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Quasiliving Carbocationic Polymerization. IX. Forced Ideal Copolymerization of Styrene Derivatives

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ABSTRACT

Forced ideal carbocationic copolymerization of α -methylstyrene (α MeSt) with p-tert-butylstyrene (ptBuSt) and (α MeSt) with styrene (St) has been achieved by continuous monomer feed addition to a cumyl chloride/ BCl_3 charge at -50°C by keeping the feeding rate of the monomer mixtures equal to the overall rate of copolymerization. The composition of the copolymers was identical to the composition of the monomer feeds over the entire concentration range. A quantitative expression has been derived to show that under forced ideal copolymerization conditions the

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composition of the copolymer can be controlled by the composition of the feed. Further, conditions have been found for forced ideal quasiliving copolymerizations, i.e., the number-average molecular weight of the copolymers increased almost linearly with the cumulative weight of consumed monomers by the use of suitably slow, continuous feed addition in the presence of relatively nonpolar solvent mixtures (60/40 v/v n-hexane + methylene chloride). In polar solvent (methylene chloride) the molecular weight increase was less pronounced due to chain transfer to monomer involving indane-skeleton formation; however, with charges containing large amounts of ptBuSt the molecular weight increase was surprisingly strong. Interestingly, ptBuSt does not homopolymerize in 60/40 v/v n-hexane/methylene chloride but it readily copolymerizes with α MeSt. This observation was explained by examining the relative rates of terminations of the cationic species involved. Conditions have been found for the pronounced quasiliving polymerization of St. In forced ideal quasiliving polymerizations neither the molecular weights of α MeSt/ptBuSt or α MeSt/St copolymers nor the initiating efficiencies of the initiating systems used show a depression. The microstructure of representative α MeSt/ptBuSt copolymers obtained under forced ideal quasiliving conditions has been analyzed by ^{13}C -NMR spectroscopy. According to these studies, true copolymers have formed and resonance peaks for various triads have been deduced.

INTRODUCTION

As shown by the previous articles of this series [1-8], quasiliving homopolymerization and block copolymerization has been achieved with a variety of representative olefins by the use of a slow, continuous monomer addition technique. In quasiliving polymerization systems initiation is instantaneous, termination is reversible (i.e., absent), and chain transfer to monomer is much depressed; the \bar{M}_n

versus consumed monomer plots of quasiliving systems start at the origin and are linear over a broad range. In the course of these investigations we theorized that the feeding of monomer mixtures instead of a single monomer with the same technique could lead to random copolymers having the same composition as the monomer mixture, i.e., the process would be an ideal copolymerization. The basic requirement for such a "forced" ideal copolymerization is that the feeding rate of the monomer mixture should be equal to the overall copolymerization rate, i.e., complete conversions should be obtained. This requirement could be attained if initiation is instantaneous and irreversible chain termination is absent, or if the rate of

initiation is faster than the rate of termination. The number of active centers should not decrease in either case.

In conventional copolymerizations, copolymer composition will be uniform and equal to the composition of the charge only if $r_1 = r_2 = 1$, or with azeotropic charges, i.e., when $m_1/m_2 = (r_2 - 1)/(r_1 - 1)$. Under all other circumstances the copolymer composition will be different from the monomer feed composition. Further, during copolymerizations the composition of copolymers will continuously shift with increasing conversions (i.e., decreasing monomer concentrations).

In regards to copolymer molecular weight, Higashimura et al. [9], and Kennedy and Chou [10] demonstrated that the molecular weights of copolymers obtained in conventional cationic copolymerizations must decrease in reference to the molecular weights of the respective homopolymers.

In quasiliving systems, chain transfer to monomer is depressed and molecular weights increase with consumed monomer. Thus it was further postulated that forced ideal quasiliving copolymerizations could be achieved provided conditions could be found under which copolymerization initiation is instantaneous, termination is reversible, and chain transfer is depressed. Under these conditions the overall composition and the molecular weight of the copolymer could be controlled, the former by the feed composition, the latter by the amount of feed consumed.

This paper concerns forced ideal quasiliving copolymerization of α -methylstyrene/p-t-butylstyrene (α MeSt/ptBuSt) and α -methylstyrene/styrene (α MeSt/St) monomer pairs with cumyl chloride/ BCl_3 initiating system. It has been demonstrated that the composition of the copolymers can be controlled by judicious feeding rate and that their molecular weights increase with monomer input.

EXPERIMENTAL

Materials

α MeSt, ptBuSt and St were extracted with 10% aqueous NaOH, washed neutral with distilled water, dried over molecular sieves (3\AA), and distilled from CaH_2 under vacuo. n-Hexane was refluxed with oleum for 2 h, then washed with distilled water, dried over molecular sieves (3\AA), and distilled from CaH_2 . Methylene chloride was purified as described [11]. BCl_3 was condensed from a lecture bottle under N_2 . Cumyl chloride (2-chloro-2-phenylpropene, CC) was prepared from purified α MeSt by hydrochlorination in methylene chloride solution; excess HCl and solvent were removed by repeated freeze-drying.

Procedures

Polymerizations were carried out in a stainless steel enclosure under dry N_2 at $-50^\circ C$ in 300 cm^3 three-neck round-bottom flasks equipped with stirrer, Teflon plug for monomer addition, and outlet for sampling. The initial volume of solvent(s) was 100 cm^3 and the initial concentrations of BCl_3 and cumyl chloride were $4.3 \times 10^{-2}\text{ M}$ and $1.3 \times 10^{-2}\text{ M}$, respectively. Monomer mixtures were fed continuously by a precision metering pump (Beckman Model 110A) through a precision glass capillary outlet. Samples (0.1 cm^3) were withdrawn with a syringe from the reaction mixture and were injected into capped vials containing excess methanol. Polymerizations were stopped by adding methanol to the reaction mixture. Final conversions were determined gravimetrically.

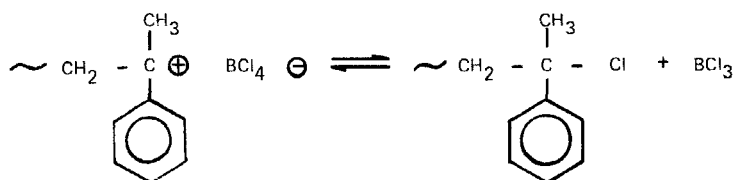
Molecular weights were determined by a Waters Associates high pressure GPC equipped with four Microstyrigel columns (10^5 , 10^4 , 10^3 , and 500 \AA) and dual UV/RI detectors. Molecular weights were calculated from a calibration curve obtained with polystyrene standards.

