Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Living Carbocationic Polymerization. Li. Living Carbocationic Copolymerization of Indene and *p*-Methylstyrene. 1. Demonstration of the Living and Random Copolymerization of Indene and *p*-Methylstyrene

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To cite this Article Tsunogae, Yasuo , Majoros, IstvÁn and Kennedy, J. P.(1993) 'Living Carbocationic Polymerization. Li. Living Carbocationic Copolymerization of Indene and *p*-Methylstyrene. 1. Demonstration of the Living and Random Copolymerization of Indene and *p*-Methylstyrene', Journal of Macromolecular Science, Part A, 30: 4, 253 — 267

To link to this Article: DOI: 10.1080/10601329308009403

URL: http://dx.doi.org/10.1080/10601329308009403

J.M.S.—PURE APPL. CHEM., A30(4), pp. 253–267 (1993)

LIVING CARBOCATIONIC POLYMERIZATION. LI. LIVING CARBOCATIONIC COPOLYMERIZATION OF INDENE AND *p*-METHYLSTYRENE. 1. DEMONSTRATION OF THE LIVING AND RANDOM COPOLYMERIZATION OF INDENE AND *p*-METHYLSTYRENE†

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ABSTRACT

The living carbocationic polymerization and copolymerization of indene (Ind) and *p*-methylstyrene (pMeSt) have been investigated by the use of the 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ and the 2-chloro-2-propylbenzene (cumyl chloride, CumCl)/BCl_3 initiating systems in the presence of triethylamine (Et_3N) as electron donor and CH_3Cl or CH_3Cl/nC_6H_{14} mixed solvents at −80°C. The TMPCl/$TiCl_4$ initiating system gives essentially living copolymerization with slow initiation up to $\overline{M}_n \approx 20{,}000$. The CumCl/$BCl_3$ initiating system also induces living Ind homopolymerization up to at least $\overline{M}_n \approx 13{,}000$. The homopolymerization of pMeSt with the latter initiating system, however, is not living as it shows evidence for a large amount of chain transfer. Thus, with the CumCl/BCl_3 combination a small amount of chain transfer has apparently been observed in the presence of 50% of pMeSt in the charge.

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†For Part L, see Y. Tsunogae and J. P. Kennedy, *Polym. Bull.*, *27*, 631 (1992).

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Reactivity ratio studies, fractionation, ^{1}H- and ^{13}C-NMR spectroscopy, and glass transition temperature (T_g) investigations indicate that virtually random Ind-*co*-pMeSt copolymers of $\overline{M}_n \approx 20{,}000$ can be obtained under suitable conditions. The T_g of the copolymers can be controlled between ~115°C (the T_g of PpMeSt) and ~194°C (the T_g of PInd) by the relative composition of the two monomers in the charge.

INTRODUCTION

We recently described the living carbocationic polymerization (LC^+Pzn) of isobutylene (IB) [1, 2], styrene [3], *p*-chlorostyrene (pClSt) [4], *p-tert*-butylstyrene (ptBuSt) [5], pMeSt [6], and Ind [7, 8], and subsequently synthesized by sequential monomer addition various glassy-rubbery-glassy triblock copolymers exhibiting thermoplastic elastomer (TPE) character [5–7, 9–13]. For example, the poly(indene-*b*-isobutylene-*b*-indene) triblock is an excellent TPE because of the high T_g (~200°C) of the PInd outer segment [7, 9, 12, 13].

Part of our current research concerns living carbocationic copolymerization (LC^+Copzn) of olefins, and we recently described the LC^+Copzn of IB/pClSt [14] and IB/2,4-dimethyl-1,3-pentadiene [15] systems. One of the objectives of these copolymerization studies is to fine-tune the T_g of the glassy outer segment of our TPEs by the synthesis of random copolymers. We have synthesized a PIB-based triblock copolymer containing a random copolymer outer segment consisting of Ind and ptBuSt, indicating the single T_g of the outer segments between the T_gs of these homopolymers [13]. The random LC^+Copzn of Ind and pMeSt would enable us to control the T_g of the glassy outer segments between ~115°C (the T_g of PpMeSt) and ~200°C (the T_g of PInd) by controlling the overall molecular weight and relative composition of these segments from homo-PpMeSt to homo-PInd.

Before the synthesis of the target triblock copolymer [P(Ind-*co*-pMeSt)-*b*-PIB-*b*-P(Ind-*co*-pMeSt)] described in the subsequent publication, a fundamental investigation of Ind-*co*-pMeSt $LC^+Copzns$ was carried out by the use of the TMPCl/$TiCl_4$ and CumCl/BCl_3 initiating systems. The TMPCl/$TiCl_4$ combination is a model for the synthesis of PIB block copolymers because the TMPCl initiator mimicks the endgroup of *tert*-chlorine capped PIB [i.e., $\sim CH_2C(CH_3)_2Cl$].

EXPERIMENTAL

Materials

The syntheses of CumCl and TMPCl have been described [16]. pMeSt (Aldrich Chemical) was washed with 10% aqueous NaOH, distilled water until neutral, dried over $CaCl_2$, and distilled over CaH_2 *in vacuo*. Ind (Aldrich Chemical) was purified by silica-gel column chromatography followed by crystallization from heptane at −50°C, washing with cool heptane, drying over $CaCl_2$ and distilling over CaH_2 *in vacuo* (purity > 98% by GC). Et_3N was distilled over KOH.

The source and purification of BCl_3, $TiCl_4$, CH_3Cl, and nC_6H_{14} have been described [1, 17]. Methanol, THF (Fisher Scientific Co.), and $CDCl_3$ (Aldrich Chemical) were used as received.

Polymerization

The overall methodology has been described [1, 17]. Polymerizations were carried out in large test tubes (75 mL) in a drybox by the conventional "All Monomer In (AMI)" technique [17].

