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Carbocationic Polymerization in the Presence of Sterically Hindered Bases. VII. The Polymerization of α-Methylstyrene with the Pentamethyl Benzyl Chloride/$SnCl_4$ Initiating System

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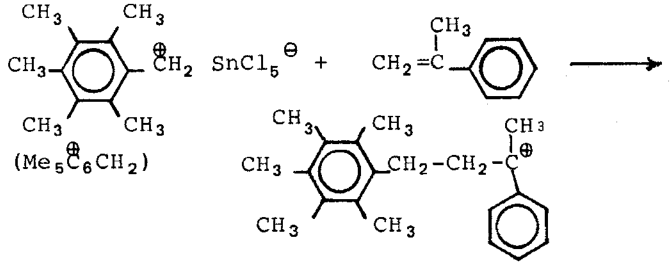
ABSTRACT

The polymerization of α-methylstyrene by the $Me_5C_6CH_2Cl$/$SnCl_4$ nonprotic initiating system has been studied in the presence and absence of 2,6-di-tert-butylpyridine (DtBP) in CH_2Cl_2 in the -30 to -80° C temperature range. Model experiments demonstrate that initiation involves direct carbocationation of the olefin by $Me_5C_6C^{\oplus}H_2$. According to kinetic studies, polymerizations in the absence of DtBP are very rapid (no induction) and terminationless, and molecular weights are determined by chain transfer to monomer. In the presence of DtBP, polymerizations do not go to completion due to terminative proton entrapment. Reducing the temperature increases the yields and molecular weights. Evidently a decrease in temperature reduces the rate of proton expulsion and thus the rate of terminative proton entrapment is also reduced. That chain transfer to monomer is absent in the presence of DtBP is demonstrated by the constancy of the number of polymer molecules formed and initiator efficiencies obtained under a variety of experimental conditions, and by Mayo plots. In addition to being an initiator, $Me_5C_6CH_2Cl$ is also an efficient chain transfer agent. The chain transfer activity of $Me_5C_6CH_2Cl$ has been quantitatively determined in the -30 to -60° C range. The effect of temperature on poly(α-methylstyrene) molecular weights has been investigated and the Arrhenius plot yielded $\Delta H_{\overline{DP}_n} = -2.15 \pm 0.2$ kcal/mol.

INTRODUCTION

Similar to our research concerning the polymerization of isobutylene where we investigated protic and nonprotic initiation (Parts III and IV of this series), we decided to extend our investigation to the polymerization of αMeSt using a nonprotic initiating system. The purposes of these investigations were 1) to deepen our understanding relative to the effect of DtBP on the mechanism of carbocationic polymerizations in general, and 2) to investigate the polymerization of αMeSt with a nonprotic initiating system in particular. The latter study was undertaken to provide guidance for our research on high-efficiency cationic grafting and blocking of polyolefins from various backbones (Parts VIII and IX). It was theorized that initiation of αMeSt polymerization by pentamethylbenzyl chloride $Me_5C_6CH_2Cl$ (PMBC) in conjunction with a suitable coinitiator, e.g., $SnCl_4$, would be nonprotic and would involve the following cationation:



Previous research has indicated that DtBP could not interfere with carbocationation of olefins (Part III), i.e., in reactions which may be regarded as models for blocking and grafting initiation of αMeSt from an active chlorine-bearing polymer site.

The function of the five $-CH_3$ groups on the initiating carbocation was to prevent possible polybenzylation and/or ring alkylation during αMeSt polymerization.

The results of experiments described in this paper provide valuable insight into the mechanism of cationic olefin polymerizations and substantiate the above expectation concerning the mechanism of initiation.

EXPERIMENTAL

Purifications of solvents, monomer, and coinitiator together with polymerization procedures and molecular weight determinations have been described (Parts V and VI). Pentamethylbenzyl chloride (Alfa) was treated with activated charcoal in CH_2Cl_2, recrystallized twice from hexane, and dried in high vacuum at room temperature.