Copolymer compositions were determined by integration of 1H -NMR resonances using a Varian T-60 NMR spectrometer at room temperature. Before NMR analysis the samples were extracted with methanol to remove residues. Copolymer structures were investigated by ^{13}C -NMR spectroscopy using a Varian FT-80A instrument and $CDCl_3$ solutions at room temperature.

RESULTS AND DISCUSSION

General Considerations

As discussed in detail in the classification of quasiling systems [1], a key demand of quasiling polymerizations is the absence or reversibility of termination. For example, in the case of α MeSt polymerization cointiated by BCl_3 termination is in fact absent because of the equilibrium [12]



By the use of a judicious monomer addition rate and relatively non-polar solvent mixtures, quasiling polymerization of α MeSt could be achieved and \bar{M}_n versus monomer addition plots were linear over a wide range [2].

We postulated that forced ideal copolymerization could be achieved in the absence of termination by the use of slow, continuous monomer addition, and thus copolymers whose composition would be uniform and identical to that of the feed could be prepared. In a living batch copolymerization the composition of the charge will continuously shift with increasing conversions (except for azeotropic copolymerizations or when $r_1 = r_2 = 1$), and at 100% conversion the average copolymer composition will reach that of the charge. The sequence distribution (microstructure) of the copolymer product will be non-uniform and will be governed by the reactivity ratios of the particular monomers used. In contrast, under quasiling conditions (i.e., by continuously feeding monomers to active charge in which instantaneous and complete monomer consumption occurs), copolymers with macroscopically uniform structures and compositions identical to that of the feed should be obtained because in the quasiling experiment living microbatch copolymerizations are continuously repeated.

The composition of a copolymer obtained by a forced ideal copolymerization can be derived as follows.

The addition of a mixture of two monomers (Monomer 1 and Monomer 2) to a copolymerization charge with an input rate of

$$A = A_1 + A_2 \quad (1)$$

(and neglecting monomer consumption due to chain transfer), leads to the respective monomer concentrations in the charge:

$$d[M_1]/dt = A_1 - [k_{11}\alpha + k_{21}(1 - \alpha)][I]_0[M_1] \quad (2)$$

$$d[M_2]/dt = A_2 - [k_{22}(1 - \alpha) + k_{12}\alpha][I]_0[M_2] \quad (3)$$

where $\alpha = [M_1^\oplus] / ([M_1^\oplus] + [M_2^\oplus])$, i.e., the fraction of propagating cations with monomer 1 as terminal units, and $[I]_0$ = the number of active centers; the rate constants have the usual meaning.

Under stationary conditions, assuming continuous 100% monomer conversion,

$$d[M_1]/dt \cong 0 \quad \text{and} \quad d[M_2]/dt \cong 0 \quad (4)$$

and

$$[M_1] = [M_1]_{st} \quad \text{and} \quad [M_2] = [M_2]_{st} \quad (5)$$

where the subscript "st" refers to the steady state. Thus the rates of incorporation of Monomers 1 and 2 into the copolymer are

$$d[M_1^P]/dt = [k_{11}\alpha + k_{21}(1 - \alpha)][I]_0[M_1]_{st} = A_1 \quad (6)$$

$$d[M_2^P]/dt = [k_{22}(1 - \alpha) + k_{12}\alpha][I]_0[M_2]_{st} = A_2 \quad (7)$$

where $[M_1^P]$ and $[M_2^P]$ are respective amounts of Monomers 1 and 2 in the copolymer. Since the input rates are constant, integration yields

$$[M_1^P] = A_1 t \quad (8)$$

$$[M_2^P] = A_2 t \quad (9)$$

and

$$\frac{[M_1^P]}{[M_2^P]} = \frac{A_1}{A_2} \quad (10)$$

which is the copolymer composition equation for this special case. Equation (10) shows that copolymer composition is determined only by the addition rate of the monomers and does not depend on r_1 and r_2 .

While in a forced ideal copolymerization the average copolymer composition is independent of the monomer reactivity ratios, the sequence distribution (microstructure) is still governed by these fundamental parameters.

The number-average degree of polymerization (\overline{DP}_n) is given by

$$\overline{DP}_n = \frac{(A_1 + A_2)t}{[I]_0 + [P^-]} \quad (11)$$

where $[P^-]$ is the amount of polymer molecules formed by chain transfer:

$$\begin{aligned}
 [P^-] = & \left\{ \left[k_{11}^{\text{tr}}\alpha + k_{21}^{\text{tr}}(1-\alpha) \right] [M_1]_{\text{st}} + \right. \\
 & \left. + \left[k_{12}^{\text{tr}}\alpha + k_{22}^{\text{tr}}(1-\alpha) \right] [M_2]_{\text{st}} \right\} [I]_0 t
 \end{aligned} \quad (12)$$

Using Eqs. (6) and (7) for A_1 and A_2 , taking into account that

$$k_{12}^{\alpha} [M_2]_{\text{st}} = k_{21}^{\alpha} (1-\alpha) [M_1]_{\text{st}} \quad (13)$$

and introducing the notations

$$\begin{aligned}
 r_1 = k_{11}^{\text{tr}}/k_{12}^{\text{tr}}, \quad C_{11} = k_{11}^{\text{tr}}/k_{11}^{\text{tr}}, \quad C_{12} = k_{12}^{\text{tr}}/k_{12}^{\text{tr}} \\
 r_2 = k_{22}^{\text{tr}}/k_{21}^{\text{tr}}, \quad C_{22} = k_{22}^{\text{tr}}/k_{22}^{\text{tr}}, \quad C_{21} = k_{21}^{\text{tr}}/k_{21}^{\text{tr}}
 \end{aligned} \quad (14)$$

we obtain from (11) and (12):

$$\frac{(A_1 + A_2)t}{\overline{DP}_n} = [I]_0 + C(A_1 + A_2)t \quad (15)$$

where C stands for the transfer constant of the copolymerization:

$$C = \frac{C_{11}r_1[M_1]_{\text{st}}^2 + (C_{12} + C_{21})[M_1]_{\text{st}}[M_2]_{\text{st}} + C_{22}r_2[M_2]_{\text{st}}^2}{r_1[M_1]_{\text{st}}^2 + 2[M_1]_{\text{st}}[M_2]_{\text{st}} + r_2[M_2]_{\text{st}}^2} \quad (16)$$