Characterization

Molecular weight and molecular weight distribution (MWD) determinations have been described [1]. The $\overline{M}_n$ of Ind-*co*-pMeSt copolymers were estimated by GPC using PSt calibration.

The overall Ind/pMeSt composition of the copolymers was determined by ^{1}H-NMR spectroscopy [18]. The characteristic resonance due to the methyl group of the pMeSt unit (2.25 ppm) in the ^{1}H-NMR spectrum of copolymers was used to calculate the pMeSt content:

$$\text{pMeSt content (mol\%)} = 4M/3A \times 100$$

where A and M are, respectively, the integrated area of aromatic protons and pMeSt methyl protons in the spectrum. The reliability of this method was examined by analyzing copolymers obtained with 100% conversion, and the average absolute error was 1.7 mol%. ^{1}H-NMR and ^{13}C-NMR spectra were obtained using a Varian Gemini 200 MHz spectrometer and $CDCl_3$ solvent.

Fractionation was carried out by silica-gel column chromatography at room temperature [19]: Silica-gel 70–270 mesh 60Å (Aldrich Chemical), column size 1.0 × 60 cm, eluent THF, sample concentration 200–250 mg/mL, elution rate 50 mL/min, fraction volume 3 mL (Table 3, Sample 1) or 2 mL (Samples 2 and 3). $\overline{M}_n$s, MWDs and Ind contents of the fractions were analyzed by GPC and ^{1}H-NMR spectroscopy.

T_g was determined by a Dupont 910 DSC module with a Dupont 9900 computer/thermal analyzer at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Living Copolymerization of Ind and pMeSt: Orienting Experiments

After some preliminary experimentation we investigated the copolymerization of Ind and pMeSt by the TMPCl/$TiCl_4$ initiating system using charges with various relative monomer compositions. Figure 1(1) shows the $\overline{M}_n$ versus W_p (g of polymer formed) and I_{eff} [initiator efficiency, i.e., $(W_p/\overline{M}_n)/I_0$ (mole of initiator)] versus W_p plots obtained under the conditions detailed in the legend. The data of homopolymerizations of Ind and pMeSt are also plotted in Fig. 1 for comparison. Evidently the experimental $\overline{M}_n$s are higher than those expected by assuming I_{eff} = 100% [see dashed lines in Fig. 1(1)]. Higher than theoretical $\overline{M}_n$s are obtained because the rate of initiation (R_i) is relatively lower than that of propagation (R_p). By plotting the data of Fig. 1(1) as $-\ln(1 - I_{eff}) - I_{eff}$ versus $([M_0] - [M])/[I_0]$ (where $([M_0] - [M])$ is the concentration of consumed monomer), i.e., by the diagnostic plot of a slowly initiating LC^+Pzn [20], a straight line without intercept is obtained, independent of monomer composition [see Fig. 1(2)]. Evidently the slopes of k_c/k_p [the ratio of rate constants of cationation (k_c) to propagation (k_p)] of Ind and pMeSt