RESULTS AND DISCUSSION

Modeling Carbocationic (Nonprotic) Initiation

The purpose of this model experiment was to prove the direct addition of the $Me_5C_6C^{\oplus}H_2$ carbocation to a nonpolymerizable olefin under simulated polymerization conditions. Cationation as shown by the equation in the Introduction would give rise to a new C–C bond whose presence could be demonstrated by ^1H NMR spectroscopy. We chose 2,4,4-trimethyl-1-pentene (TMP) as the model olefin since its structure adjacent to the double bond is quite similar to that of αMeSt and because a large body of experience in working with this nonpolymerizable monomer was available in our laboratories [1]. Experimentally we added a cooled (-60°C) solution of $SnCl_4$ (4.34×10^{-3} mol) in CH_2Cl_2 to a mixture of 1.25×10^{-2} mol of pure and dry TMP, 6.11×10^{-4} mol $Me_5C_6CH_2Cl$, and 25 mL CH_2Cl_2 at -60°C under vacuum. The reaction was stopped by adding chilled methanol. The reaction mixture was washed with water 4-5 times, filtered, dried over anhydrous Na_2SO_4, and distilled under reduced pressure to remove traces of TMP. The residue was dissolved in CCl_4, and the ^1H NMR spectrum was recorded. Table 1 shows the chemical shifts of the resonances in the spectra of $Me_5C_6CH_2Cl$, TMP, and the reaction products. According to these data, the structure of the product formed in this model experiment (shown in Table 1) indicates direct cationation of the model olefin by the $Me_5C_6C^{\oplus}H_2$ cation.

Kinetic Investigations

Systematic kinetic research started by establishing convenient conditions for the reproducible polymerization of αMeSt by the $Me_5C_6CH_2Cl/SnCl_4$ initiating system in the absence and presence of DtBP. Runs carried out in the absence of DtBP but in the presence of $SnCl_4$ or $Me_5C_6CH_2Cl/SnCl_4$ yielded 100% polymer at every temperature. "Control" runs, i.e., polymerizations carried out in the absence of $Me_5C_6CH_2Cl$ but in the presence of $SnCl_4$ and DtBP, yielded 5, 7, 11, 20, and 24% conversions at -40, -50, -60, -70, and -80°C, respectively.

TABLE 1. ^1H Chemical Shift Assignments for the Model Compound Formed in the $(CH_3)_5C_6CH_2Cl/SnCl_4/TMP$ System

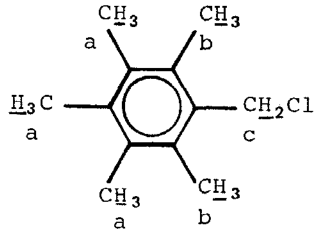
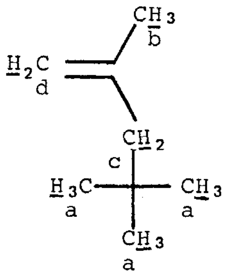
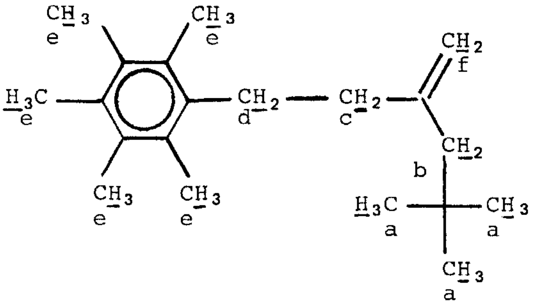
Structures	Chemical shifts (ppm)
	a 2.15 b 2.30 c 4.59
	a 0.93 b 1.76 c 1.91 d 4.58, 4.78
	a 0.93 b 1.90 c and d 1.90-2.00 e 2.15 f 4.65, 4.85

Figure 1 shows conversion-time plots for the $Me_5C_6CH_2Cl/SnCl_4/\alpha MeSt/CH_2Cl_2$ systems in the presence of DtBP in the -40 to -80° C range. Rapid homogeneous polymerization (no induction period) occurred upon $SnCl_4$ addition and ultimate conversions were reached within ~10 min. In view of this observation, subsequent kinetic experiments were uniformly conducted for 30 min. The molecular weights