The first term of Eq. (15) becomes negligible with increasing time; thus \overline{DP}_n approaches a maximum value:

$$\lim_{t \rightarrow \infty} \overline{DP}_n = \overline{DP}_{n,\text{max}} = 1/C \quad (17)$$

Of course, if $C = 0$, i.e., in the absence of chain transfer (e.g., in QL_{R0} systems), $\overline{DP}_{n,\text{max}} = \infty$ and the molecular weight increase is unlimited:

$$\overline{DP}_n = \frac{(A_1 + A_2)t}{[I]_0} \quad (18)$$

Forced Ideal Quasiliving Copolymerization of α -Methylstyrene and p-t-Butylstyrene

To suppress irreversible chain transfer to monomer involving indane-skeleton formation [2, 5], experiments have been carried out by using 60/40 v/v n-hexane/methylene chloride solvent mixtures. The composition of the initial monomer mixtures, the composition and molecular weight of the copolymers obtained, and the final conversions together with other pertinent information are listed in Table 1.

In the first two experiments (SS 1-5 and SS 6-10) a stream of undiluted monomer was added. When the α MeSt content in the feed was increased from 53 to 77 mol% the conversion increased from 60 to 80%. The molecular weights of the copolymers increased with monomer addition in both cases.

Copolymer compositions in Samples SS 1 and 6 were essentially identical to that of the monomer feeds, but later, in Samples 2-5 and 7-10, the amount of α MeSt in the copolymer became increasingly higher than in the feed. Evidently the monomers accumulated in the reactor during the reaction. While the reactivity ratios of α MeSt and ptBuSt are unavailable, α MeSt is presumably more reactive than ptBuSt (indeed, according to Ref. 13, the r values for α MeSt and p-ethylstyrene are $r_{\alpha\text{MeSt}} = 3.0$ and $r_{\text{pEtSt}} = 0.3$). We found that the UV intensity by GPC of residual monomers gradually increased from sample to sample and the concentration of unreacted ptBuSt was higher than that of α MeSt.

In order to increase conversions the monomer feed was diluted with a solvent mixture (25 vol% monomer mixture + 75 vol% solvent mixture) and in this manner the input rate was decreased to 0.5 cm³/min (SS 11-15). As a consequence the conversion rose to 90% and copolymer compositions approached the expected value (see Table 1). The decrease of the input rate also resulted in a linear molecular weight increase (Fig. 1). Figure 2 shows the corresponding unimodal GPC traces obtained.

Figure 3 is a plot of the number of polymer molecules (calculated by $[P] = (A_1 + A_2)t/\overline{DP}_n$) against the cumulative amount of monomers consumed in Experiments SS 1-15. The $\overline{DP}_{n,\text{max}}$ and $[I]_0$ values shown in Table 1 were calculated by using Eqs. (15) and (17). For convenience, the values are given in moles. Evidently, by decreasing the input rate from 14.25×10^{-3} mol/min (2 cm³/min, SS 6-10) to 3.5×10^{-3} mol/min (0.5 cm³/min, SS 11-15), we could avoid extensive chain transfer, reach high $\overline{DP}_{n,\text{max}}$, and obtain practically 100% initiator efficiency.

To clarify these results the homopolymerization of ptBuSt was investigated in solvent mixtures of different polarity under the same conditions. Surprisingly, ptBuSt was found not to homopolymerize in 60/40 v/v n-hexane/methylene chloride solvent mixture! The

TABLE 1. Copolymerization of α -Methylstyrene and p-t-Butylstyrene with BCl_3 /Cumyl Chloride Initiation System in 60/40 v/v Hexane/Methylene Chloride Solvent Mixture^a

Sample	Cumulative Mole amount of fraction consumed of αMeSt monomers $\times 10^3$ mol	$\bar{M}_n \times 10^{-3}$	$\bar{DP}_n \times 10^{-3}$	Number of polymer molecules $\times 10^3$ mol	\bar{M}_w/\bar{M}_n	$\bar{DP}_{n,\text{max}}$ (calcd)	$[\text{I}]_0 \times 10^3$ mol (calcd)
$A_1 = 6.9 \times 10^{-3}$ mol/min, $A_2 = 6.1 \times 10^{-3}$ mol/min ($A = A_1 + A_2 = 13 \times 10^{-3}$ mol/min); mole fraction of αMeSt : 0.53; conversion = 60%							
SS 1	11.7	0.56	15.96	0.73	1.80		
2	23.4	0.61	26.26	0.89	1.85		
3	35.1	0.63	32.28	1.09	1.90	52.4	0.47
4	46.8	0.66	34.10	1.37	1.95		
5	58.5	0.68	36.27	1.61	1.95		
$A_1 = 11 \times 10^{-3}$ mol/min, $A_2 = 3.25 \times 10^{-3}$ mol/min ($A = 14.25 \times 10^{-3}$ mol/min); mole fraction of αMeSt : 0.77; conversion = 80%							
6	17.1	0.80	17.01	1.05	1.84		
7	34.2	0.89	33.38	1.03	1.85		
8	51.3	0.90	40.45	1.27	1.83	80	0.60
9	68.8	0.88	48.55	1.42	1.91		
10	85.0	0.83	50.70	1.69	1.94		

(continued)

TABLE 1 (continued)

Sample	Cumulative amount of monomers consumed $\times 10^3$ mol	Mole fraction of α MeSt in the copolymer	$\bar{M}_n \times 10^{-3}$	\bar{DP}_n	Number of polymer molecules $\times 10^3$ mol	\bar{M}_w/\bar{M}_n	$\bar{DP}_{n, \max}$ (calcd)	$[I]_0 \times 10^3$ mol (calcd)
$A_1 = 2.7 \times 10^{-3}$ mol/min, $A_2 = 0.8 \times 10^{-3}$ mol/min ($A = 3.5 \times 10^{-3}$ mol/min); mole fraction of α MeSt: 0.77;								
conversion = 90%								
11	22.1	0.76	2.23	17.44	1.26	1.76		
12	44.2	0.80	4.20	32.86	1.35	2.26		
13	66.3	0.75	5.23	40.92	1.62	3.02	387.7	1.26
14	88.4	0.75	8.10	63.37	1.40	2.50		
15	110.5	0.82	9.30	72.76	1.52	3.40		

^a Monomer 1 = α MeSt, Monomer 2 = ptBuSt.