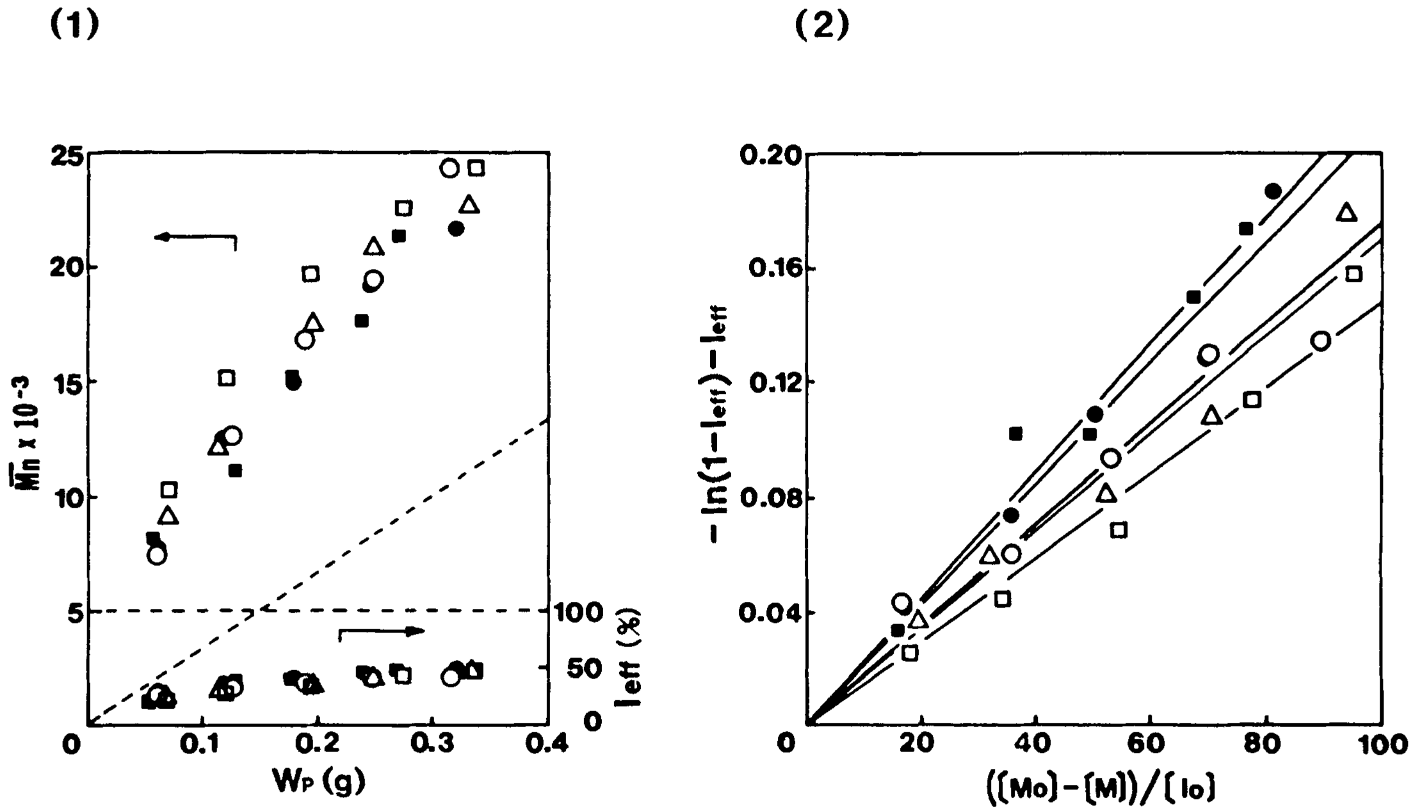

FIG. 1. Copolymerization of Ind and pMeSt and homopolymerization of Ind and pMeSt initiated by the TMPCl/$TiCl_4$ system [AMI method; TMPCl = 1.0 mM; $TiCl_4$ = 40.0 mM; Ind = 0.0043-0.0861 M; pMeSt = 0.042-0.0846 M; Monomer compositions in charge: Ind/pMeSt (w/w) = 0/100 (●), 25/75 (○), 50/50 (△), 75/25 (□), and 100/0 (■); Et_3N = 5.0 mM; Ch_3Cl/nC_6H_{14} = 4/6 (v/v); V_0 = 30 mL; 30 min; −80°C]. (1): $\overline{M}_n$ versus W_p, and I_{eff} versus W_p plots (conversions = 100%; the dashed lines are theoretical, calculated for I_{eff} = 100%). (2): The same data plotted by $-\ln(1 - I_{eff}) - I_{eff}$ versus $([M_0] - [M])/[I_0]$.

homopolymerization are very close under the conditions shown in the legend of Fig. 1: $k_c/k_{p(\mathrm{Ind})} = 2.21 \times 10^{-3}$ and $k_c/k_{p(\mathrm{pMeSt})} = 2.11 \times 10^{-3}$. The apparent k_c/k_p values of Ind/pMeSt copolymerization decrease with increasing Ind composition in the charge [$k_c/k_p = 1.75 \times 10^{-3}$ (Ind/pMeSt = 25/75), 1.70×10^{-3} (50/50), 1.48×10^{-3} (75/25)]. These results suggest that Ind is more reactive than pMeSt (see also next section). According to this evidence the copolymerization of Ind and pMeSt under the above conditions is living with $R_i < R_p$. This treatment has been used previously to gain insight into the mechanism of LC^+Pzn of Ind [7, 8] and pMeSt [6], and led to similar results.

We have also investigated the homopolymerization of Ind and pMeSt, and the copolymerization of these monomers by the CumCl/BCl_3 initiating system in CH_3Cl at −80°C. Table 1 shows the results of a representative set of experiments. In contrast to control experiments carried out in the absence of Et_3N, well-defined molecular weights and relatively narrow MWD products were obtained in the presence of this electron donor. Figure 2 shows the $\overline{M}_n$ and I_{eff} versus W_p/I_0 plots. As

TABLE 1. Ind, pMeSt, and Ind-*co*-pMeSt Polymerizations by the CumCl/BCl_3 Initiating System (AMI method, I_0 = CumCl = 2.0–16.0mM, BCl_3 = 20.0 mM, Et_3N = 5.0 mM, CH_3Cl, V_0 = 30 mL, 30 min, −80°C)

$W_p/[I_0]$, g/M	Conversion, %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	I_{eff}, %
	(1) Ind Homopolymerization (Ind = 0.34 M)			
71	95	2,700	1.22	88
149	100	5,200	1.18	97
250	84	9,400	1.18	89
377	63	13,300	1.23	95
72[a]	97	3,200	1.34	75
	(2) pMeSt Homopolymerization (pMeSt = 0.34 M)			
69	92	3,700	1.36	62
121	81	5,600	1.33	72
186	62	6,700	1.41	92
240	60	7,000	1.47	115
334	55	8,500	1.46	129
68[a]	91	5,100	2.62	44
(3) Ind-*co*-pMeSt Copolymerization (Ind = 0.17 M, pMeSt = 0.17 M)				
69	92	3,300	1.23	69
135	90	5,300	1.28	84
222	74	8,200	1.33	91
270	67	9,000	1.37	99
332	55	9,700	1.41	113
71[a]	94	3,600	1.55	66

[a]Control, in the absence of Et_3N.

