

LIVING CARBOCATIONIC COPOLYMERIZATIONS. I. SYNTHESIS AND CHARACTERIZATION OF ISOBUTYLENE/*p*-METHYLSTYRENE COPOLYMERS

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The isobutylene (IB)-*p*-methylstyrene (pMeSt) monomer pair readily produces by living copolymerization nearly random copolymers with up to $\bar{M}_n \approx 50,000 \text{ gmol}^{-1}$ and $\bar{M}_w/\bar{M}_n \approx 1.4$. The livingness of the copolymerization process and the compositional homogeneity of the copolymers have been demonstrated by the following four diagnostic plots: (A) \bar{M}_n (number-average molecular weight) and corresponding N (number of moles of copolymer formed) vs W_p (weight of copolymer formed) for the diagnosis of chain transfer; (B) $-\ln(1 - C)$ (C = conversion of monomers) vs time for the diagnosis of termination; (C) copolymer composition vs molecular weight; and (D) cumulative copolymer composition vs conversion for the diagnosis of true homogeneous copolymers. The theory for the use of the $-\ln(1 - C)$ vs time plot for the quantitation of irreversible termination in copolymerization has been developed. The exact conditions (i.e. nature of reagents, reagent concentrations, temperature, etc.) which lead to desirable products in terms of conversion, molecular weight, molecular weight distribution (MWD) and copolymer composition, were developed systematically by analyzing the results of a large number of experiments. The following combination of chemicals was found to lead to living copolymerization, and uniform high molecular weight, narrow MWD copolymers: IB-*p*MeSt 97:3 mol/mol with 5-*tert*-butyl-1,3-dicumyl methyl ether (5-*t*Bu-1,3-DiCumOMe) initiator, TiCl_4 coiniciator, ethyl chloride (EtCl) solvent, triethylamine (TEA) electron pair donor (ED) and 2,6-di-*tert*-butylpyridine (DtBP) proton trap at -52 , -65 and -85°C .

INTRODUCTION

Living carbocationic polymerizations have been repeatedly demonstrated and extensively discussed during the early 1990s.^{1,2} Recently, thoughtful authors warned against the use of the expression 'truly living'³⁻⁷ and suggested the use of quantitative parameters (e.g. chain-transfer and termination constants) to characterize the limits of 'livingness.' Majoros *et al.*⁸ recognized the fundamentally simple manner in which conventional and living carbocationic polymerizations are interconnected, and united these processes into a comprehensive closed-loop model.

In contrast to living homopolymerizations, very little information is available on living carbocationic copolymerization, particularly of dissimilar monomers, i.e.

aliphatic-aromatic monomer pairs. While the living random copolymerization of similar (in terms of structure and reactivity) comonomers is relatively easily achievable,^{9,10} the living copolymerization of dissimilar monomers and particularly the synthesis of random copolymers is very difficult because the more reactive comonomer will tend to homopolymerize and thus blocky copolymer segments will be formed.¹¹⁻¹³ If the reactivity difference between comonomers is large, inhibition will arise¹⁴ and copolymerization may not even occur.^{15,16} With respect to molecular weights, it is well known¹⁷ that the molecular weights of copolymers obtained by conventional processes are strongly depressed relative to the corresponding homopolymers, probably owing to rapid cross-transfer relative to propagation. The synthesis of random copolymers (i.e.

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copolymers in which the different monomer units are distributed randomly along the chain) have been claimed only in very few instances.^{9,15,18} Nonetheless, the living random copolymerization of monomer pairs having dissimilar reactivities could be of great technological interest^{19,20} because they may give rise to a wide variety of new products with new combinations of properties.

Led by these considerations, we decided to investigate the living random copolymerization of the isobutylene (IB)-*p*-methylstyrene (pMeSt) monomer pair, the conventional (non-living) suspension copolymerization of which by the $\text{AlCl}_3\text{-CH}_2\text{Cl}$ (-90°C) system has recently been described by industrial investigators.^{21a-c} According to these authors, the reactivity ratios of IB and pMeSt are $r_{\text{IB}}=0.99$ and $r_{\text{pMeSt}}=1.43$.^{21a,d} IB-pMeSt copolymers are of great current interest as starting materials for the latest generation of butyl rubbers.

