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Quasiliving Carbocationic Polymerization. XIII. Polymerization of 2,4,6-Trimethylstyrene

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ABSTRACT

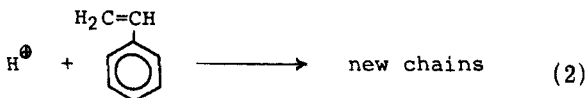
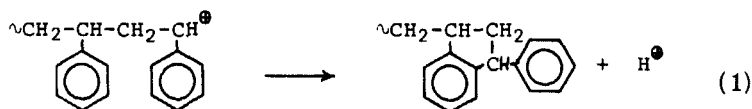
The polymerization of 2,4,6-trimethylstyrene (vinyl mesitylene) has been investigated, and quasiliving polymerizations have been achieved under a comfortably wide experimental condition range. This monomer is particularly suitable for quasiliving polymerizations because the methyl groups in the 2 and 6 positions prevent chain transfer to monomer involving indanyl-skeleton formation. Quasiliving polymerizations readily occurred by the use of cumyl chloride/ TiCl_4 or BCl_3 initiating systems in various $n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ mixtures at -50°C . Because indanyl-skeleton formation

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is impossible, the rate of monomer addition can be safely decreased to very low values without risking chain transfer by intramolecular alkylation.

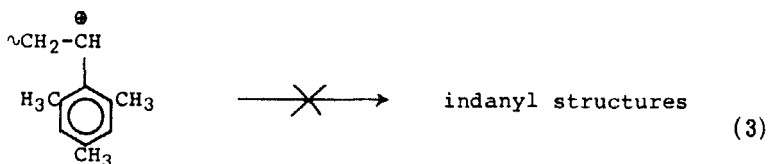
INTRODUCTION

The quasiliving polymerization of styrene [1] and several styrene derivatives, i.e., α -methylstyrene [2], *p*-tert-butylstyrene [3], and indene [4], has been studied. While in all these cases quasiliving polymerization could be demonstrated by linear \bar{M}_n versus monomer input plots passing through the origin, unacceptable chain transfer by intramolecular alkylation (indanyl skeleton formation)



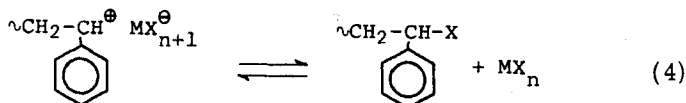
was a frequent problem, particularly when the rate of monomer addition was too low. Intramolecular alkylation leading to the indanyl skeleton almost certainly did not occur with indene; however, chain transfer was found to operate under the conditions examined [4].

Thus it seemed of interest to investigate the quasiliving polymerization of 2,4,6-trimethylstyrene, TrMeSt, a monomer in which intramolecular alkylation is impossible because the 2 and 6 positions are occupied:

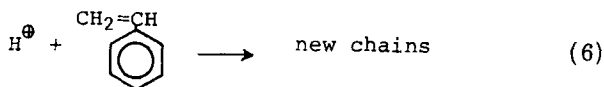
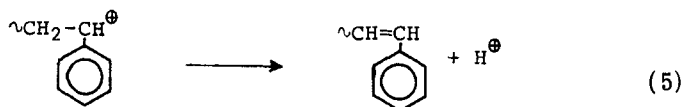


In regard to the other elementary steps anticipated to occur during the polymerization of TrMeSt, the mechanism of initiation of styrene and styryl derivatives is fairly well understood; for example, it has been shown that cumyl chloride in the presence of strong Friedel-Crafts acids, such as TiCl_4 and BCl_3 , rapidly and efficiently initiates quasiliving polymerization. As to permanent termination, kinetic analy-

ses with styrene and styrene derivatives very similar to TrMeSt have demonstrated that is absent, most likely because of the equilibrium:



Thus the only chain breaking event of consequence that has to be suppressed is chain transfer by proton elimination:



It was anticipated that experimental conditions can be found under which the rate of monomer addition does not exceed the rate of propagation, and chain breaking processes can be avoided; thus quasiling conditions with TrMeSt will be achieved.

This paper concerns the quasiling polymerization of TrMeSt, and the effect of temperature, medium polarity, monomer introduction rate, and nature of the coinitiator on the polymerization.