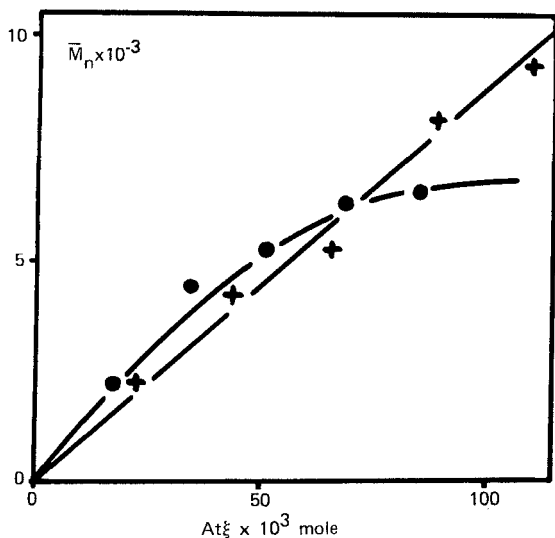


FIG. 1. \bar{M}_n vs cumulative amount of consumed monomer in the copolymerization of α -MeSt and ptBuSt in nonpolar solvent. (●) SS 6-10: $A = 14.25 \times 10^{-3}$ mol/min. (+) SS 11-15: $A = 3.50 \times 10^{-3}$ mol/min.

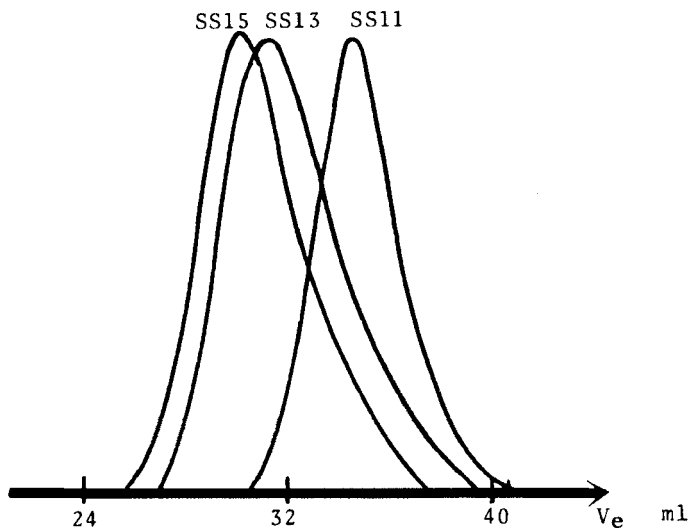


FIG. 2. GPC curves of Samples SS 11, SS 13, and SS 15.

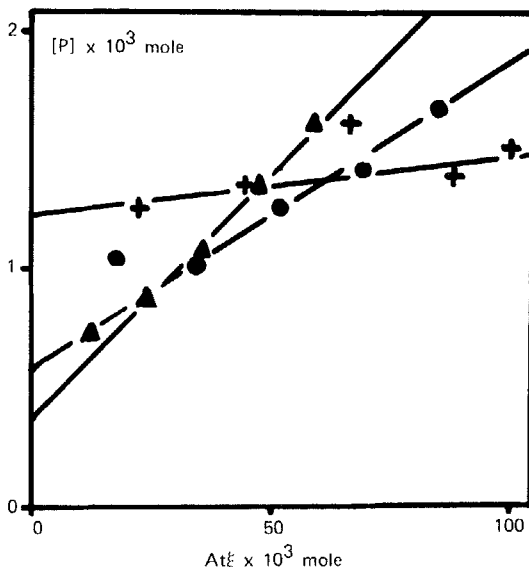
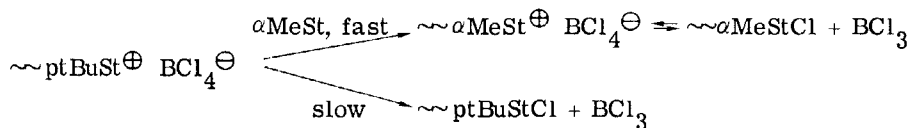


FIG. 3. Number of α MeSt/ptBuSt copolymer molecules $[P]$ vs cumulative amount of monomers consumed in Experiments SS 1-15 (nonpolar solvent): (\blacktriangle) SS 1-5, (\bullet) SS 6-10, ($+$) SS 11-15.

fact that ptBuSt does not homopolymerize under the conditions used in copolymerization experiments is proof positive for copolymerization.

Evidently, in the homopolymerization of ptBuSt, irreversible chain termination occurs or reionization of the chlorine-terminated chain end is reduced in relatively nonpolar media. However, in the copolymerization of α MeSt and ptBuSt, cross-propagation is faster than termination of the ptBuSt $^{\oplus}$ unit:



If the feed is rich in α MeSt, propagation may proceed; however, the active center concentration will decrease because of irreversible termination of the ptBuSt unit.

Reionization of the tertiary chlorine terminus of α MeSt is faster than that of the secondary chlorine terminus of ptBuSt. Probably in the polar methylene chloride solvent reionization of the secondary chlorine terminus is also accelerated, thus homopolymerization occurs and the molecular weight of the ptBuSt increases (Table 2). Also

TABLE 2. Copolymerization of α -Methylstyrene and p-t-Butylstyrene with BCl_3 /Cumyl Chloride Initiating System in Methylene Chloride Solvent, and Homopolymerization of These Monomers under the Same Conditions