The main objective of the present research was to explore the possibility of living IB-pMeSt copolymerizations and to determine whether random IB-pMeSt copolymers could be obtained in the technologically meaningful $[\text{IB}]/[\text{pMeSt}] = (90-97):(10-3)$ mol/mol range. We were able to demonstrate that under well defined conditions, living IB-pMeSt copolymerization can indeed proceed and that nearly random copolymers can be obtained up to $\bar{M}_w/\bar{M}_n \approx 1.4$. The effects of chain transfer to monomer and irreversible termination were investigated quantitatively by diagnostic plots. The validity of $-\ln(1-C)$ (C = conversion of monomers) vs time plots for quantitative analysis of irreversible termination in the IB-pMeSt copolymerization system was established.

EXPERIMENTAL

Materials. The synthesis of 1,3-di(2-methoxy-2-propyl)-5-*tert*-butylbenzene (or 5-*tert*-butyl-1,3-dicumyl methyl ether, 5-tBu-1,3-DiCumOMe) was carried out by refluxing a solution of 5-*tert*-butyl-1,3-dicumyl alcohol (19.0 g, 0.076 mol) in methanol (300 ml) with 98% sulfuric acid (0.004 ml) for 23 h. The solution was neutralized with anhydrous Na_2CO_3 (0.1 g) and most of the methanol (250 ml) was evaporated at 30°C . The charge was cooled to 20°C and *n*-hexane (100 ml) was added and stirred for 5 min. The organic layer was separated and washed four times with water (100 ml each time) and dried with anhydrous Na_2SO_4 (10 g). The *n*-hexane was evaporated at ambient temperature and the liquid was stored at 5°C overnight. The crystals were filtered off and washed with *n*-hexane; yield 14.2 g (74%). This procedure is an optimized version of that published earlier.²² The purity of the product (99.2%) was ascertained by ^1H NMR spectroscopy and gel permeation chromatography (GPC).

Ethyl chloride (Matheson) was dried by passing the gas through a column packed with anhydrous CaSO_4 (Drierite), molecular sieves (Fisher) and powdery barium oxide. The source and the purification of IB have been described.²³ TiCl_4 , DtBP, CDCl_3 , methanol, *n*-hexane (Aldrich) and sulfuric acid, Na_2SO_4 and Na_2CO_3 (Fisher) were used as received. Triethylamine (TEA) was distilled over KOH.

Procedures. Copolymerizations were carried out in a stainless-steel glove-box under a dry nitrogen atmosphere in large (75 ml) test-tubes. Molecular weights were determined using a Waters high-pressure GPC instrument. Details of polymerization and characterization methods, including NMR spectroscopic analysis, have been described.^{24,25} Absolute molecular weights were measured with a laser scattering (LS) detector (MiniDAWN, Wyatt Technologies) attached to the GPC instrument.

RESULTS AND DISCUSSION

Definitions and diagnostic methodology for living copolymerization

Similarly to the term 'living polymerization,' which refers to homopolymerizations occurring in the absence of chain transfer and termination,² the term 'living copolymerization' will be used to describe copolymerizations which proceed in the absence of kinetically significant irreversible chain transfer and termination. By definition, even the simplest copolymerizations involve two different monomers and kinetically different growing cations, so that the number of possible termination and/or chain-transfer reactions is much larger than those in homopolymerizations.

For the quantitative analysis of living copolymerizations we had to develop new analytical methodologies. In living homopolymerizations, livingness can be demonstrated by linear molecular weight (\bar{M}_n) vs conversion or horizontal number of polymer chains (N) vs conversion plots, either of which indicate the absence of chain transfer (see, e.g., Ref. 2), and by first order in monomer kinetic behavior, i.e. by linear $[-\ln(1-C)]$ vs time plots, which indicate the absence of termination.⁸ \bar{M}_n (or N) vs W_p (weight of polymer formed) plots can be applied without modification for the diagnosis of livingness of copolymerization: the linearity of the \bar{M}_n vs W_p plot indicates that N = constant, that is, the absence of chain transfer. (For simplicity, we disregard the compensating effect of simultaneous chain transfer and slow initiation discussed previously.⁸) However, the validity of the first order in monomer kinetic plot used for the quantitative analysis of termination in homopolymerizations has to be demonstrated for copolymerization systems. The