EXPERIMENTAL

Materials

2,4,6-Trimethylstyrene was synthesized from 1,3,5-trimethylbenzene (Aldrich) by the method described by Zwegers and Maréchal [5].

n-Hexane and methylene chloride were purified as described [6, 7]. Cumyl chloride (2-chloro-2-phenyl-propane) was obtained by hydrochlorination of purified α -methylstyrene in methylene chloride solution. TiCl_4 was distilled from P_2P_5 under nitrogen. BCl_3 was condensed from a lecture bottle under N_2 in a dry box.

Procedures

Polymerizations were carried out in a stainless steel enclosure under dry N_2 at -50, -25, and 0°C, using 250 cm³ three-neck round-

bottom flasks equipped with stirrer, Teflon plug for monomer addition, and outlet for sampling. The initial volume of solvent (mixture) was 100 cm³. Initiator and coinitiator were added to the solvent 5 min before starting monomer addition. Monomer/CH₂Cl₂ mixtures were introduced into the flask at controlled rate by a precision metering pump (Beckman Model 110 A) through a precision glass capillary inlet. During polymerization, samples (0.1 cm³) were withdrawn with a syringe and injected into capped vials containing excess methanol. At the end of monomer feeding, methanol was added to the charge. Conversions were determined gravimetrically.

Molecular weights were determined on samples in THF solutions by gel permeation chromatography using a Waters Associates High Pressure GPC equipped with five Microstyrigel columns (10⁵, 10⁴, 10³, 5 × 10², and 10² Å) and dual UV and RI detectors. The flow rate was 1 mL/min. Molecular weights were calculated from a calibration curve obtained with polystyrene standards.

RESULTS AND DISCUSSION

In view of past experience with quasiliving olefin polymerizations, we decided to investigate the polymerization of TrMeSt by using cumyl chloride as the initiator in the presence of TiCl₄ or BCl₃ coinitiators in various n-C₆H₁₄/CH₂Cl₂ media in the temperature range from -50 to 0°C.

A. Rate of Monomer Addition

In theory, quasiliving polymerizations may be achieved in the rates of monomer introduction and of monomer consumption are equal [8]. Thus the experimental determination of the correct monomer introduction rate for a particular system (monomer, coinitiator, medium polarity, impurity level) to achieve quasiliving conditions is of paramount importance.

Figure 1 shows the effect of monomer addition rate on the conversion of TrMeSt under a certain set of conditions indicated in the legend. Evidently, complete monomer consumption has been achieved in the 1 to 3 × 10⁻³ mol TrMeSt/min range. If the introduction rate is higher than about 3 × 10⁻³ mol TrMeSt/min, the monomer starts to accumulate and consequently the danger of chain transfer to monomer arises.

B. The Effect of Temperature

Having determined the correct range of monomer addition rates, we explored the effect of temperature on the quasiliving polymerization of

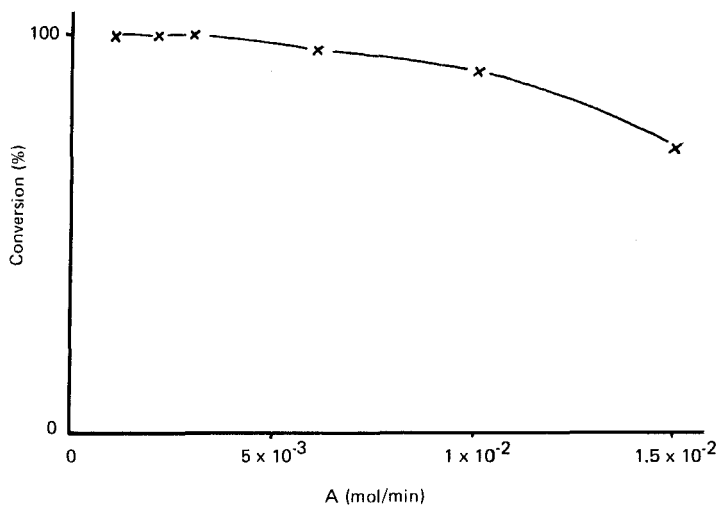


FIG. 1. The effect of the monomer addition rate on the conversion. Solvent: 20/80 v/v n-C₆H₁₄/CH₂Cl₂. Temperature = -50°C; initiator (CC) concentration = 10⁻² M; coinitoriator (TiCl₄) concentration = 2 10⁻² M.

TrMeSt. In view of our past experience in this field, where most polymerizations were carried out at rather low temperatures, we were interested in determining the highest temperature at which quasiliving conditions could still be obtained with TrMeSt.