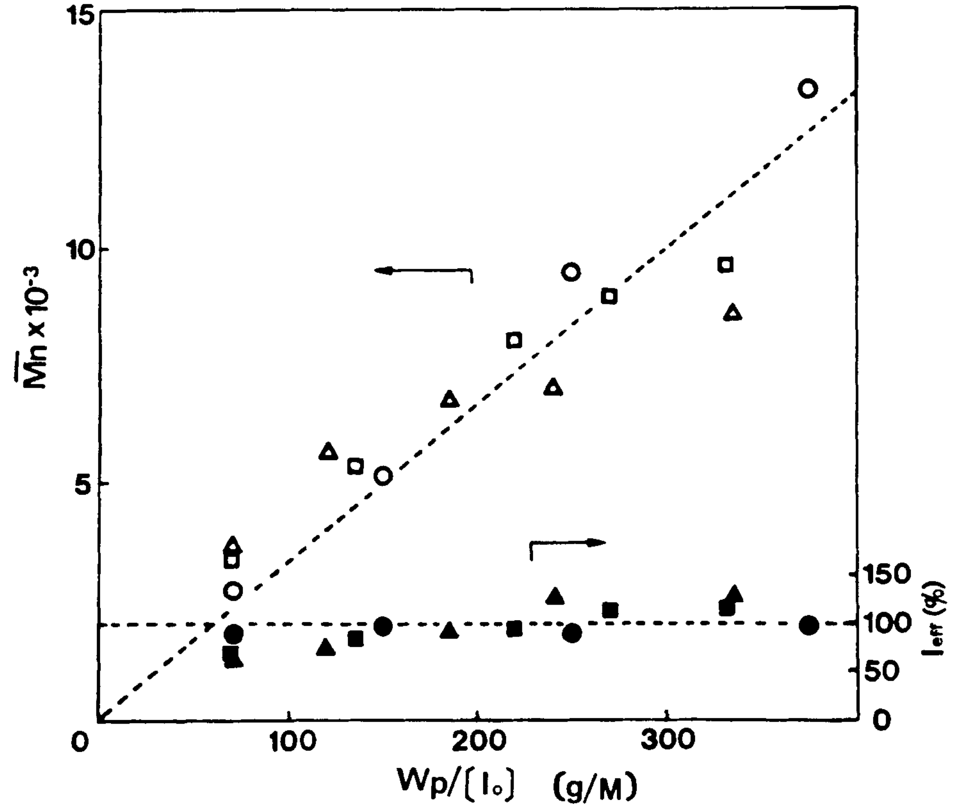

FIG. 2. The $\overline{M}_n$ and I_{eff} versus $W_p/[I_0]$ plots constructed from the data of Table 1. Ind homopolymerization (○, ●); pMest homopolymerization (△, ▲); Ind-*co*-pMeSt copolymerization (□, ■). The dashed lines are theoretical, calculated for I_{eff} = 100%.

indicated by the linear $\overline{M}_n$ versus W_p/I_0 plot starting at the origin, the horizontal I_{eff} versus W_p/I_0 plot, and the narrow MWDs ($\overline{M}_w/\overline{M}_n$ = 1.18–1.23), the homopolymerization of Ind was living. To-date, these are the narrowest MWD PInd's described.

In contrast to the homopolymerization of Ind which occurred in the virtual absence of chain transfer in the range investigated, the plot for the homopolymerization of pMeSt showed evidence for chain transfer (see the characteristic deviations of the experimental data from the theoretical values).

The data for the copolymerization of equimolar Ind and pMeSt charges indicate a small extent of chain transfer, as shown by the higher than 100% I_{eff} values in Table 1. The extent of chain transfer increases with the pMeSt concentration in the charge.

In similar experiments we have also examined the CumCl/$TiCl_4$ and TMPCl/BCl_3 systems using CH_3Cl solvent (data not shown). According to these studies, the CumCl/$TiCl_4$ and TMPCl/$TiCl_4$ systems gave very similar results, i.e., living polymerizations with slow initiation. The TMPCl/BCl_3 system gave very slow initiation (I_{eff} = 1–2%) so that the molecular weight of the products were much higher than expected.

According to these investigations, the relative rates of cationation and propagation strongly depend on the nature of the initiators, coinitiators, and solvents. However, under suitable conditions, living copolymerizations can apparently be

TABLE 2. Reactivity Ratios of Ind-*co*-pMeSt Copolymerization

(1) CumCl/BCl_3 System[a]

(a) BCl_3 = 20 mM, Et_3N = 0 mM, 15 seconds

Mole fraction of Ind		Conversion, %
In charge	In polymer	
0.244	0.380	33.2
0.361	0.553	33.6
0.475	0.619	22.0
0.585	0.716	16.8
0.693	0.808	15.2
0.798	0.852	10.1

r_{Ind} = 1.47 ± 0.31
r_{pMeSt} = 0.25 ± 0.16

(b) BCl_3 = 20 mM, Et_3N = 5 mM, 1 minute

Mole fraction of Ind		Conversion, %
In charge	In polymer	
0.124	0.246	12.0
0.244	0.396	12.7
0.361	0.511	13.0
0.475	0.601	13.3
0.585	0.681	14.1
0.693	0.607	12.1
0.798	0.864	8.9

r_{Ind} = 1.50 ± 0.26
r_{pMeSt} = 0.37 ± 0.10

(2) TMPCl/$TiCl_4$ System[b]

(a) $TiCl_4$ = 10 mM, Et_3N = 0 mM, 5 seconds

Mole fraction of Ind		Conversion, %
In charge	In polymer	
0.124	0.190	15.6
0.244	0.324	14.9
0.475	0.591	9.1
0.585	0.678	5.5
0.693	0.787	3.8
0.798	0.831	3.0

r_{Ind} = 1.37 ± 0.27
r_{pMeSt} = 0.55 ± 0.15

(b) $TiCl_4$ = 10 mM, Et_3N = 5 mM, 15 seconds

Mole fraction of Ind		Conversion, %
In charge	In polymer	
0.124	0.203	5.1
0.361	0.467	6.0
0.475	0.572	5.5
0.585	0.667	4.6
0.693	0.726	3.2

r_{Ind} = 1.09 ± 0.20
r_{pMeSt} = 0.49 ± 0.10

[a] Conditions: CumCl = 2.0 mM, Ind = 0.06–0.46 M, pMeSt = 0.05–0.40 M, CH_3Cl, V_0 = 30mL, −80°C

[b] Conditions: TMPCl = 2.0 mM, Ind = 0.06–0.46 M, pMeSt = 0.05–0.40 M, CH_3Cl/nC_6H_{14} = 4/6 (v/v), V_0 = 30 mL, −80°C.

obtained across the copolymer composition range up to at least $\overline{M}_n \approx 20{,}000$ [see Fig. 1(2)].

Randomness of Ind-co-pMeSt Copolymer

Reactivity Ratio Studies

In order to control the T_g of a copolymer between the T_gs of the two components, random copolymerization should prevail. Investigations in this direction started by determining the relative reactivities of Ind and pMeSt under various conditions by the expanded Kelen-Tüdös method which can be used up to rather high conversions (~40%) [21, 22]. Experimental details and results are summarized in Table 2, and Fig. 3 shows a representative η versus ξ plot of the data in Table 2(1)(b). According to these data, Ind is two to six times more reactive than pMeSt. The Et_3N does not seem to influence the reactivity ratios. The rates of polymerization in the presence of Et_3N are much reduced. However, they remain reasonably constant and independent of the relative Ind/pMeSt composition. In contrast, in the absence of Et_3N the rates of polymerization decrease strongly with increasing Ind composition in the charge.

