been found that in these media the polymerizations are living and that they occur in two phases: an "initial phase" during which simultaneous slow initiation and chain transfer to DiCumCl ("inifering") plus propagation and reversible termination occur (i.e., a phase characterized by simultaneous inifering and living polymerization) and, after the DiCumCl is consumed, a "living phase" during which only propagation and reversible termination proceed (i.e., a phase characterized by exclusively living polymerization). Further, the initial phase is characterized by low initiating efficiencies ($I_{\mathrm{eff}} < 100\%$) while in the subsequent living phase $I_{\mathrm{eff}} \sim 100\%$. The absence of irreversible termination ($k_t/k_p \sim 0$) during the initial phase has been demonstrated by inifer plots, which also led to the inifer constants ($k_{\mathrm{tr,I}}/k_p = C_I$) of 0.96 in CH_3Cl and 0.49 in CH_2Cl_2 diluent. Diagnostic $-\ln(1 - I_{\mathrm{eff}}^j) - I_{\mathrm{eff}}^j$ versus jC_j plots indicate that DiCumCl is consumed by slow initiation and chain transfer. Evidently DiCumCl is a true inifer (*ini*tiator and trans*fer* agent), and inifering proceeds till it is completely consumed. After the inifer has been depleted, the living phase commences during which $\bar{M}_n$ increases linearly with the amount of polymer formed. Termination is reversible (i.e., for all practical purposes absent) and involves polyisobutylene ended with chlorine on the tertiary carbon (PIB-Cl^t) plus excess BCl_3 in polar media at low temperature. By increasing the temperature or by decreasing the medium polarity, termination becomes irreversible. Carbocation stability during the polymerization is strongly affected by solvation effects.

Introduction

IB polymerization induced by inifer/BCl_3 systems leads to linear and star-shaped polyisobutylenes (PIB) which carry $CH_2C(CH_3)_2Cl$ end groups.[1–5] These perfectly telechelic polymers have opened numerous avenues toward the preparation of other novel telechelics (see refs 6–8) and sequential copolymers.[9] Kennedy and Smith[1] interpreted the results obtained with the DiCumCl/BCl_3 system (where DiCumCl represents 1,4-bis(1-chloro-1-methylethyl)benzene) by introducing the inifer concept, according to which DiCumCl functions both as initiator and chain-transfer agent. Both chain-breaking processes, i.e., chain transfer to DiCumCl and termination, yield tertiary chlorine termini, and exact telechelics can be prepared provided chain transfer to monomer and indanyl ring formation are absent.[10] Wondraczek et al.[11] tried to explain the results by neglecting transfer to the inifer and considering only the effect of counteranion stability; however, recently collected data[2–5,12,13] support the presence of transfer to the inifer in line with the original proposition.[1] The aliphatic tertiary Cl termini in PIB-Cl^t were believed to be inactive under the experimental conditions used, and therefore it was assumed that the end groups resulting from inifering and/or termination do not sustain propagation.[1–5] However, Nuyken and co-workers,[12,13] on the basis of their findings with the DiCumCl/BCl_3/IB/CH_2Cl_2 and 2-chloro-2,4,4-trimethylpentane/BCl_3 systems, have found evidence for reversible termination involving the PIB-Cl^t chain ends in the presence of excess BCl_3.

Not long after the introduction of the inifer concept, the living polymerization of IB induced by tertiary ester/Lewis acid[14,15] and tertiary ether/Lewis acid systems[16] has been discovered. However, the mechanism of these polymerizations has not yet been completely elucidated.[14–16,23,24] To gain further insight into the mechanism of the inifer and living processes, we have carried out polymerization studies with the DiCumCl/BCl_3/IB system in various solvents and have discovered that both processes are in fact governed by the same principles. This paper concerns efforts to conceptually unite the inifer and living methodologies and provides experimental evidence for a comprehensive view of these two systems.

Experimental Section

A. Materials. Details of the preparation of dicumyl chloride (DiCumCl) have been described.[17] It was recrystallized from petroleum ether the day before the experiments. Sources and purification of isobutylene (IB), boron trichloride, methyl chloride (MeCl), methylene chloride, ethyl chloride (EtCl), and *n*-hexane have been described.[15]

B. Procedures. IB polymerizations were carried out in a drybox under a dry nitrogen atmosphere. The charges were quenched with prechilled methanol. In incremental monomer addition (IMA) experiments,[15] a series of large (~75 mL) test tubes were charged with the initiator, monomer, and solvent, and at time zero BCl_3 coiniator was added to the charges. After a predetermined time interval (Δt), the polymerization was quenched in the first test tube, whereas an additional amount of IB (ΔM) was added to all the other test tubes. After the same time interval, quenching was carried out in the second test tube, and IB was added to the rest of the tubes. This procedure was continued until all the charges were quenched. After evaporation of solvents and removal of boron-containing residues by filtration, the weights of polymers formed were determined. Further experimental details are given in Table I and figure captions.