Sample	Cumulative amount of monomers consumed $\times 10^3$ mol	Mole fraction of αMeSt in the copolymer	$\bar{M}_n \times 10^{-3}$	$\frac{\text{DP}}{n} \times 10^{-3}$	Number of polymer molecules $\times 10^3$ mol	$\frac{\bar{M}_w}{\bar{M}_n}$	$\frac{\text{DP}}{n, \text{max}}$ (calcd)	$[\text{I}]_0 \times 10^3$ mol (calcd)
$A_1 = 0.76 \times 10^{-3}$ mol/min, $A_2 = 2.25 \times 10^{-3}$ mol/min ($A = A_1 + A_2 = 3.01 \times 10^{-3}$ mol/min; mole fraction of $\alpha\text{MeSt} = 0.25$; conversion = 97%)								
vv 1	22.04	0.25	2.20	14.72	1.50	1.90		
2	44.08	0.25	4.50	30.10	1.46	2.20		
3	66.12	0.25	5.99	40.07	1.65	2.15	113.0	1.26
4	88.16	0.17	7.40	49.50	1.78	2.10		
5	110.09	0.23	7.99	53.44	2.06	2.10		
$A_1 = 1.6 \times 10^{-3}$ mol/min, $A_2 = 1.63 \times 10^{-3}$ mol/min ($A = 3.23 \times 10^{-3}$ mol/min); mole fraction of $\alpha\text{MeSt} = 0.50$; conversion = 98%								
6	12.73	0.50	3.20	23.00	1.03	4.09		
7	47.48	0.54	3.30	23.70	2.00	5.02		
8	71.22	0.55	3.80	27.32	2.61	4.80	45.8	1.00
9	95.12	0.54	4.30	30.91	3.08	4.50		
10	118.70	0.54	4.62	33.21	3.57	4.40		
$A_1 = 2.71 \times 10^{-3}$ mol/min, $A_2 = 0.88 \times 10^{-3}$ mol/min ($A = 3.59 \times 10^{-3}$ mol/min); mole fraction of $\alpha\text{MeSt} = 0.75$; conversion = 35%								
11	25.58	0.77	2.50	19.43	1.32	4.50		
12	51.15	0.75	2.70	28.76	1.78	3.60		

(continued)

TABLE 2 (Continued)

Sample	Cumulative amount of monomers consumed $\times 10^3$ mol	Mole fraction of α MeSt in the copolymer	$\bar{M}_n \times 10^{-3}$	\overline{DP}_n	Number of polymer molecules $\times 10^3$ mol	\bar{M}_w/\bar{M}_n	$\overline{DP}_{n, \max}$ (calcd)	$[\eta]_0 \times 10^3$ mol (calcd)
13	76.74	0.72	4.20	32.65	2.35	3.00	56.8	0.90
14	102.31	0.65	5.00	38.87	2.63	2.90		
15	127.90	0.75	4.60	35.76	3.58	2.60		
$A_1 = 2.79 \times 10^{-3}$ mol/min, $A_2 = 0.75 \times 10^{-3}$ mol/min ($A = 3.54 \times 10^{-3}$ mol/min); mole fraction of α MeSt = 0.79; conversion = 99%								
16	26.55	0.80	2.30	18.10	1.47	5.25		
17	53.10	0.79	3.30	25.99	2.10	3.00		
18	79.65	0.80	3.95	31.11	2.56	3.00	43.4	0.84
19	106.20	0.77	4.03	31.74	3.35	2.95		
20	132.75	0.79	4.32	34.02	3.90	2.62		
Homopolymerization of α MeSt: $A_1 = 3.89 \times 10^{-3}$ mol/min; conversion = 99%								
	29.18		1.50	12.69	2.30	2.45		
	58.35		1.60	13.54	4.31	2.65		
	87.54		1.50	12.69	9.90	2.59	14.6	0.46
	116.72		1.60	13.54	8.62	2.45		
	145.90		1.70	14.38	10.14	2.63		
Homopolymerization of ptBuSt: $A_2 = 2.75 \times 10^{-3}$ mol/min; conversion = 73%								
	15.06		1.85	11.59	1.30	1.35		
	30.11		3.58	22.37	1.35	1.70		
	45.18		4.52	28.24	1.60	1.87	113.0	1.20
	60.22	5.67	6.88	35.43	1.70	1.90		
	75.29		6.88	43.03	1.75	2.04		

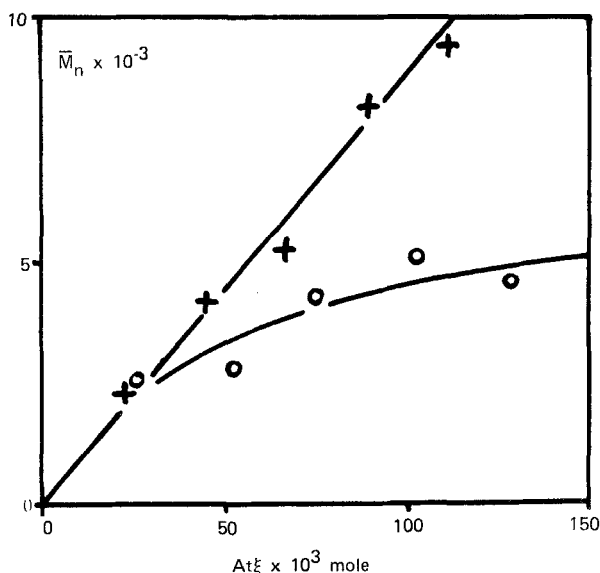


FIG. 4. The effect of solvent polarity on \bar{M}_n of α MeSt/ptBuSt copolymers: \bar{M}_n vs cumulative amount of consumed monomer. (+) SS 11-15: 60 vol% n-hexane + 40 vol% methylene chloride. (o) VV 11-15: methylene chloride.

forced ideal copolymerization was achieved in this solvent (Experiments VV 1-20). Results are shown in Table 2. The experiments were carried out by the use of 25/75 v/v mixed monomer/methylene chloride solution. Conversions were essentially 100%, thus copolymer compositions were equal to the composition of the monomer feed. Evidently the use of polar solvent also increased the rate of chain transfer (indane-skeleton formation) and thus the molecular weight increase was less pronounced than in nonpolar solvent (Fig. 4). Interestingly, in Experiments VV 1-5 where the ptBuSt content was high (75 mol%), the molecular weight strongly increased although polar solvent was used (Fig. 5). A plot of the number of polymer molecules $[P]$ against the cumulative amount of consumed monomers for the copolymerization Experiments VV 1-20 and for the homopolymerization of the two monomers (not shown) supplies $\bar{DP}_{n, \max}$ and $[I]_0$ values (calculated by using Eqs. 15 and 17) and are listed in Table 2.