Kinetic Studies: Conversion versus Time, $\overline{M}_n$ versus Conversion, and Copolymer Composition versus Conversion

A series of kinetic experiments has been carried out in which conversion, $\overline{M}_n$, and overall copolymer composition were determined as a function of time. The results, together with experimental details, are summarized in Figs. 4 (for the

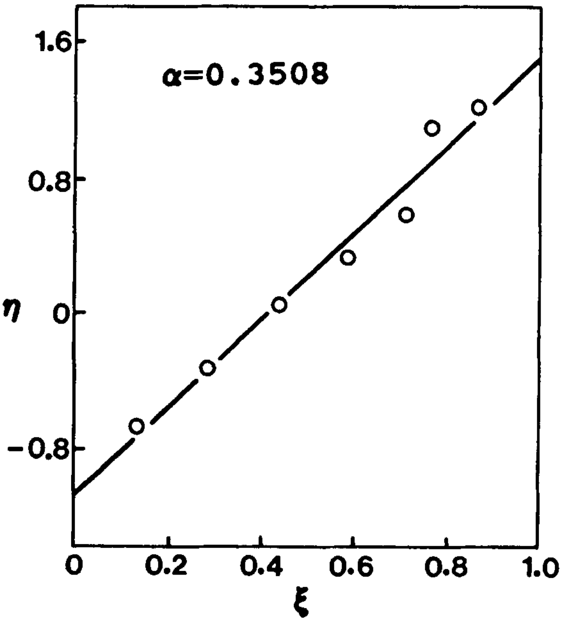

FIG. 3. Kelen-Tüdös plot constructed from the data of Table 2(1)(b).

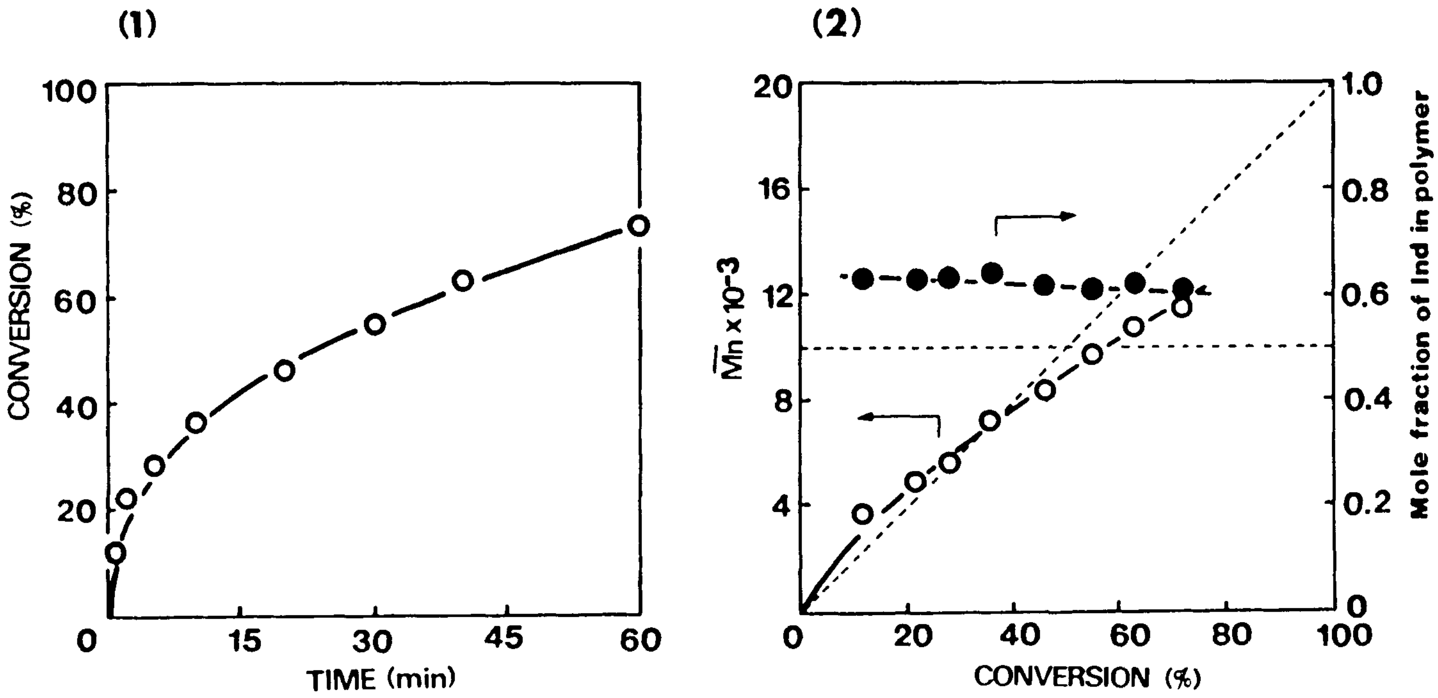

FIG. 4. Copolymerization of Ind and pMeSt charges initiated by the CumCl/BCl$_3$ system (CumCl = 2.0 mM, BCl$_3$ = 20.0 mM, Ind = 0.17 M, pMeSt = 0.17 M, Et$_3$N = 5.0 mM, CH$_3$Cl, V_0 = 30 mL, 1-60 min, −80°C). (1): Overall conversion versus time. (2) Overall $\overline{M}_n$ and Ind content in the copolymer versus conversion. The dashed lines are theoretical molecular weights calculated for I_{eff} = 100% and theoretical compositions calculated for mole fraction of Ind in charge.