Table 1 and Figs. 2 and 3 show the results of TrMeSt polymerizations carried out at -50, -25, and 0°C using the cumyl chloride/TiCl₄ initiating system and a 20/80 v/v n-C₆H₁₄/CH₂Cl₂ solvent mixture.

The monomer input rate was $2.7 \times 10^{-3} \pm 2\%$ mol/min to insure close to 100% monomer conversion. Figures 1 and 2 demonstrate convincingly that quasiliving conditions have been achieved at -50°C. At the higher temperatures the number of molecules increases during the runs, which indicates chain transfer to monomer. It is noteworthy that conversions were 100% at the higher temperatures as well, and that the \bar{M}_n 's increased with monomer addition even at 0°C (cf. Fig. 2).

Complete monomer consumption in these experiments seems to indicate the absence of termination or rather the operational presence of an equilibrium such as that shown in Eq. (4).

We anticipated the presence of terminal unsaturations because of β -proton elimination, particularly in polymers obtained at 0°C. Indeed, the ¹H-NMR spectrum of a rather low molecular weight sample ($\bar{M}_n =$

TABLE 1. The Effect of Temperature on the Quasiliving Polymerization of TrMeSt (20 vol% n-hexane + 80 vol% methylene chloride, initial volume = 100 mL; [cumyl chloride] = 10^{-2} M; [TiCl₄] = 2×10^{-2} M)

Temperature (°C)	Time of sampling (min)	Cumulative amount of consumed monomer (mol × 10 ³)	\bar{M}_n	\overline{DP}_n	[P] × 10 ³ mol	\bar{M}_w/\bar{M}_n	[I] ₀ × 10 ⁵ mol
-50	10	27.4	4,620	31.59	0.86	2.59	0.85
	20	54.8	7,740	52.93	1.04	1.93	
	30	82.2	10,700	73.17	1.12	1.60	
	40	109.6	16,400	112.1	0.98	1.58	
	50	137	19,650	146.2	0.94	1.48	
-25	10	26.4	3,900	26.67	0.99	3.47	0.90
	20	52.8	6,420	43.90	1.20	2.60	
	30	79.2	9,640	65.92	1.20	2.62	
	40	106	11,600	79.33	1.33	2.48	
	50	132	12,160	83.16	1.59	2.29	
0	10	27.0	1,200	8.21	3.28	3.35	1.10
	20	54.0	3,420	23.40	2.31	3.42	
	30	81.0	3,930	26.87	3.0	3.20	
	40	108	5,020	34.33	3.14	3.28	
	50	135	4,840	33.10	4.08	2.92	

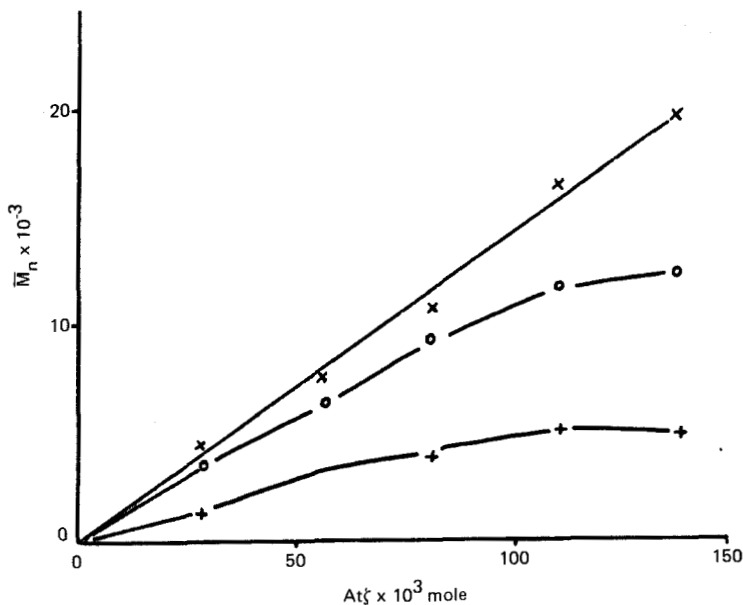
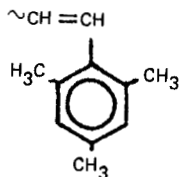


FIG. 2. \bar{M}_n versus monomer consumed at different temperatures: (x) -50°C , (o) -25°C , (+) 0°C . Solvent: 20/80 v/v n- $\text{C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$. $[\text{CC}] = 10^{-2} \text{ M}$, $[\text{TiCl}_4] = 2 \times 10^{-2} \text{ M}$, monomer addition rate = 3×10 mol/min. ξ = conversion.