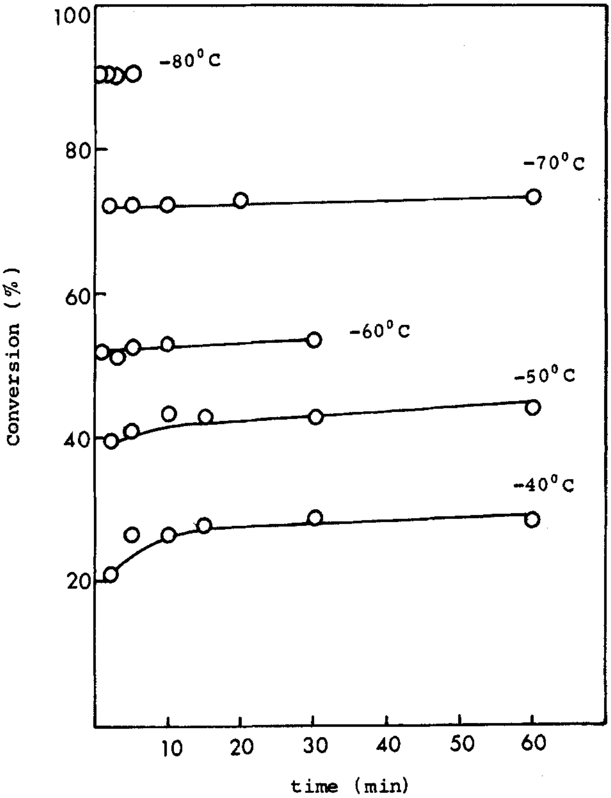


FIG. 1. Conversion vs time at different temperatures. ([PMBC] = 2.24×10^{-3} $\underline{M}$, [$SnCl_4$] = 5.70×10^{-3} $\underline{M}$, $[M]_0$ = 0.768 $\underline{M}$, [DtBP] = 6.00×10^{-3} $\underline{M}$, CH_2Cl_2 diluent, total volume 30 mL.)

and molecular weight dispersities of select samples after the plateau of ultimate conversions has been reached were determined (the data are collected in Table 2). The relationship between conversion, molecular weight, and temperature is shown in Fig. 2 where average values of 2-4 experiments are plotted.

Evidently both conversions and molecular weights increase at approximately the same rate the temperature is lowered. These observations can be readily explained by analyzing the effect of temperature on termination and proton expulsion (chain transfer to monomer): In the $Me_5C_6CH_2Cl/SnCl_4/\alpha MeSt/CH_2Cl_2$ system in the absence of the DtBP proton trap, conversions invariably reach 100% at every temperature level (control runs), indicating that kinetic termination is absent. Molecular weights, however, increase by lowering the

TABLE 2. Initiator Efficiency in the Pentamethyl Benzyl Chloride/$SnCl_4$/αMeSt System ([$SnCl_4$] = 5.7 × 10^{-3} M, [DtBP] = 6.0 × 10^{-3} M, [αMeSt] = 0.768 M; CH_2Cl_2 diluent, 30 min, total volume 30 mL)

Temperature (°C)	[PMBC] (M × 10^3)	Yield (g)	Conversion[a] (%)	$M_n \times 10^{-4}$	MWD	$\overline{N} \times 10^5$	I_{eff}[b]
-30	2.24	0.50 ± 0.3	18 ± 2	3.00	1.92	1.82	0.28
-30	2.24			2.18	1.96	2.16	0.32
-40	2.24	0.60	22	2.80	2.20	2.14	0.32
-50	2.24	1.01	37	5.15	1.98	1.98	0.30
-60	2.24	1.33	50	6.20	2.10	2.15	0.32
-70	2.24	1.48 ± 0.02	54 ± 1	6.30	1.70	2.32	0.35
-70	2.24			6.00	1.75	2.50	0.38
-80	2.24	1.82 ± 0.03	67 ± 1	7.50	1.70	2.39	0.36
-80	2.24			8.90	1.70	2.08	0.32