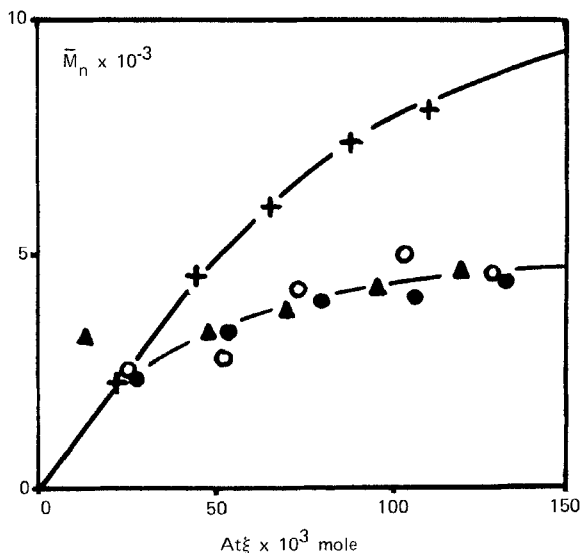


FIG. 5. Effect of monomer mixture composition ($f_1 = \alpha\text{MeSt}$ mole fraction in the feed) on \bar{M}_n of $\alpha\text{-MeSt/ptBuSt}$ copolymers: \bar{M}_n vs cumulative amount of consumed monomer. (+) VV 1-5: $f_1 = 0.25$. (▲) VV 6-10: $f_1 = 0.50$. (○) VV 11-15: $f_1 = 0.75$. (●) VV 16-20: $f_1 = 0.79$.

Copolymerization of α -Methylstyrene and Styrene in Methylene Chloride

The copolymerization of αMeSt and St was investigated at three monomer feed compositions. Conditions were identical to those used in Experiments VV 1-20. Results are listed in Table 3. Conversions were essentially 100% in every case. Copolymer composition data obtained by $^1\text{H-NMR}$ spectroscopy are somewhat uncertain due to the small difference in the number of protons between the two monomers, but the agreement between the composition of monomer feeds and that of copolymers is excellent. With increasing αMeSt content in the feed, the molecular weight increase was less pronounced.

A plot of the number of polymer molecules $[P]$ against the cumulative amount of consumed monomers for the copolymerization Experiments A 6-20 and for the homopolymerization of the two monomers (not shown) supplies $\overline{DP}_{n,\text{max}}$ and $[I]_0$ values (calculated by using Eqs. 15 and 17) and are listed in Table 3.

TABLE 3. Copolymerization of α -Methylstyrene and Styrene with BCl_3 /Cumyl Chloride Initiating System in Methylene Chloride Solvent, and Homopolymerization of Styrene under the Same Condition^a

Sample	Cumulative amount of monomers consumed $\times 10^3$ mol	Mole fraction of αMeSt in the copolymer	$\bar{M}_n \times 10^{-3}$	$\overline{\text{DP}}_n$	Number of polymer molecules $\times 10^3$ mol	\bar{M}_w/\bar{M}_n	$\overline{\text{DP}}_{n, \text{max}}$ (calcd)	$[\text{I}]_0 \times 10^3$ mol (calcd)
$A_1 = 1.1 \times 10^{-3}$ mol/min, $A_2 = 3.17 \times 10^{-3}$ mol/min ($A = A_1 + A_2 = 4.27 \times 10^{-3}$ mol/min); mole fraction of $\alpha\text{MeSt} = 0.25$; average $\bar{M}_s = 107.66$; conversion = 97%								
A 6	31.06	0.31	2.05	19.04	1.63			
7	62.13	0.23	3.23	30.00	2.07	2.15		
8	93.18	0.17	3.81	35.39	2.63	2.15	54.88	0.97
9	124.26	0.26	4.42	41.06	3.03	2.20		
10	155.30	0.21	4.2	39.01	3.98	2.30		
$A_1 = 2.03 \times 10^{-3}$ mol/min, $A_2 = 2.02 \times 10^{-3}$ mol/min ($A = 4.05 \times 10^{-3}$ mol/min); mole fraction of $\alpha\text{MeSt} = 0.50$; average $\bar{M}_s = 111.17$; conversion = 99%								
11	30.07	0.56	1.80	16.19	1.86	2.75		
12	60.14	0.57	2.40	21.60	2.80	2.61		
13	90.21	0.44	2.90	26.09	3.46	2.70	57.12	1.10
14	120.28	0.36	3.20	28.78	4.18	2.80		
15	150.35	0.48	3.20	28.78	5.22	2.81		

(continued)

TABLE 3 (Continued)

Sample	Cumulative amount of monomers consumed $\times 10^3$ mol	Mole fraction of α MeSt in the copolymer	$\bar{M}_n \times 10^{-3}$	\overline{DP}_n	Number of polymer molecules $[P] \times 10^3$ mol	\bar{M}_w/\bar{M}_n	$\overline{DP}_{n, \max}$ (calcd)	$[I]_0 \times 10^3$ mol (calcd)
$A_1 = 2.96 \times 10^{-3}$ mol/min, $A_2 = 0.96 \times 10^{-3}$ mol/min ($A = 3.92 \times 10^{-3}$ mol/min); mole fraction of α MeSt = 0.75; average $\bar{M}_s = 114.69$; conversion = 98%								
16	28.81	0.83	1.30	11.33	2.59	3.05		
17	57.62	0.75	1.70	14.82	3.89	2.90		
18	86.43	0.78	1.90	16.57	5.22	2.75	23.0	1.40
19	115.25	0.78	2.00	17.44	6.61	2.60		
20	144.05	0.75	2.20	19.18	7.50			
Homopolymerization of styrene: $A_2 = 4.33 \times 10^{-3}$ mol/min; conversion = 100%								
28.52			11.50	110.42	0.26	2.80		
57.04			21.80	209.33	0.27	2.85		
85.56			31.00	297.68	0.29	2.52	∞	0.26
114.08			44.70	429.23	0.27	1.97		
147.60			45.30	434.99	0.33	2.03		

^a Monomer 1 = α MeSt. Monomer 2 = St. Average \bar{M}_s = average molecular weight of the monomers in the mixture.