4800) indicated (at 50 \times magnification) the presence of unsaturations consistent with the group



A closer examination of the spectrum, however, showed that the number of terminal unsaturations was lower than calculated for a poly-TrMeSt of $\bar{M}_n = 4800$, assuming every chain end to carry the above structure. (The ratio of olefinic to aromatic protons $R = 2/(\overline{\text{DP}}_n \times 2) = 1/\overline{\text{DP}}_n$, for $\bar{M}_n = 4800$, $R = 3 \times 10^{-2}$. Found $R = 2.2 \times 10^{-2}$.) The

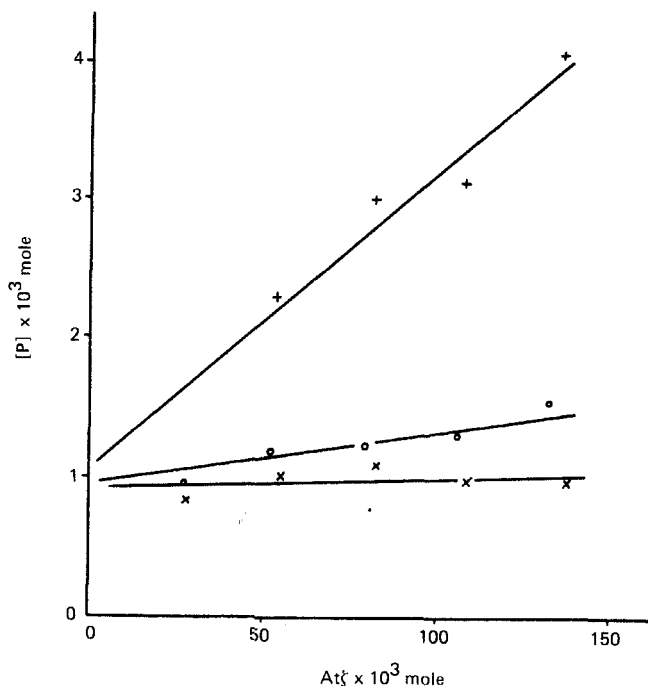
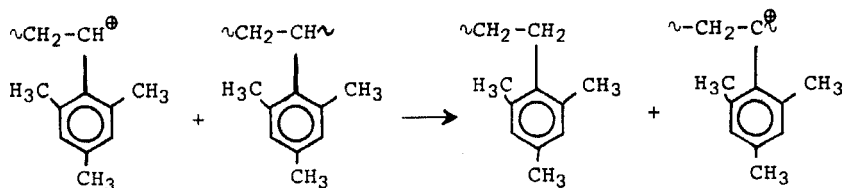


FIG. 3. Number of polymer molecules versus monomer consumed at different temperatures: (x) -50°C , (o) -25°C , (+) 0°C . Solvent: 20/80 v/v n- $\text{C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$. $[\text{CC}] = 10^{-2}$ M, $[\text{TiCl}_4] = 2 \times 10^{-2}$ M, monomer addition rate = 3×10^{-3} mol/min.

somewhat lower than expected number of unsaturated endgroups may be explained by assuming that in addition to chain transfer to monomer, chain transfer to polymer may also occur, particularly at higher temperatures:



In regard to the molecular weight dispersities, the $\overline{M}_w/\overline{M}_n$ values steadily decrease from 2.59 to 1.48 in the experiments where quasi-

living conditions have been achieved. This effect has been anticipated and indeed it is considered to be an important diagnostic sign for the presence of quasiliving conditions. It has been predicted that the molecular weight dispersion limit in quasiliving carbocationic polymerizations is 1.33 [9, 10].

C. The Effect of Solvent Polarity

According to earlier experience in this field, the nature and polarity of the medium greatly affects the outcome of quasiliving polymerizations [11]. Table 2 and Figures 4 and 5 show the effect of solvent composition on the quasiliving polymerization of TrMeSt. Polymerizations have been carried out using pure CH_2Cl_2 and 20/80 and 40/60 v/v n- C_6H_{14} / CH_2Cl_2 mixtures under conditions shown in the legend to Table 2.