Molecular weights and molecular weight distributions (MWD) were determined by a Waters high-pressure GPC instrument (Model 6000Å pump) with a series of five μ-Styragel columns (10^5, 10^4, 10^3, 500, and 100 Å), a differential refractometer (Waters, Model 401), and a UV absorbance detector (Waters, Model 440). Calibration was made by narrow MWD PIB standards.

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Table I
Polymerization of Isobutylene by the DiCumCl/BCl_3 System in Various Solvents[a]

solvent	j	W_p, g	yield, %	$\bar{M}_n \times 10^{-3}$, g/mol	$\bar{M}_w/\bar{M}_n$	I_{eff}, %
CH_3Cl	1	0.1404	98	2.5	1.95	49
	2	0.2871	100	3.5	1.70	71
	3	0.4211	98	4.4	1.52	83
	4	0.5720	100	5.0	1.43	100
	5	0.6773	95	5.8	1.33	101
	6	0.7626	89	6.4	1.34	103
	7	0.8739	87	7.3	1.33	103
10:90 v/v CH_3Cl/ *n*-hexane	1	0.1236	86	2.8	2.06	38
	2	0.2354	82	3.8	1.93	54
	3	0.3072	72	4.2	2.01	64
	4	0.3867	68	4.8	1.97	70
	5	0.4823	68	5.3	1.98	80
	6	0.5542	65	5.4	2.14	89
	7	0.5989	60	6.3	2.13	83
	8	0.7045	62	6.7	2.14	91
EtCl	1	0.1418	99	6.3	2.33	20
	2	0.2274	80	7.0	2.64	28
	3	0.2805	65	8.3	2.32	29
	4	0.3343	59	8.9	2.51	33
	5	0.4015	56	11.1	2.46	32
	6	0.4441	52	11.3	2.69	34
	7	0.5108	51	12.0	2.92	37
	8	0.5183	45	10.7	3.48	42
CH_2Cl_2[b]	1	0.1395	98	2.5	3.22	61
	2	0.2597	91	4.5	3.11	63
	3	0.3973	93	5.1	2.60	84
	4	0.5427	95	6.7	2.39	88
	5	0.6804	95	7.1	2.32	102
	6	0.7989	93	8.8	2.31	98
	7	0.8747	86	9.2	2.36	102

[a] −75 °C. IMA method: [DiCumCl] = 4.6×10^{-3} mol/L, [BCl_3] = 0.16 mol/L, [ΔM] = 0.1 mol/L, V_0 = 25 mL, Δt = 20 min, j is the number of monomer increments. [b] [DiCumCl] = 3.7×10^{-3} mol/L.

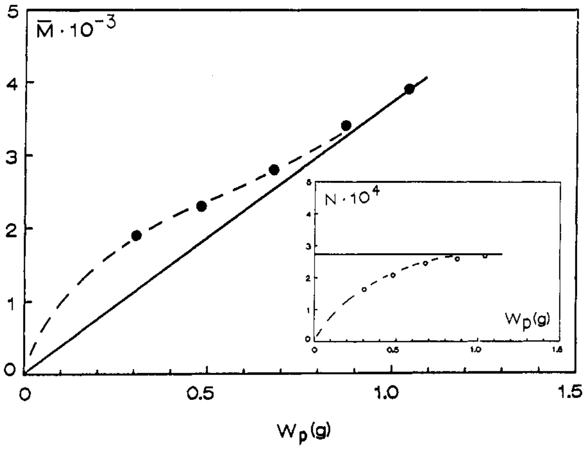


Figure 1. $\bar{M}_n$ versus weight of polymer (W_p) and number of polymer chains (N) versus W_p (inset) plots for the DiCumCl/BCl_3/*i*-C_4H_8/CH_3Cl/−75 °C system. IMA method: [DiCumCl] = 1.1×10^{-2} mol/L, [BCl_3] = 0.1 mol/L, [ΔM] = 0.25 mol/L, V_0 = 25 mL, Δt = 15 min.