-30	1.49	-	17	2.30	2.03	-	-
-30	2.98	-	21	1.80	2.06	-	-
-30	3.73	-	23	1.70	2.39	-	-
-40	2.98	0.68	25	2.60	2.10	2.62	0.30
-40	3.73	0.73	27	2.40	2.00	3.00	0.28
-50	2.98	1.09	40	3.10	2.08	3.50	0.40
-50	3.73	1.16	43	3.50	2.20	3.30	0.30
-50	4.47	1.17	43	2.70	2.10	4.30	0.33
-60	2.98	1.43	53	5.40	2.20	2.70	0.31

[a] Corrected conversions (conversions obtained in the presence of PMBC - conversion obtained in the absence of PMBC.)

[b] $$I_{eff} = \frac{\text{moles of P}\alpha\text{MeSt}}{\text{moles of initiator}}.$$

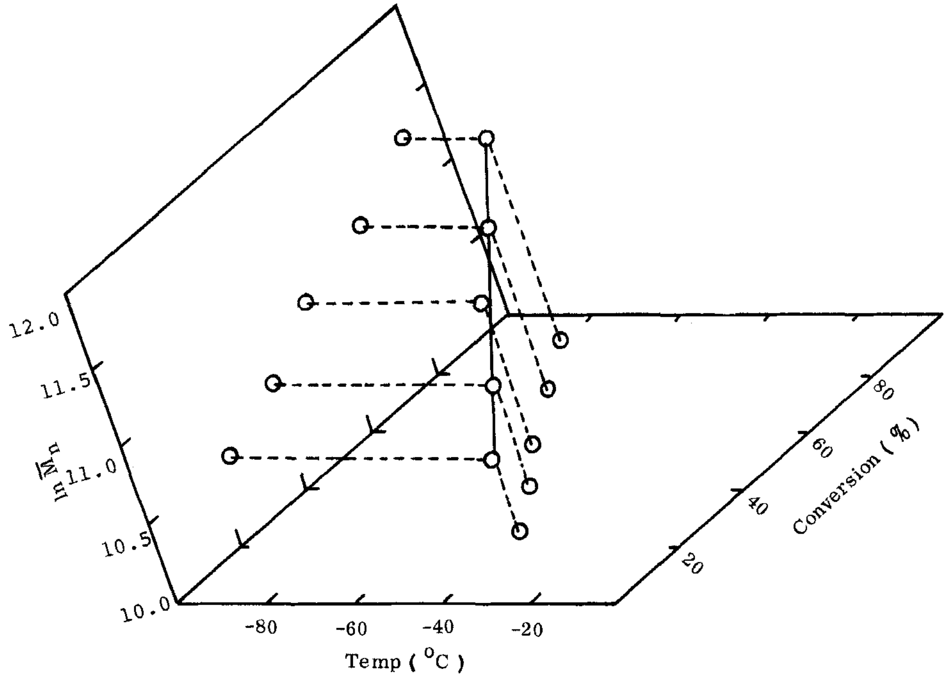


FIG. 2. Effect of temperature on conversions and molecular weights. ([PMBC] = 2.24 × 10^{-3} M, [$SnCl_4$] = 5.70 × 10^{-3} M, $[M]_0$ = 0.768 M, [DtBP] = 6.00 × 10^{-3} M, CH_2Cl_2 diluent, total volume 30 mL.)

temperature, indicating that the length of the polymer chain is determined by the rate of proton expulsion (or more precisely, by $R_{tr,M}/R_p$, the relative rate of chain transfer to monomer and that of propagation). In the presence of DtBP, kinetic termination appears; conversions cannot reach 100% because the proton trap intercepts the proton expelled in the course of chain transfer to monomer. Lowering the temperature reduces the rate of proton expulsion, i.e., the period of uninterrupted propagation is lengthened, and this in turn gives rise to increased conversions and molecular weights. According to Fig. 2, conversions should reach ~100% at about -90°C at which point $\overline{M}_n \approx 120{,}000$.