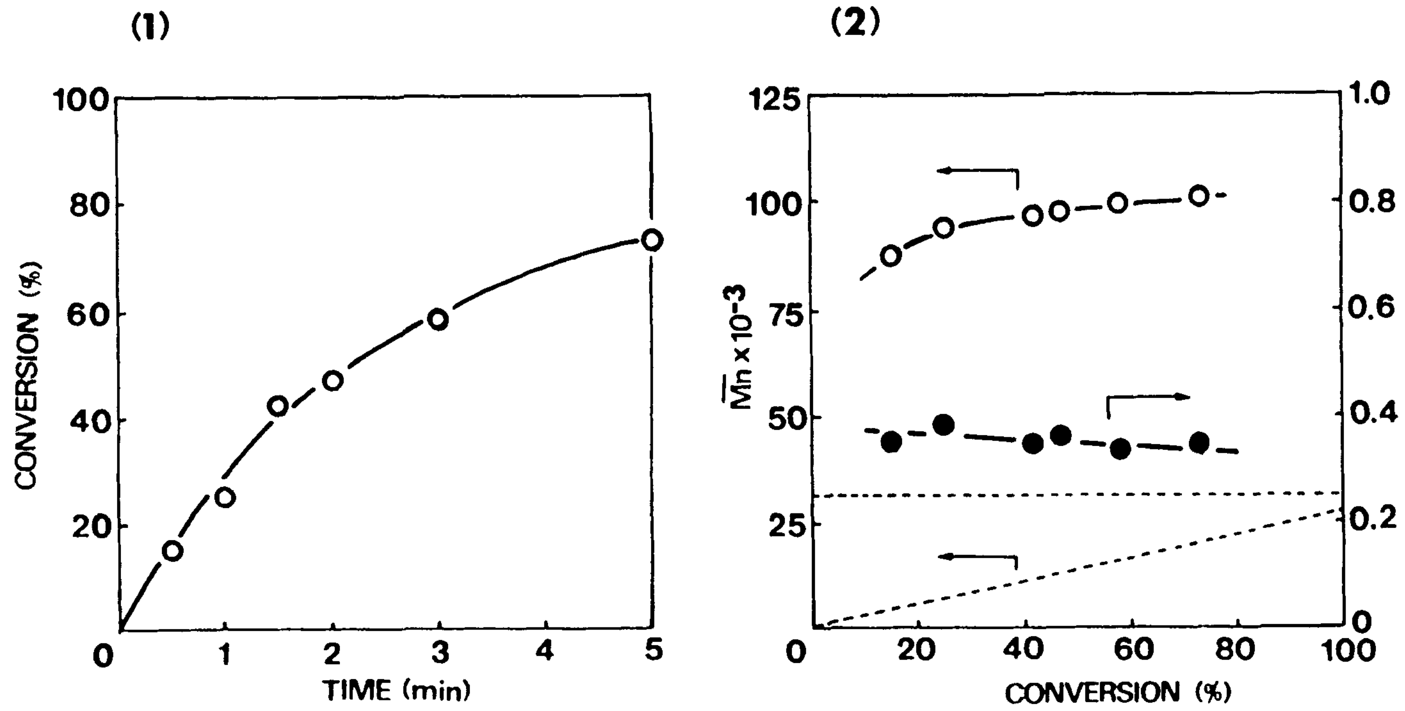

FIG. 5. Copolymerization of Ind and pMeSt charges initiated by the TMPCl/$TiCl_4$ system [TMPCl = 2.0 mM, $TiCl_4$ = 10.0 mM, Ind = 0.114 M, pMeSt = 0.354 M, Et_3N = 5.0 mM, CH_3Cl/nC_6H_{14} = 4/6 (v/v), V_0 = 30 mL, 0.5-5 min, −80°C]. (1): Conversion versus time. (2): $\overline{M}_n$ of and Ind content in copolymer versus conversion. The dashed lines are theoretical molecular weights calculated for I_{eff} = 100% and theoretical compositions calculated for mole fraction of Ind in charge.

TABLE 3. Fractionation of Ind-*co*-pMeSt Copolymer

No. of fraction	W_p (mg)	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Ind content, wt%
		Sample 1[a]		
Crude	240.0	19,300	2.59	23.3
1	20.0	35,300	1.74	28.1
2	53.5	24,900	2.21	27.7
3	51.1	21,000	2.53	26.0
4	46.5	19,100	2.71	19.0
5	37.3	18,200	2.76	22.6
6	17.0	14,800	3.07	15.7
		Sample 2[a]		
Crude	210.0	20,900	2.87	51.0
1	20.0	33,000	2.06	54.3
2	36.7	26,800	2.42	55.5
3	34.1	25,500	2.51	54.1
4	28.9	22,800	2.75	52.1
5	31.7	20,400	2.97	53.1
6	21.2	18,400	3.19	46.3
7	16.4	19,900	3.02	48.7
		Sample 3[a]		
Crude	250.0	22,600	2.64	78.5
1	27.7	34,500	1.90	78.9
2	36.2	26,400	2.36	80.8
3	30.6	24,100	2.55	80.3
4	29.2	23,600	2.59	77.9
5	27.5	22,700	2.69	72.7
6	21.6	22,700	2.69	75.4
7	26.3	21,400	2.82	74.4
8	20.4	21,400	2.82	73.6
9	16.5	21,700	2.75	72.6

[a] Synthesis conditions of these samples are given in the legend to Fig. 1.