According to the data, quasiliving conditions prevail in the 20/80 v/v n- C_6H_{14} / CH_2Cl_2 mixture, and most likely in the 40/60 v/v mixture as well. This slight reservation in regard to the 40/60 mixture is due to the somewhat lower than theoretical $[\text{P}]$ and conversion values obtained (cf. Table 2 and Fig. 3); however, the deviation from $[\text{P}] = 1.0$ may be within experimental error.

Quasiliving conditions do not exist in pure CH_2Cl_2 , and the data indicate a measure of chain transfer activity in this system. A similar phenomenon has been observed [1].

Increasing the amount of the nonpolar component in the solvent mixture increases the extent of chain transfer and somewhat decreases the initiator efficiency (see Table 2).

The narrowing of the molecular weight distributions during the experiments is quite evident in these runs also. Figure 6 shows a set of representative GPC traces obtained in experiments with 20/80 v/v n- C_6H_{14} / CH_2Cl_2 (cf. Table 2). All the distributions are monomodal. The shift toward lower elution counts indicates increasing molecular weight, and their sharpening is an indication of a narrowing of the molecular weight distributions. The lowering of $\overline{M}_w/\overline{M}_n$ values is viewed as an important sign for quasiliving conditions (see comments above).

D. Quasiliving Polymerizations with TiCl_4 and BCl_3 Coinitiators

It was of interest to examine the quasiliving polymerization of TrMeSt with more than one Friedel-Crafts acids. For this purpose

TABLE 2. The Effect of the Solvent Polarity on the Quasiling Polymerization of TrMest ([cumyl chloride] = 10^{-2} M, $[TiCl_4] = 2 \times 10^{-2}$ M, temperature = $-50^\circ C$)

Time of sampling (min)	Cumulative amount of consumed monomer ($mol \times 10^3$)	\bar{M}_n	$\frac{DP}{n}$	$[P] \times 10^3$ mol	$\frac{\bar{M}_w}{\bar{M}_n}$	$[I]_0 \times 10^3$ mol
Pure methylene chloride						
10	29.2	3,200	21.91	1.33	2.73	1.04
20	58.4	6,000	41.09	1.42	2.48	
30	87.6	8,400	56.37	1.55	1.92	
40	116.8	9,920	67.94	1.72	1.84	
50	146.0	10,510	71.98	2.02	1.86	
$n-C_6H_{14}/CH_2Cl_2 = 20/80$						
10	27.6	4,150	28.42	0.97	2.62	0.94
20	55.2	6,600	45.20	1.22	2.25	
30	82.8	9,420	64.52	1.28	1.88	
40	110.4	12,140	83.15	1.32	1.62	
50	138.0	18,030	123.49	1.11	1.58	
$n-C_6H_{14}/CH_2Cl_2 = 40/60$						
10	28.1	5,548	38.00	0.75	2.52	0.70
20	56.2	10,005	68.53	0.82	2.62	
30	84.3	14,147	96.90	0.87	2.14	
40	112.4	21,300	145.9	0.77	1.87	
50	140.5	22,290	152.7	0.92	1.68	