Results and Discussion

A. Diagnosis of Inifering and Living Processes. The living polymerization of IB by the DiCumCl/BCl_3 system has been investigated by the diagnostic incremental monomer addition (IMA) method[15] at −75 °C so as to avoid indanyl ring formation.[10] Figure 1 summarizes the results of a set of orienting experiments. The $\bar{M}_n$ of the polymer formed upon the first three or four monomer additions (increments) is above the solid line expected for a rapidly initiated living polymerization (theoretical line) in the $\bar{M}_n$ versus weight of polymer (W_p) plot (i.e., $I_{eff} < 100\%$). This effect is even more apparent in the plot of number of polymer molecules (N) versus W_p (inset), where the horizontal line indicates the number of initiator molecules (I_0) added. After four to five monomer increments, all the DiCumCl is consumed, i.e., $I_{eff} \sim 100\%$, and the data points reach the theoretical lines both in the $\bar{M}_n$ versus W_p and the N versus W_p plots. To diagnose with certainty living polymerization, the addition of further monomer increments would be required. Unfortunately, polar solvents like CH_3Cl and CH_2Cl_2 are poor solvents for high molecular weight PIB, and the polymer rapidly precipitates above $\bar{M}_n \sim 5000$.[18] Thus, to avoid precipitation the amount of monomer added in the increments (ΔM) was reduced, and the polymerizations were carried out also in a 90:10 v/v CH_3Cl/*n*-hexane solvent mixture or in C_2H_5Cl. The data obtained are summarized in Table I and Figures 2–5. In these figures, the solid lines represent theoretical values assuming living polymerization with I_{eff} = 100%. Figures 2 and 3 show the $\bar{M}_n$ versus W_p and N versus W_p plots, respectively, for polymerizations carried out by the use of CH_3Cl, CH_3Cl/*n*-hexane mixture, and C_2H_5Cl solvents. Evidently, in CH_3Cl the DiCumCl is consumed after four monomer increments; thereafter, the $\bar{M}_n$ increases linearly with W_p, and the number of polymer chains remains constant and becomes equal to the number of the DiCumCl molecules employed. Thus, after the initial phase, the linear increase of $\bar{M}_n$ is exclusively due to propagation by polymer chains formed of slow DiCumCl consumption; in other words, after four monomer additions only the living phase remains.

As shown in Table I in the series with CH_3Cl solvent, polydispersity (i.e., $\bar{M}_w/\bar{M}_n$) decreases with j (the number of monomer increments), and after the fourth monomer addition $\bar{M}_w/\bar{M}_n$ drops *below* 1.5, the theoretical value for the DiCumCl/BCl_3 system.[19] This effect is readily explained by the transition from the initially slow DiCumCl consumption phase to the living phase.

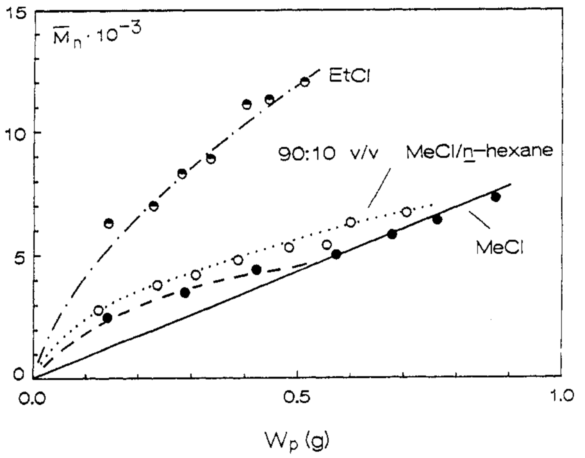


Figure 2. $\bar{M}_n$ as a function of polymer weight (W_p) formed in the DiCumCl/BCl_3/i-C_4H_8/−75 °C systems in various solvents. IMA method: [DiCumCl] = 4.6×10^{-3} mol/L, [BCl_3] = 0.16 mol/L, [ΔM] = 0.1 mol/L, V_o = 25 mL, Δt = 20 min.

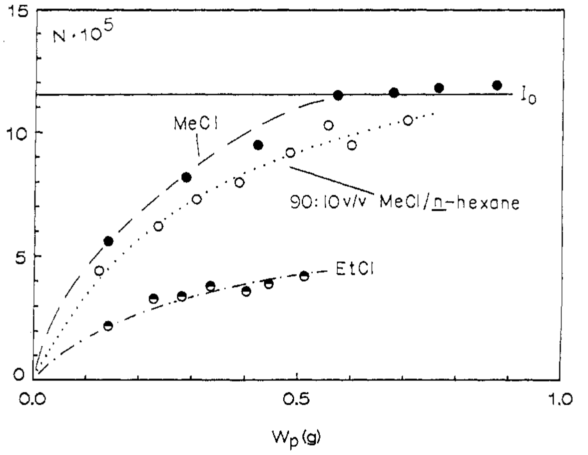


Figure 3. Number of polymer chains (N) as a function of polymer weight (W_p) formed in DiCumCl/BCl_3/i-C_4H_8/−75 °C systems in various solvents. Experimental conditions as in Figure 1.