$CumCl/BCl_3$ system) and 5 (for the $TMPCl/TiCl_4$ system). The significant finding in regard to our primary objective is the remarkable constancy of the overall compositions (i.e., Ind in the copolymer as a function of conversion) found in both the $CumCl/BCl_3$ and $TMPCl/TiCl_4$ initiating systems. Specifically, except for a slight downward drift in the Ind content with conversion, the overall copolymer compositions are largely uniform and close to those of the charge compositions. With the $CumCl/BCl_3$ system, the $\overline{M}_n$ versus conversion plot indicates somewhat slow initiation and a small amount of chain transfer. With the $TMPCl/TiCl_4$ combination, the rate of copolymerization was very high at $[TiCl_4] = 40$ mM so that this concentration was decreased to 10 mM; however, under these conditions the relative rate of initiation decreased considerably, which resulted in much higher than theoretical molecular weights.

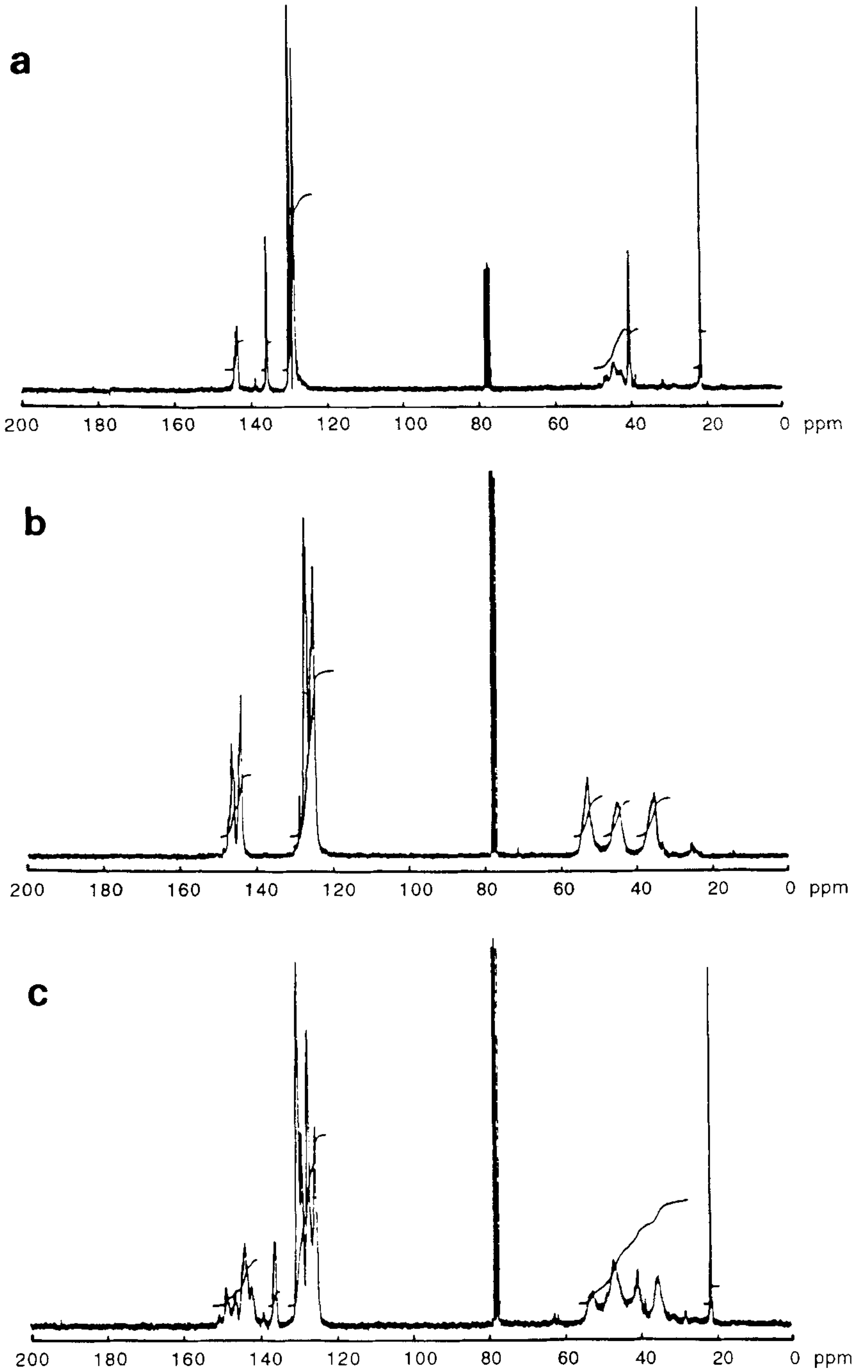

FIG. 6. ^{13}C-NMR spectra of a pMeSt homopolymer (a), an Ind homopolymer (b), and an Ind-*co*-pMeSt copolymer (53 wt% Ind, c). Synthesis conditions are given in Table 1 as lines (1), (2), and (3) of the three experiments indicated.