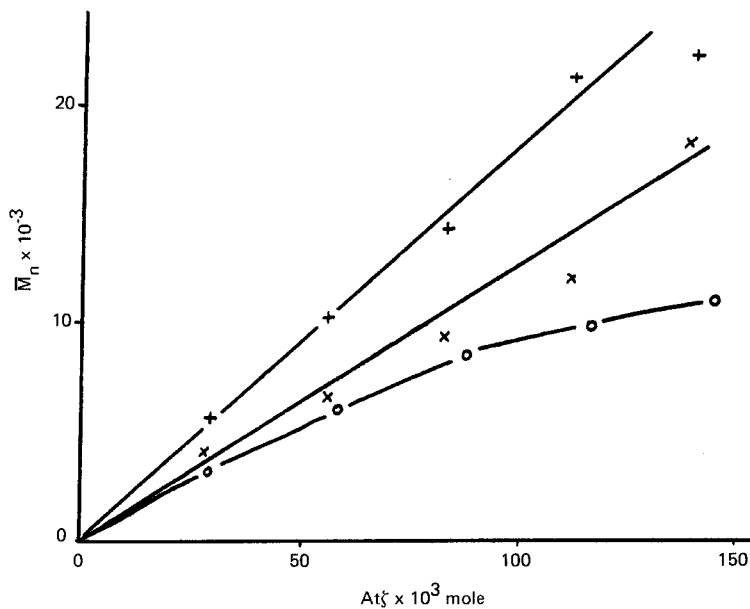


FIG. 4. \bar{M}_n versus monomer consumed for different solvents: (+) 40/60 v/v n-C₆H₁₄/CH₂Cl₂, (x) 20/80 v/v n-C₆H₁₄/CH₂Cl₂, (o) pure CH₂Cl₂. Temperature = 50°C, [CC] = 10⁻² M, [TiCl₄] = 2 × 10⁻² M, monomer addition rate = 3 × 10⁻³ mol/min.

we selected TiCl₄ and BCl₃. The results of two sets of experiments are shown in Table 3 and Figs. 7 and 8. The data indicate quasiling polymerizations with both coiniciators, i.e., linear molecular weight growth with monomer introduction (Fig. 7), theoretical number of molecules versus monomer input plots (Fig. 8), and decreasing molecular weight dispersities with molecular weight growth (Table 3). Evidently there is very little difference between the two initiating systems cumyl chloride/TiCl₄ and cumyl chloride/BCl₃, and quasiling conditions can be easily achieved with either system.

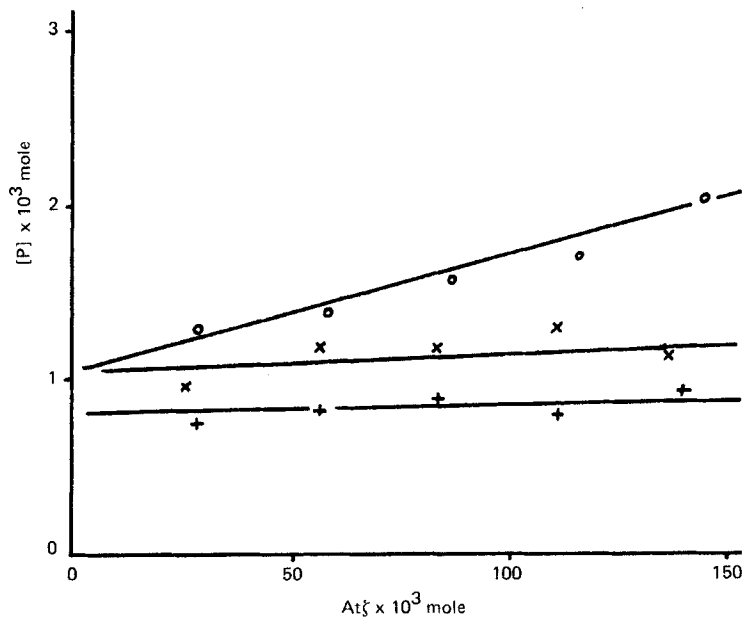


FIG. 5. Number of polymer molecules versus monomer consumed for different solvents (see legend to Fig. 4).

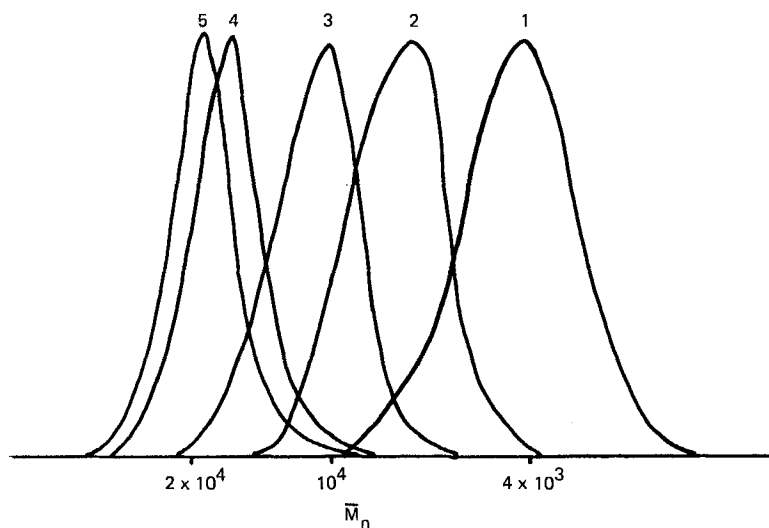


FIG. 6. GPC traces of polyTrMeSt samples obtained with cumyl chloride/ $TiCl_4$ initiating system using continuous monomer addition (see Table 1, run at $-50^\circ C$).