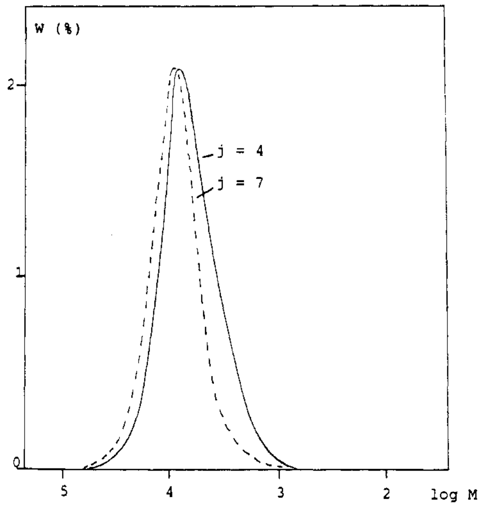


Figure 4. Molecular weight distribution traces of PIB samples formed in the DiCumCl/BCl_3/i-C_4H_8/CH_3Cl/−75 °C system in the fourth and seventh monomer addition steps (j). Experimental conditions as in Figure 2.

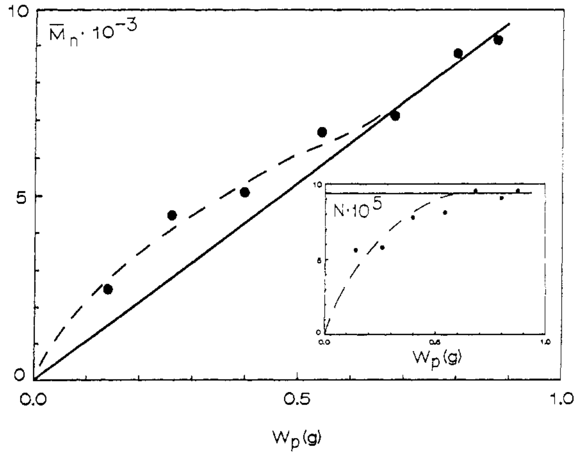


Figure 5. $\bar{M}_n$ versus weight of polymer (W_p) and number of polymer chains (N) versus W_p (inset) plots for the DiCumCl/BCl_3/i-C_4H_8/CH_2Cl_2/−75 °C system. IMA method: [DiCumCl] = 3.7×10^{-3} mol/L, [BCl_3] = 0.16 mol/L, [ΔM] = 0.1 mol/L, V_o = 25 mL, method Δt = 20 min.

Interestingly, according to normalized MWD traces (i.e., weight percent of polymer versus log of molecular weights), representative samples of which are shown in Figure 4, the polymer molecules grew approximately at the same rate in the precipitated phase as in the homogeneous phase (precipitation was apparent by milkiness in the reactor at $\bar{M}_n \sim 5000$). This indicates that precipitation of the polymer did not affect MWD and that precipitation did not significantly affect propagation rates under the conditions studied. Due to possible diffusion control, lower polymerization rates may be expected in the precipitated phase than in the homogeneous phase. However, as our data indicate, monomer diffusion to the active sites was not rate determining, which suggests that swelling of the precipitated polymer by the solvent was sufficient to provide enough monomer for growth. Evidently the decrease of $\bar{M}_w/\bar{M}_n$ with increasing number of monomer increments is mainly due to the living nature of the polymerization and not to physical effects.

To prevent precipitation, i.e., to increase $\bar{M}_n$ in a homogeneous system, a series of experiments have been carried out by the use of a mixture of 10% n-hexane and 90% CH_3Cl. However, as shown by the data in Figures 2 and 3 and in Table I, even this low amount of nonpolar solvent caused a marked decrease in the rates and I_{eff} values, and even after eight monomer increments I_{eff} remained below 100%. This effect is even larger with use of the less polar C_2H_5Cl solvent. Thus, these polymerizations are very sensitive toward even small changes in medium polarity.