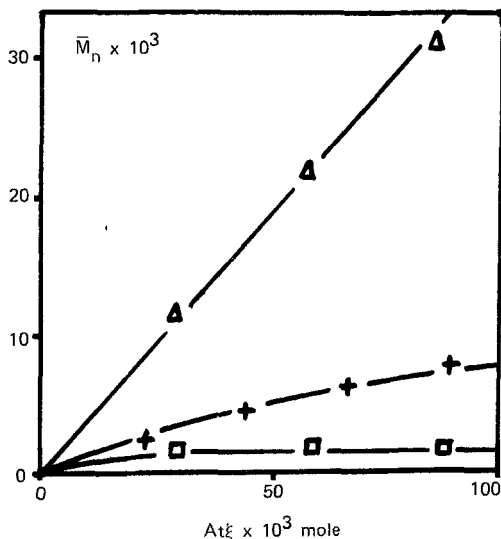


FIG. 6. \bar{M}_n vs cumulative amount of consumed monomer plots: a comparison of the homopolymerizations of styrene (Δ) and α -methylstyrene (\square) and the copolymerization of styrene with α -methylstyrene ($+$, Experiments A1-5).

In the homopolymerization of St the molecular weight increased linearly with time or added monomer in spite of the less than 100% (i.e., 88%) conversion (Fig. 6); however, the initiator efficiency was very low (26%).

Molecular Weights and Initiator Efficiencies in Forced Ideal Copolymerization

In the α MeSt/ptBuSt and α MeSt/St copolymerization systems the limiting molecular weights of copolymers are between the respective molecular weights of the homopolymers (Figs. 7 and 8), and the initiator efficiencies are high, although in the homopolymerization of α MeSt and St the initiator efficiencies are low, 46 and 26%, respectively. We did not detect molecular weight depression in any of our systems. Since the monomer concentrations used were low and chain transfer to monomer was much reduced, the theory developed by Kennedy and Chou [10] to explain molecular weight depressions in conventional cationic copolymerizations seems not to be valid here.

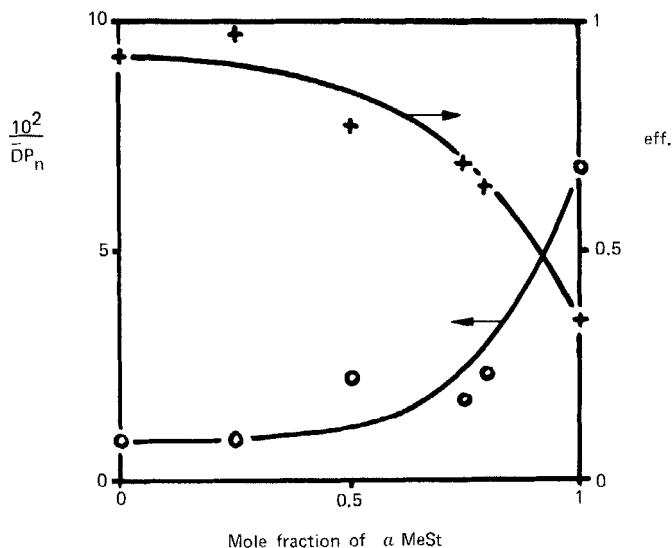


FIG. 7. $1/\overline{DP}_{n,\max}$ (\circ) and $I_{\text{eff.}} = [I]_{0,\text{calc.}}/[I]_0$ (+) vs copolymer composition plots of the $\alpha\text{MeSt}/\text{ptBuSt}$ copolymerization in methylene chloride.

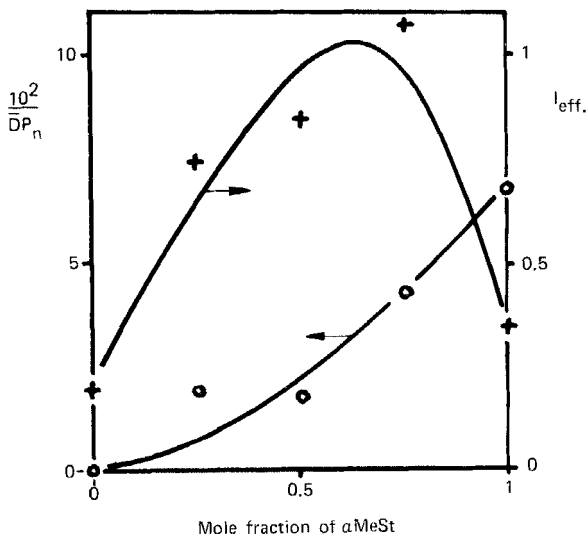


FIG. 8. $1/\overline{DP}_{n,\max}$ (\circ) and $I_{\text{eff.}} = [I]_{0,\text{calc.}}/[I]_0$ (+) vs copolymer composition plots of the $\alpha\text{MeSt}/\text{St}$ copolymerization system in methylene chloride.

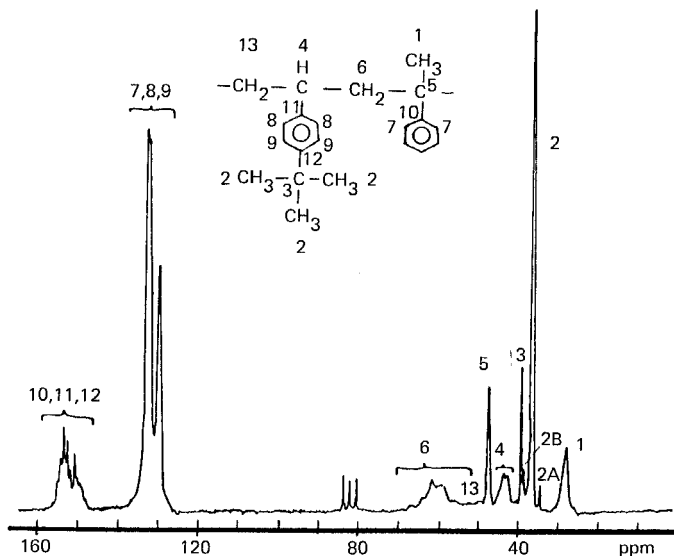


FIG. 9. ^{13}C -NMR spectrum of an $\alpha\text{MeSt}/\text{ptBuSt}$ copolymer (mole fraction of αMeSt is 0.54, deuteriochloroform solvent).

^{13}C -NMR Investigation of Copolymers

Spectroscopic analysis of the microstructure of the products obtained in these experiments provides direct proof for the formation of true copolymers. Figure 9 and Table 4 show the ^{13}C -NMR spectrum and peak assignments, respectively, of representative $\alpha\text{MeSt}/\text{ptBuSt}$ copolymer. (The mole fraction of αMeSt units, $f_1 = [M_1^P] / ([M_1^P] + [M_2^P])$, is 0.54).