The effect of temperature on conversions and molecular weights are the same in a system in which kinetic termination does exist in the absence of proton trap, e.g., in the "H_2O"/BCl_3/IB system [2]. In this system, termination occurs by irreversible chlorination of the

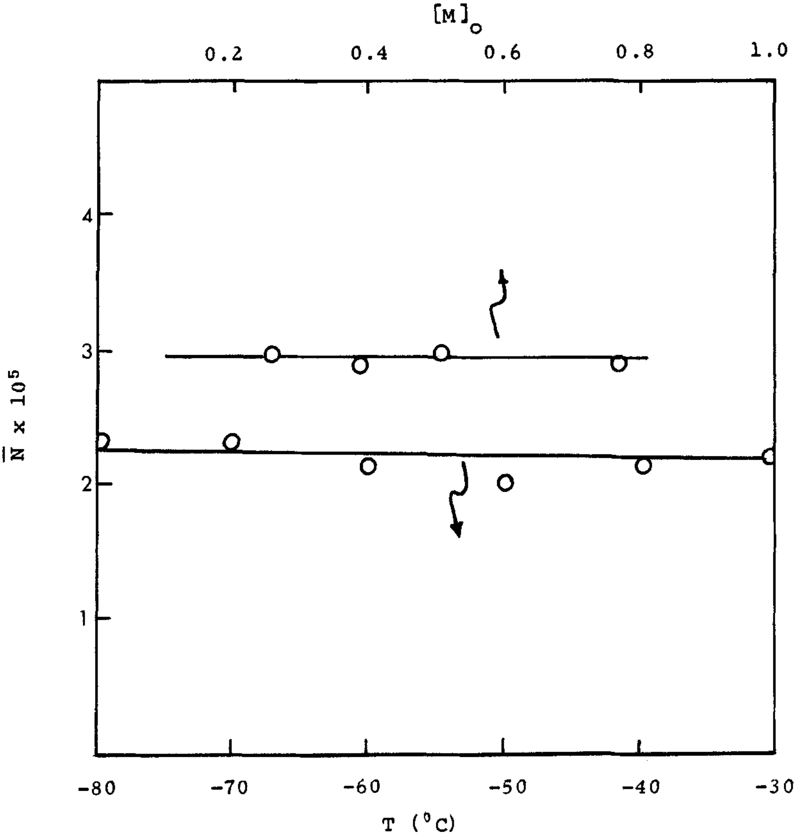


FIG. 3. Plots of moles of PαMeSt vs temperature ([PMBC] = 2.24 × 10^{-3} M, [$SnCl_4$] = 5.70 × 10^{-3} M, $[M]_o$ = 0.768 M, [DtBP] = 6.00 × 10^{-3} M, CH_2Cl_2 diluent, total volume 30 mL) and ([PMBC] = 2.24 × 10^{-3} M, [$SnCl_4$] = 5.70 × 10^{-3} M, [DtBP] = 6.00 × 10^{-3} M, CH_2Cl_2, compensating solvent cyclohexane, total volume 30 mL, -60° C).

propagating carbocation, and lowering the temperature reduces the rate of kinetic termination which in turn leads to higher conversions and molecular weights. According to the data in Table 2, molecular weight dispersities (MWD) are ~2.0 in the range from -30 to -60° C whereas a narrowing ($\bar{M}_w/\bar{M}_n$ = 1.70) is evident at -70 and -80° C. The most probable MWD, i.e., $\bar{M}_w/\bar{M}_n$ = 2.0, is in line with the concept of random terminative proton entrapment; however, the lower