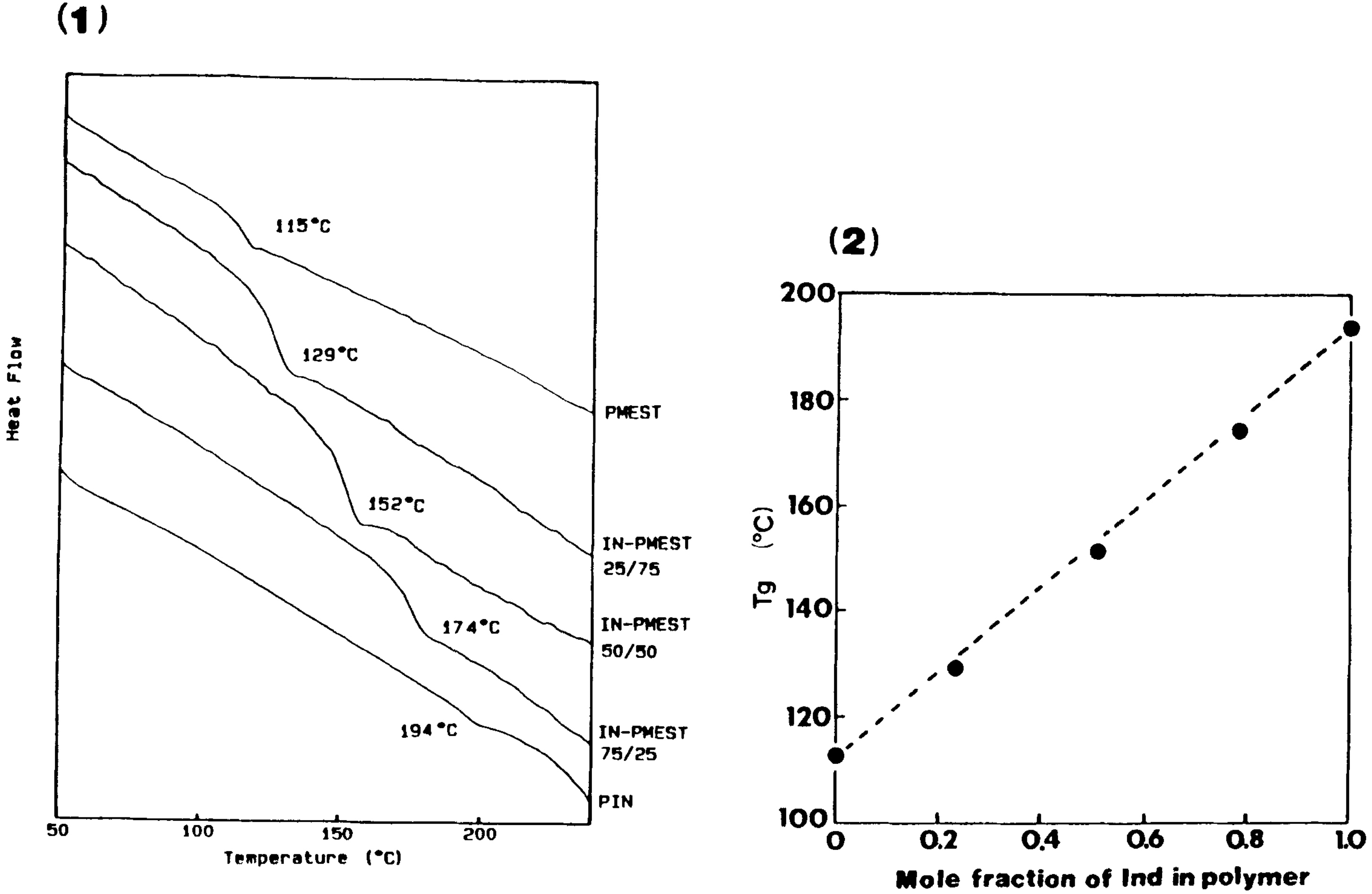

FIG. 7. T_g of PpMeSt, PInd, and P(Ind-*co*-pMeSt). (1): DSC traces of P(Ind-*co*-pMeSt), PInd, and PpMeSt (see Fig. 1 for origin of samples). (2): T_g as a function of Ind/pMeSt composition. The dashed straight line connects the T_gs of the homopolymers.

Fractionation of Ind-*co*-pMeSt Copolymer

An effort was made to demonstrate the uniformity of copolymer composition and the independence of copolymer compositions of molecular weights by GPC equipped with dual UV and RI detectors [23]. Unfortunately, however, the UV and RI coefficients of the homopolymers PInd and PpMeSt were too close [i.e., $C_{\mathrm{UV(PInd)}} = (1.92 \pm 0.11) \times 10^{13}$, $C_{\mathrm{UV(PpMeSt)}} = (8.89 \pm 0.53) \times 10^{12}$, $C_{\mathrm{RI(PInd)}} = (1.84 \pm 0.01) \times 10^{11}$, and $C_{\mathrm{RI(PpMeSt)}} = (1.50 \pm 0.10) \times 10^{11}$] for meaningful analysis.

The needed analytical information was obtained by column chromatography [19]. We charged THF solutions of three representative copolymers (compositions with 23.3, 51.0, and 78.5 wt% Ind) to a silica-gel filled column and fractionated the products into 6 to 9 fractions. Table 3 summarizes the results.

While the $\overline{M}_n$s decrease with elution volume (i.e., fractionation occurs as a function of molecular weight), the Ind contents do not significantly change; indeed, in Samples 2 and 3 the compositions change only about ±5%. Significantly, the largely constant copolymer compositions over the entire molecular weight range indicates random Ind and pMeSt incorporation into the product. Overall, the data suggest that the reactivity of Ind is somewhat higher than that of pMeSt.

^{13}C-NMR Spectroscopy Studies

^{13}C-NMR spectroscopy is of inestimable value for copolymer composition analysis. Figure 6 shows the ^{13}C-NMR spectra of a representative copolymer (c) and the corresponding homopolymers (a and b). The spectrum of the copolymer (c) shows a sharp peak near 21.5 ppm attributed to the methyl carbon of the pMeSt unit. Further, the significant peak-broadening in the methine and methylene region (30–60 ppm) and the new peaks which appear in the aromatic region (142.0 and 148.5 ppm) suggest a largely random copolymer and not a mixture of PInd and PpMeSt.

T_g Determination

The T_gs of Ind-*co*-pMeSt copolymers have been investigated. Figure 7(1) shows the DSC traces of three copolymers (Ind content = 23.3, 51.0, and 78.5 wt%), together with those of PInd and PpMeSt. Synthesis conditions are given in the legend to Fig. 1. All the DSC traces exhibit only one T_g, and they increase linearly with increasing Ind content [see Fig. 7(2)]. This linear relationship indicates that the copolymer is random and that the T_g of the copolymer can be controlled by the relative composition of the two monomers in the charge.

ACKNOWLEDGMENTS

Financial support by the NSF (Grant 89-20826) is gratefully acknowledged. Y.T. is grateful to Nippon Zeon Co. for an educational leave of absence.

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Received June 5, 1992
Revision received August 18, 1992