Figure 10 shows the aliphatic region of a ptBuSt homopolymer together with a series of $\alpha\text{MeSt}/\text{ptBuSt}$ copolymers with different overall compositions. With decreasing mole fraction of αMeSt in the copolymer the resonances associated with the carbon in the $-\text{CH}_2-$ group (50–63 ppm, peak no. 6) shifts downfield.

A closer inspection of the resonances in the 40–43 ppm range, i.e., the resonances associated with the tertiary carbon in the ptBuSt unit (peak no. 4) led to a tentative triad assignment. The spectrum of the homopolymer of ptBuSt exhibits only one resonance at 43.1 ppm. The spectrum of the product formed with $f_1 = 0.25$ αMeSt in the feed exhibits the resonance at 43.1 ppm plus another at 42 ppm. Next, in the spectrum of the copolymer obtained with $f_1 = 0.54$ αMeSt in the feed, the

TABLE 4. Chemical Shifts in the ^{13}C -NMR Spectrum of an $\alpha\text{MeSt}/\text{ptBuSt}$ Copolymer

Peak no. ^a	Chemical shift (ppm)	Identification of the carbon atom				
		αMeSt -Unit (1)	ptBuSt-Unit (2)			
1	26.0	$-\text{CH}_3$	-			
2	34.6	-	$-(\text{CH}_3)_3$			
2A	33.3	-	$-(\text{CH}_3)_3$ in the indane end group			
2B	35.9	-				
3	37.3	-	$-\overset{ }{\text{C}}-$			
4	43.1	-	$-\overset{ }{\text{CH}}-$ $\left\{ \begin{array}{l} \text{in 222 triad} \\ \text{in 212 triad} \\ \text{in 121 triad} \end{array} \right.$			
	42.0	-				
	40.7	-				
5	45.6	$-\overset{ }{\text{C}}-$	-			
6	63-50	$-\text{CH}_2-$	-			
7 } 8 } 9 }	133-125	CH groups in the aromatic ring	CH groups in the aromatic ring			
10 } 11 } 12 }				143-151	C atoms in the aromatic ring	C atoms in the aromatic ring
13						

^aPeak numbers in Figs. 9 and 10; $f_1 = 0.54$.

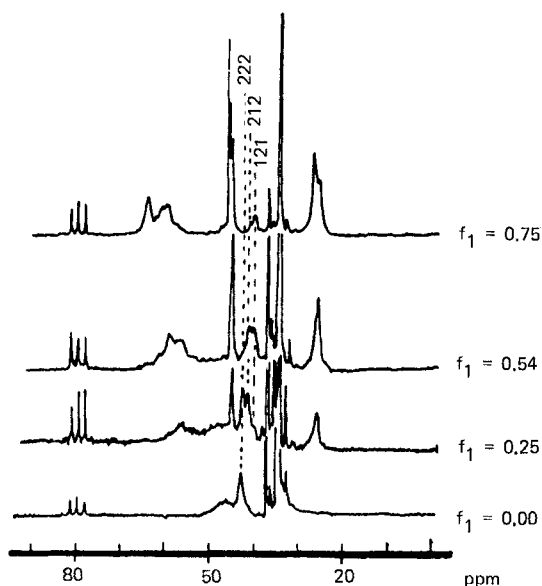


FIG. 10. ^{13}C -NMR spectra of various $\alpha\text{MeSt}/\text{ptBuSt}$ copolymers (f_1 = mole fraction of αMeSt in the feed) in the aliphatic region.

Solvent: deuteriochloroform.

resonance at 43.1 ppm is hardly noticeable as a shoulder, the resonance at 42 ppm is still strong, and a new strong resonance appears at 40.7 ppm. Finally, in the spectrum of the polymer obtained with $f_1 = 0.75$ αMeSt in the feed, the resonance at 43.1 ppm disappeared, the intensity of the resonance at 42 ppm strongly decreased, while that at 40.7 ppm became dominant. On the basis of these findings it is suggested that the resonances at 43.1, 42.0, and 40.7 ppm indicate the presence of $\text{ptBuSt}-\text{ptBuSt}-\text{ptBuSt}$, $\text{ptBuSt}-\alpha\text{MeSt}-\text{ptBuSt}$, and $\alpha\text{MeSt}-\alpha\text{MeSt}-\alpha\text{MeSt}$ triads, respectively.

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REFERENCES

- [1] J. P. Kennedy, T. Kelen, and F. Tüdös, J. Macromol. Sci.-Chem., **A18**(9), 1189 (1982).

- [2] R. Faust, A. Fehérvári, and J. P. Kennedy, Ibid., A18(9), 1209 (1982).
- [3] J. Puskás, G. Kaszás, J. P. Kennedy, T. Kelen, and F. Tüdös, Ibid., A18(9), 1229 (1982).
- [4] J. Puskás, G. Kaszas, J. P. Kennedy, T. Kelen, and F. Tüdös, Ibid., A18(9), 1245 (1982).
- [5] J. Puskás, G. Kaszás, J. P. Kennedy, T. Kelen, and F. Tüdös, Ibid., A18(9), 1263 (1982).
- [6] M. Sawamoto and J. P. Kennedy, Ibid., A18(9), 1275 (1982).
- [7] M. Sawamoto and J. P. Kennedy, Ibid., A18(9), 1293 (1982).
- [8] M. Sawamoto and J. P. Kennedy, Ibid., A18(9), 1301 (1982).
- [9] Y. Imanishi, T. Higashimura, and S. Okamura, J. Polym. Sci., A3, 2455 (1965).
- [10] J. P. Kennedy and T. Chou, Adv. Polym. Sci., 21, 1 (1976).
- [11] J. P. Kennedy and R. A. Smith, J. Polym. Sci., Polym. Chem. Ed., 18, 1523 (1980).
- [12] J. P. Kennedy, S. Y. Huang, and S. C. Feinberg, J. Polym. Sci., Polym. Chem. Ed., 15, 2869 (1977).
- [13] J. Brandrup and E. H. Immergut (eds.), Polymer Handbook, Wiley, New York, 1975, p. II-105.