A series of IMA experiments have also been carried out with CH_2Cl_2 as diluent. The findings are collected in Figure 5 and Table I. $\bar{M}_n$ is above the theoretical line during the first four monomer increments, and then it reaches the theoretical line and increases linearly with the weight of polymer formed. Similarly, the number of polymer chains (N) increases by increasing the number of monomer increments, and after reaching the number of DiCumCl inifer molecules (I_o) N remains constant and equal to I_o. Evidently, in the latter phase the increase of $\bar{M}_n$ is due to chain growth by monomer addition to living chains. Similar to the results with CH_3Cl diluent, $\bar{M}_w/\bar{M}_n$ decreases with the number of monomer increments; however, the MWDs are broader in CH_2Cl_2 than in CH_3Cl.

Attempts were made to determine the fate of DiCumCl during the initial relatively slow initiator consumption phase. Thus, experiments were designed to obtain inifer plots at a relatively low monomer concentration. Figures 6 and 7 show such plots by the use of CH_3Cl and CH_2Cl_2, respectively. The slope of the inifer plot gives the ratio of chain transfer to inifer over propagation rate

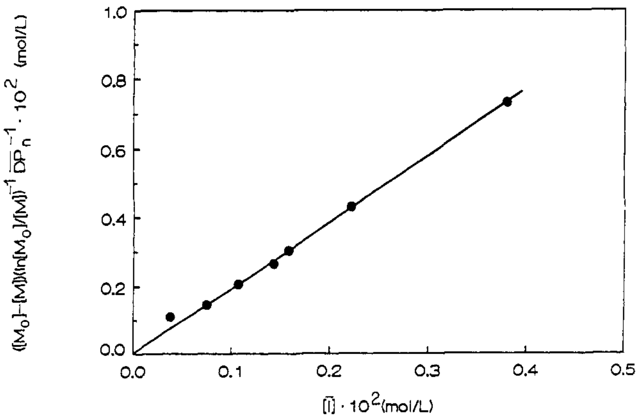


Figure 6. Inifer plot for the DiCumCl/BCl_3/i-C_4H_8/CH_3Cl/-75 °C system.

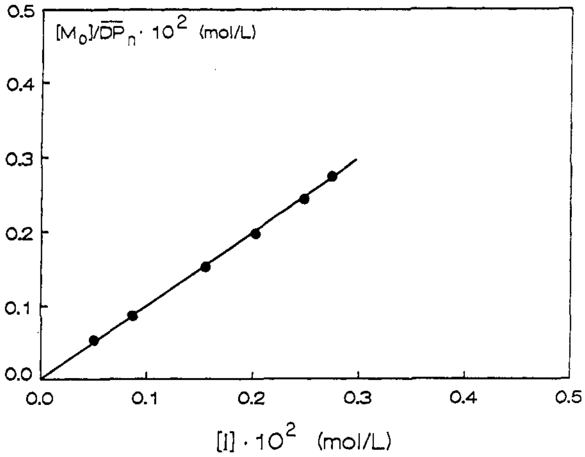


Figure 7. Inifer plot for the DiCumCl/BCl_3/i-C_4H_8/CH_2Cl_2/-75 °C system.

constants $k_{tr,I}/k_p$ (=C_I inifer constant), while the intercept gives the ratio of termination over propagation rate constants k_t/k_p.[19] The integrated form of the inifer equation[19] was used when yields were less than 100% (in CH_3Cl), and the plot was constructed according to Kennedy and Hiza[3] when the monomer conversion was close to 100% (in CH_2Cl_2). In CH_3Cl solvent (Figure 6), $C_I = 0.96$ is virtually identical with a value (0.95) obtained earlier with a similar system.[4] The fact that $k_t/k_p \sim 0$ indicates the absence of permanent termination, i.e., the living nature of this system. A similar inifer plot obtained with CH_2Cl_2 (Figure 7) gave $C_I = 0.49$ and $k_t/k_p \sim 0$, indicating the absence of permanent termination in that system. According to these findings, DiCumCl is relatively slowly consumed during the initial phase, and continuous initiation by and chain transfer to this inifer occur simultaneously. The higher C_I value obtained with CH_3Cl may be due to its higher polarity than that of CH_2Cl_2 (dielectric constants: $\epsilon_{CH_3Cl} = 17.5$ and $\epsilon_{CH_2Cl_2} = 14.5$, both at -75 °C). These inifer plots indicate that DiCumCl is consumed not only by initiation but also by chain transfer and that termination is virtually absent in these polymerization systems.