TABLE 3. Comparison of TiCl_4 and BCl_3 Coinitiators (20 vol% n-hexane + 80 vol% methylene chloride, initial volume = 100 mL, [cumyl chloride] = 10^{-2} M; $[\text{TiCl}_4] = 2 \times 10^{-2}$ M; $[\text{BCl}_3] = 2 \times 10^{-2}$ M; temperature = 50°C)

Time of sampling (min)	Cumulative amount of consumed monomer (mol $\times 10^3$)	\bar{M}_n	$\frac{\overline{DP}}{DP_n}$	$[\text{P}] \times 10^3$ mol	$\frac{\bar{M}_w}{\bar{M}_n}$
TiCl_4 :					
10	25.8	4,320	29.54	0.87	2.29
20	51.6	7,940	54.29	0.95	1.95
30	77.4	10,410	71.19	1.09	1.86
40	103.2	15,930	108.9	0.95	1.61
50	129.0	18,640	127.5	1.01	1.57
BCl_3 :					
10	26.2	3,990	27.28	0.96	2.47
20	52.4	6,820	46.64	1.12	2.20
30	78.6	10,950	74.88	1.05	1.72
40	104.8	15,200	103.94	1.01	1.73
50	131	17,260	118.03	1.11	1.69

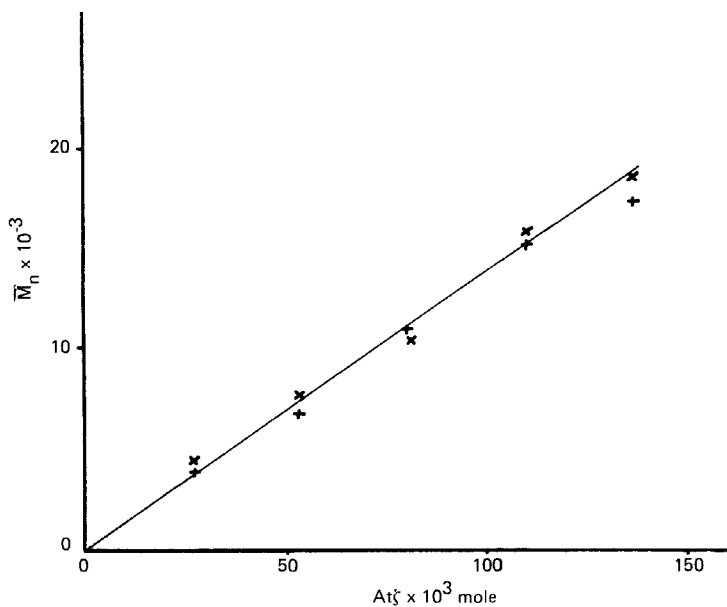


FIG. 7. \bar{M}_n versus the cumulative amount of consumed monomer: (x) coinitiator = 2×10^{-2} M TiCl_4 , (+) coinitiator = 2×10^{-2} M BCl_3 .

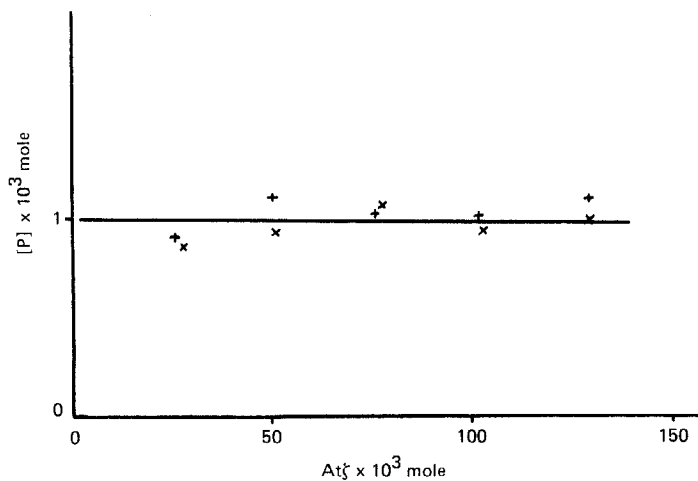


FIG. 8. Number of polymer molecules versus the cumulative amount of monomer consumed (see legend to Fig. 7).

ACKNOWLEDGMENTS

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