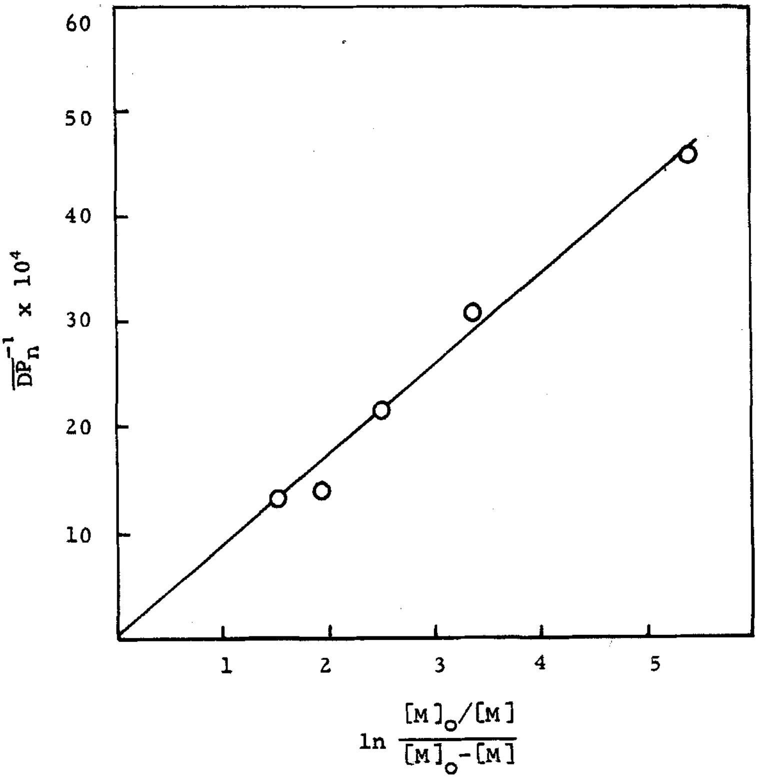


FIG. 4. Mayo plot: [PMBC] = 2.24 × 10^{-3} M, [$SnCl_4$] = 5.70 × 10^{-3} M, [DtBP] = 6.00 × 10^{-3} M, CH_2Cl_2 diluent, compensating solvent cyclohexane, total volume 30 mL, -60° C.

value is difficult to explain. It is possible that at very low temperatures the transfer to monomer is frozen out and the rate of the terminative proton entrapment by DtBP also decreases considerably. Interestingly, the MWD of polymers obtained in control runs in the absence of $Me_5C_6CH_2Cl$ but in the presence of DtBP was ~1.5. Observations and theories concerning the narrowing of MWD in the presence of DtBP will be discussed separately [3].

Table 2 also shows $\overline{N}$, the number of moles of PαMeSt formed (g PαMeSt/$\overline{M}_n$), and I_{eff}, initiator efficiencies (moles PαMeSt/moles $Me_5C_6CH_2Cl$). Figure 3 illustrates the constancy of $\overline{N}$ over a range of monomer concentrations and temperatures. Evidently both $\overline{N}$ and I_{eff} remain essentially unchanged by varying the experimental conditions within quite broad ranges. According to these data, chain transfer to monomer is absent in the system under investigation.

Although I_{eff} remains constant under the various conditions investigated, it is much less than unity, i.e., $I_{eff} \sim 0.3$. Low I_{eff} values may be due to a low degree of ionization of $Me_5C_6CH_2Cl$ in the presence of $SnCl_4$. Further, the quantity of $SnCl_4$ available for nonprotic initiation would be reduced by the quantity of H_2O impurities in the reactor. Moisture reacts with $SnCl_4$ to form various hydrates and/or $H^{\oplus}SnCl_4OH^{\ominus}$, and DtBP would promptly intercept the proton which would lead to a reduction of free $SnCl_4$ in the system. The use of large stoichiometric excesses of $SnCl_4$ would tend to increase I_{eff}; however, experiments to test this hypothesis have not been carried out.

The absence of chain transfer to monomer in the $Me_5C_6CH_2Cl$/$SnCl_4$/αMeSt system in the presence of DtBP has also been proven by determining the effect of monomer concentration on the degree of polymerization ($\overline{DP}_n$). Figure 4 shows the corresponding Mayo plot, and the absence of intercept indicates the absence of chain transfer to monomer in this system. Since conversions were in the 30-50% range in this series of experiments, an integrated form of the Mayo equation has been employed. The slope provides k_t/k_p of 7.3×10^{-4}.