Further evidence for the presence of two simultaneous DiCumCl-consuming processes (i.e., initiation and chain transfer) has been obtained from $-\ln(1 - I_{eff}^j) - I_{eff}^j$ versus jC_j plots (where I_{eff}^j and C_j are the initiating efficiency and monomer conversions, respectively, after the jth monomer increment in an IMA experiment) that were found to be nonlinear. Thus, a variety of relatively slowly initiating living IB polymerizations[26-28] exhibit kinetics very similar to those obtained with the systems under investigation (e.g., similar $\bar{M}_n$ versus W_p plots by the IMA technique). It has been shown[26-29] that these polymerizations yield linear $-\ln(1 - I_{eff}^j) - I_{eff}^j$ versus jC_j plots starting from the origin if the rate-determining event of initiation is cationation (as is the case in the DiCumCl/BCl_3/IB system). In contrast to this analysis, however, as shown by the data in Figure 8, such plots constructed for the systems under investigation for the initial phase (during the first four monomer additions) are decidedly nonlinear. This deviation from linearity suggests that the DiCumCl is consumed not only by slow initiation but also by another process, chain transfer; i.e., infering operates during the initial phase.

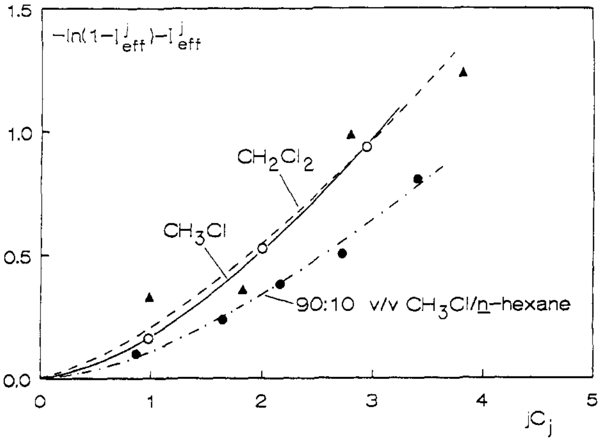
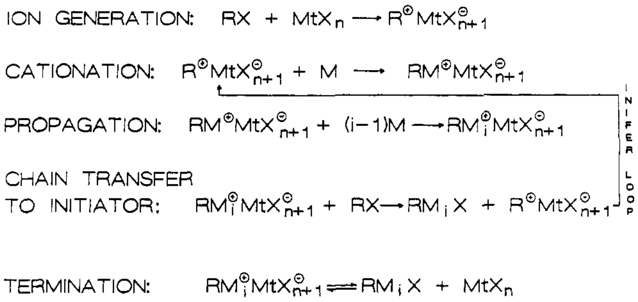


Figure 8. Diagnostic $-\ln(1 - I_{eff}^j) - I_{eff}^j$ versus jC_j plots for the slow DiCumCl consumption phase for DiCumCl/BCl_3/i-C_4H_8/-75 °C system in various solvents. Experimental conditions as in Table I.

Scheme I
Inifer and Living Carbocationic Polymerization Mechanisms



$$RX + MtX_n \longrightarrow R^{\oplus}MtX_{n+1}^{\ominus}$$

$$R^{\oplus}MtX_{n+1}^{\ominus} + M \longrightarrow RM^{\oplus}MtX_{n+1}^{\ominus}$$

$$RM^{\oplus}MtX_{n+1}^{\ominus} + (i-1)M \longrightarrow RM_i^{\oplus}MtX_{n+1}^{\ominus}$$

$$RM_i^{\oplus}MtX_{n+1}^{\ominus} + RX \longrightarrow RM_iX + R^{\oplus}MtX_{n+1}^{\ominus}$$

$$RM_i^{\oplus}MtX_{n+1}^{\ominus} \rightleftharpoons RM_iX + MtX_n$$

B. Mechanistic Considerations. According to the above data, the DiCumCl/BCl_3 system not only induces infering but also living polymerization. The polymerizations occur in two phases in polar solvents such as CH_3Cl or CH_2Cl_2. During the initial phase, simultaneous slow initiation by DiCumCl and chain transfer to DiCumCl (which summarily are termed infering by DiCumCl), propagation, and reversible termination proceed, while during the subsequent living phase, after the DiCumCl is consumed, only propagation and reversible termination occur. Thus, the inifer and living polymerizations may be combined into a unified mechanistic scheme. Scheme I shows the comprehensive mechanism.

According to this scheme, the initial phase involves ion generation, cationation, propagation, chain transfer to initiator, and reversible termination. Ion generation occurs by a reaction between the RX initiator (DiCumCl) and the MtX_n (BCl_3). Cationation is the addition of a monomer M (IB) to the ion pair formed in the first step. Propagation is the repetitive addition of monomer to the growing site. The RX is not only the initiator but also a chain-transfer agent (inifer, hence the expression inifering) that produces a functionally terminated chain RM_iX. The inifer loop yields the same ion pair that has formed by *ion generation*. Inifering as such has been discussed in detail earlier.[1-5,12,13,19] After the inifer RX (DiCumCl binifer in the present investigations) is depleted by slow initiation and chain transfer, only propagation and reversible termination remain; that is, the polymerization becomes living.