While the data in Table 2 indicate the absence of chain transfer to monomer, they also provide evidence for chain transfer to the initiator $Me_5C_6CH_2Cl$ (note the decreasing $\overline{M}_n$ with increasing $[Me_5C_6CH_2Cl]$ under otherwise identical conditions). This phenomenon was expected in light of the well-known chain transfer activity of organic halides in cationic polymerizations [4]. This lead was followed up by carrying out a series of experiments to investigate quantitatively the $Me_5C_6CH_2Cl$ concentration at different temperatures on the molecular weight of PαMeSt. Thus the number average degree of polymerization ($\overline{DP}_n$) is defined by

$$\overline{DP}_n = \frac{k_p[M]}{k_p[M] + k_{tr,M}[M] + k_{tr,I}[I] + k_t} \qquad (1)$$

where the brackets indicate concentrations and k_p, $k_{tr,M}$, $k_{tr,I}$, and k_t are rate constants of propagation, chain transfer to monomer and initiator, and termination. Further

$$\overline{DP}^{-1} = C_I[I]/[M] + C_M + k_t/k_p[M] \qquad (2)$$

where

$C_I = k_{tr,I}/k_p$ and $C_M = k_{tr,M}/k_p$

This equation can be transformed to (see Ref. 5 for details)

$$\overline{DP}_n^{-1} = C_I[I]\frac{\ln\frac{[M]_0}{[M]}}{[M]_0-[M]} + \frac{k_t}{k_p}\frac{\ln\frac{[M]_0}{[M]}}{[M]_0-[M]} + C_M \tag{3}$$

It has been assumed that d[I]/d[M] = 0 because the ratio of initiator consumption to monomer consumption at -30°C is $\sim 5 \times 10^{-3}$ and decreases further with decreasing temperatures. Since $C_M \simeq 0$, Eq. (3) reduces to

$$\overline{DP}_n^{-1}([M]_0 - [M])\ln\frac{[M]_0}{[M]} = C_I[I] + k_t/k_p \tag{4}$$

Figure 5 shows plots of Eq. (4) which yield C_I (slope) and k_t/k_p (intercept) at various temperatures. The latter data have been assembled in Table 3. Decreasing the temperature from -30 to -60°C evidently decreases C_I by a factor of 10 and that of k_t/k_p by 3.5. The effect of temperature on these parameters is close to linear. The value of k_t/k_p obtained from Fig. 5 at -60°C is in close agreement with that obtained from the Mayo plot (Fig. 4).

The last two columns in Table 3 show activation energy differences obtained from the plots in Fig. 5 for the -30 to -60°C range. $H_{tr,I} - H_p = 7.4$ kcal/mol is higher than the 1.4 kcal/mol obtained for the p-dicumyl chloride/BCl_3/isobutylene system [5], and this reflects the greater ease of chain transfer to the organic chloride in the latter.

The fact that kinetic termination is absent in the $Me_5C_6CH_2Cl$/$SnCl_4$/αMeSt system must be kept in mind when evaluation k_t and H_t since these parameters reflect terminative proton entrapment by DtBP. Termination in the system under study involves proton expulsion followed by immediate proton entrapment. Kinetically, this event may be regarded either as termination or terminative proton entrapment because the rate-determining step in either case is proton loss. Terminative proton entrapment is in fact an aborted chain transfer to monomer, a process which cannot go to completion because the proton is consumed by the hindered amine prior to