In respect to the living nature of these polymerizations, reversible termination becomes of paramount importance. Living polymerizations arise in the absence of termination (truly living polymerizations) *or* in the presence of rapid reversible termination (quasiliving polymerization), and these two types of living polymerizations are kinetically indistinguishable.[21] In truly living polymerizations, only initiation and propagation by *stable species occur until monomer is depleted*. In quasiliving polymerizations with reversible termination (for a classification of living polymerization systems, see ref 21), initiation, propagation, and reversible termination occur. Due to the specific structure of the DiCumCl binifer, the DiCumCl/BCl_3 combination leads to quasiliving IB polymerization comprising an initial slow DiCumCl consumption phase with simultaneous inifering, propagation, and reversible termination, followed by a living phase comprising only of propagation and reversible termination.

It is of interest to examine the reason(s) why the dual (first mainly inifering and then living) nature of inifer systems has remained hidden for so long. The answer comes from several sources: from an insufficient analysis of the effect of temperature on k_t/k_p, from not investigating the effect of polymerization time on inifer consumption, and from not appreciating the extraordinary sensitivity of inifer systems to medium polarity. In regard to the effect of temperature on the relative rate of termination, an analysis of pertinent inifer data published by Santos et al.[4] and Fehervari et al.[19] holds important clues: according to these sources, k_t/k_p obtained for similar binifer systems decreases as the polarity of the medium increases and the temperature decreases. Thus, it is not too surprising that at -75 °C (used in the present study) $k_t/k_p \sim 0$, in other words, irreversible termination was "frozen out". In regard to the effect of polarity, the extreme sensitivity of the systems toward even very small changes in medium polarity has not been fully appreciated. It is remarkable that even a minor polarity reduction, for example, the addition of only 10% *n*-hexane to CH_3Cl or the use of C_2H_5Cl (cf. Figures 2 and 3) instead of pure CH_3Cl (Figures 2 and 3) or CH_2Cl_2 (Figure 5), tremendously extends the initial (predominantly inifer) phase and thus in effect prevents living polymerization to arise. Evidently, reversible termination is extremely sensitive to even a minor reduction in medium polarity.

The conclusions in respect to reversible termination are also in line with Nuyken et al.'s findings.[12,13] These authors showed that IB polymerization can be initiated by $(CH_3)_3CCH_2C(CH_3)_2Cl$ (i.e., by a model compound that mimicks the end of a PIB terminated by chlorine on a tertiary carbon; RM_iX in Scheme I), and by PIB-Cl^t in conjunction with BCl_3 in polar solvent (CH_2Cl_2) at -85 °C.

Thus, on the basis of our data, observations by others,[4,12,13,19] and the fact that inifering and termination yield PIB-Cl^t,[1-6,19,20,22] it is concluded that DiCumCl/BCl_3-induced IB polymerizations are living due to reversible termination–reinitiation in polar solvents at low temperatures and that the concentration of the propagating species is determined by the termination $\rightleftharpoons$ reinitiation equilibrium.

In view of the high sensitivity of the system to polarity and the nonpolar nature of the monomer, even small changes in monomer concentration will affect the overall polarity and thus influence the results. In other words, the addition of even small amounts of monomer at the beginning of polymerization decreases the polarity of the medium and may lead to slower initiation, inifering, and thus to broader MWD. Improved control for the synthesis of telechelic PIBs by the DiCumCl/BCl_3 inifer system in polar solvents should be obtained by continuous slow nonpolar monomer addition. By this technique, the highest medium polarity could be maintained, and thus well-defined products by inifering and subsequent living polymerization could be obtained.

Deviations from the Poisson distribution arise in general in living polymerizations because of slow initiation and the presence of more than one kind of propagating species having different k_p values.[25] During the initial phase of DiCumCl/BCl_3-induced IB polymerizations, slow initiation and chain transfer to the initiator are additional causes of MWD broadening. The MWDs obtained in CH_3Cl are narrower than in CH_2Cl_2 diluent, conceivably because the distribution of the reactive species is more uniform in the more polar CH_3Cl than in CH_2Cl_2. Due to better cation solvation in the more polar diluent, the concentration of rapidly initiating and propagating species is probably higher in CH_3Cl than in CH_2Cl_2, leading to narrower MWD.

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Syntheses of Acetophenone Enol Ester Polymers and Their Conversion to Poly(phenylacetylenes)

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ABSTRACT: α-Acetoxystyrene (ACOST), 4-methylene-4*H*-1,3-benzodioxin-2-one (MBDOON), and 3-methylenephthalide (MP) readily undergo radical polymerization although they are α-substituted styrene derivatives. While poly(α-acetoxystyrene) (PACOST) is syndiotactic-rich due to the severe steric hindrance, the α,α-cyclic analogues are almost perfectly atactic (heterotactic-rich), indicating that the cyclization reduces the steric hindrance. PACOST and poly(4-methylene-4*H*-1,3-benzodioxin-2-one) (PMBDOON) release acetic acid and carbon dioxide upon heating to 200 °C, being converted to poly(phenylacetylene) (PPA) and poly((*o*-hydroxyphenyl)acetylene) (PHOPA), respectively. PPA thus obtained has a trans structure. The thermolysis temperature can be lowered to ca. 100 °C by generating a strong acid in the PACOST film through photolysis of a sulfonium salt cationic photoinitiator. PPA produced by acidolysis at the lower temperature contains a significant amount of cis sequences. PMBDOON can be also converted to PHOPA by heating the polymer powder with an acid at ca. 100 °C. However, thermolysis and acidolysis of PACOST and PMBDOON are accompanied by depolymerization. In contrast, poly(3-methylenephthalide) (PMP) is very stable toward thermolysis and acidolysis.

Introduction

We have been interested in reactions of radiochemically generated acids with polymer matrices especially for lithographic applications. Acid-catalyzed cross-linking, depolymerization, and deprotection reactions were first utilized in 1982 in the design of sensitive resist systems incorporating "chemical amplification",[2–4] and many publications have followed.[5–7] One such example is acid-catalyzed deprotection reactions (A_{AL}-1 acidolysis[8]) involving polymer pendant groups.[2–5,9–11] In this scheme, conversion of lipophilic polymers to hydrophilic phenol or carboxylic acid polymers allows either positive imaging with a polar developer or negative imaging with use of a nonpolar organic developer without swelling (Scheme I). Triarylsulfonium salts are typical radiochemical acid generators,[12] and nitrobenzyl esters[13,14] have been also used recently in resist applications.

Poly(α,α-dimethylbenzyl methacrylate) (PDMBZMA) (Scheme I) bearing a tertiary benzyl group in the ester side chain is thermolyzed or acidolyzed to form poly(methacrylic acid) and α-methylstyrene.[10,11,15] Hence, poly(α-acetoxystyrene) (PACOST) with a tertiary benzylic carbon adjacent to ester oxygen in the polymer backbone is expected to release acetic acid to form poly(phenylacetylene) (PPA) upon thermolysis or acidolysis (Scheme I). Thus, we have extended our research on thermal and acid-catalyzed deprotection of polymer pendant groups to the cases where the backbone α-carbon participates in the reaction. In Chart I are presented some polymers bearing tertiary ester functionalities and their mutual structural relationships. PACOST is structurally similar to cyclic benzoate or carbonate as shown in Chart I, which may be considered to be cyclic analogues of poly(((*tert*-butoxycarbonyl)oxy)styrene) (PBOCST)[2–5,16] and poly(*tert*-butyl vinylbenzoate) (PTBVB).[9] As Scheme I indicates, PBOCST and PTBVB undergo thermolysis or acidolysis to form poly(hydroxystyrene) (PHOST) and poly(vinylbenzoic acid) (PVBA), releasing isobutene/carbon dioxide and isobutene, respectively. Thus, poly((*o*-hydroxyphenyl)acetylene) (PHOPA) and poly(*o*-ethynylbenzoic acid) are expected to be produced through thermolysis or acidolysis of poly(4-methylene-4*H*-1,3-benzodioxin-2-one) (PMBDOON) and poly(3-methylenephthalide) (PMP), respectively. While polyacetylenes are typically synthesized by polymerization of acetylene monomers,[17,18] use of processable polymers as precursors to highly conjugated conducting polymers has attracted much attention recently.[19,20] Formation of acetylenic structures by treating PACOST with acid has been mentioned in the literature[21] but no detailed studies on the subject are available to our best knowledge. We have been also interested in lithographic imaging of polyacetylene films by photochemically induced acidolysis of precursor polymers.

In addition to the polymer reactions mentioned above, we have been engaged in investigations of the polymerization behavior of α-substituted styrene derivatives[22,23]

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