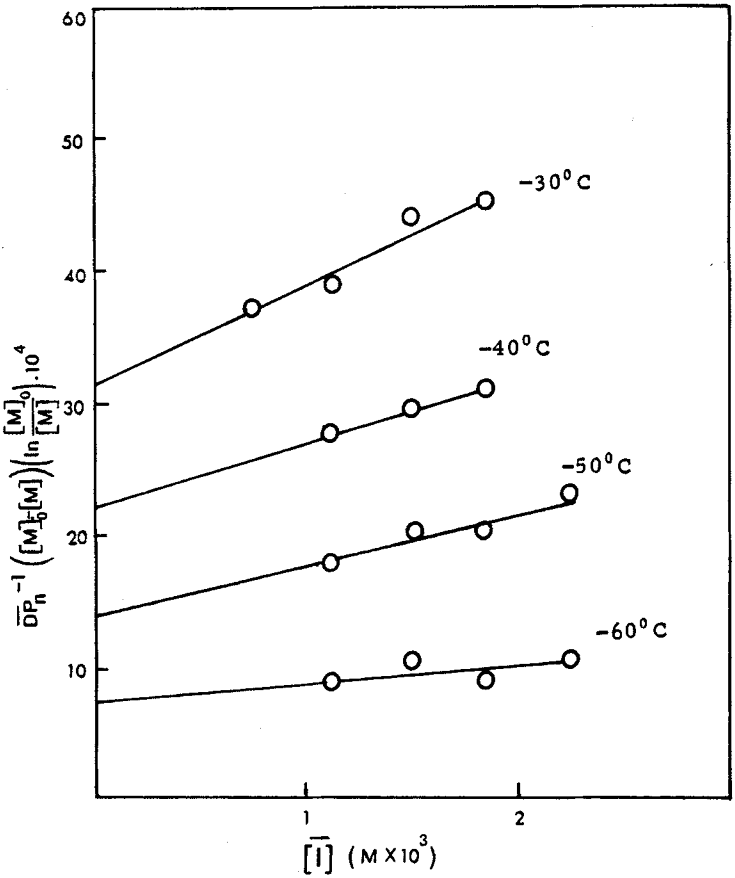


FIG. 5. Determination of C_I at different temperatures.

TABLE 3. The Effect of Temperature on Chain Transfer Constants C_I and k_t/k_p Ratios for the PMBC/$SnCl_4$/αMeSt/CH_2Cl_2 System

Temperature (°C)	Conversion (%)	C_I	k_t/k_p $\times 10^4$	$H_t - H_p$ (kcal/mol)	$H_{tr,I} - H_p$ (kcal/mol)
-30	17-23	0.40	30.86	4.6 ± 0.4	7.4
-40	27-34	0.22	22.74		
-50	44-50	0.19	13.70		
-60	60-68	0.04	8.26		

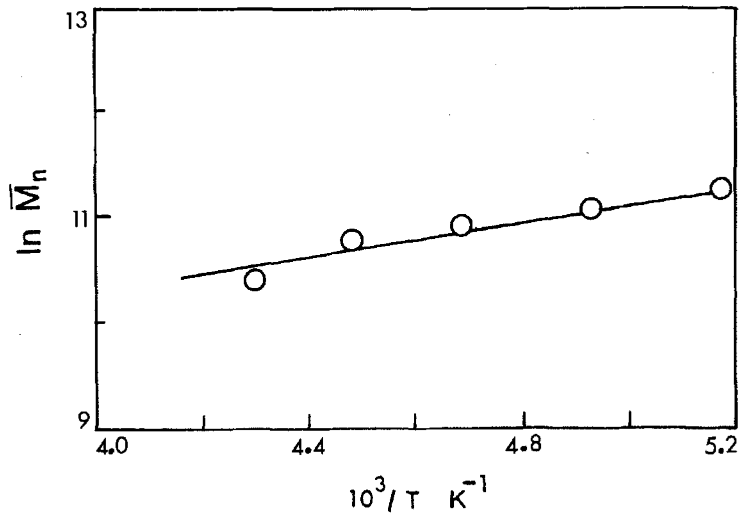


FIG. 6. Arrhenius plot for $\overline{M}_n$. ([PMBC] = 2.24 × 10^{-3} M, [$SnCl_4$] = 5.70 × 10^{-3} M, $[M]_0$ = 0.768 M, [DtBP] = 6.00 × 10^{-3} M, CH_2Cl_2 diluent, total volume 30 mL.)

protonation of a monomer molecule. The activation energy difference $H_t - H_p$ calculated from the plots in Fig. 5 (4.6 ± 0.3 kcal/mol) and that of the Arrhenius plot shown in Fig. 6 (2.1 ± 0.2 kcal/mol) are different. It is difficult to explain this discrepancy; however, the 2.1 ± 0.2 kcal/mol value is probably the more reliable one since it has been obtained from absolute experimental values (i.e., molecular weights) whereas the 4.6 ± 0.30 value has been derived by employing approximations and data obtained at ~30% initiation efficiencies.

ACKNOWLEDGMENTS

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