following chain of thought was employed to prove the validity of the $-\ln(1-C)$ vs time plot for copolymerizations. In the simplest case, the rate of homopolymerization can be expressed by

$$-\frac{d[M]}{dt} = k_p^{\text{app}}[M^+][M] \quad (1)$$

where $[M^+]$ and $[M]$ are the concentrations of the growing cation and monomer, respectively, and k_p^{app} is the apparent propagation rate constant (k_p^{app} may be a composite of individual propagation rate coefficients and concentrations of various propagating species; for further discussions see, e.g., Refs 2, 8, and 26). The integrated form of equation (1) contains experimentally measurable quantities:

$$-\ln(1-C) = k_p^{\text{app}}[M^+]t \quad (2)$$

where C is conversion and t is time. In truly living systems $[M^+] = [I]_0$ (initiator concentration) or in systems in which termination is rapidly reversible (quasi-living systems) $[M^+] \sim [I]_0$.² Thus a plot of $-\ln(1-C)$ vs t will be linear, provided $[M^+] = \text{constant}$, that is, the number of growing chains remains unchanged and does not decrease by termination.

First order in monomer kinetics should also be valid for copolymerization systems. Thus, the overall rate of copolymerization, $-d([M_1] + [M_2])/dt$, where $[M_1]$ and $[M_2]$ are the concentrations of the two monomers, can be described by the sum of the four rates of propagation:

$$\begin{aligned} -\frac{d([M_1] + [M_2])}{dt} &= k_{11}[M_1^+][M_1] + k_{21}[M_2^+][M_1] \\ &+ k_{22}[M_2^+][M_2] + k_{12}[M_1^+][M_2] \end{aligned} \quad (3)$$

where k_{11} and k_{22} are the homo- and k_{12} and k_{21} are the cross-propagation rate constants, and $[M_1^+]$ and $[M_2^+]$ are the concentrations of the two growing cations. By using the simplifying assumption of short sequences²⁷ (sometimes erroneously interpreted as the steady-state concept²⁶):

$$k_{12}[M_1^+][M_2] \approx k_{21}[M_2^+][M_1] \quad (4)$$

and expressing $[I]_0$ by

$$[M_1^+] + [M_2^+] = \alpha[I]_0 \quad (5)$$

(in truly living copolymerizations $\alpha = 1$; in quasi-living systems $\alpha < 1$ ²⁸), we obtain

$$\begin{aligned} -\frac{d([M_1] + [M_2])}{dt} &= k_{12}\alpha[I]_0([M_1] + [M_2]) \\ &\times \frac{r_1(1-\chi_2)^2 + 2\chi_2(1-\chi_2) + r_2\chi_2^2}{1 + \chi_2\left(\frac{k_{12}}{k_{21}} - 1\right)} \\ &= K[I]_0([M_1] + [M_2]) \end{aligned} \quad (6)$$

where r_1 and r_2 are the reactivity ratios:

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \quad (7)$$

and χ_2 is the partial mole fraction of monomer 2:

$$\chi_2 = \frac{[M_2]}{[M_1] + [M_2]} \quad (8)$$

If r_1 , r_2 , χ_2 , k_{12} and k_{21} are constant, integration of equation (6) gives

$$-\ln(1-C) = K[I]_0t \quad (9)$$

where C is the total monomer conversion. Equation (9) is formally identical with equation (2). Therefore, provided the assumptions used in this derivation are valid, a linear first order in monomer plot will be proof for the absence of irreversible termination in copolymerizations.

As a result of the above considerations, we propose that living copolymerizations can be conclusively diagnosed with the help of four plots readily obtainable from routine experimental data: (A) \bar{M}_n (and N) vs W_p plot for the diagnosis of chain transfer; (B) $-\ln(1-C)$ (and C) vs time plot (or 'first-order' plot) for the diagnosis of chain termination; (C) copolymer composition vs molecular weights (i.e. GPC RI and UV traces normalized in arbitrary units to the same height for better comparison); and (D) cumulative copolymer composition vs conversion (expressed by weight of sample). Plots (C) and (D) provide insight into the composition of the copolymer by Fodor's algorithm.²⁹ The application of these diagnostic plots is demonstrated later.

Orienting experiments

Led by extensive experience with living carbocationic homopolymerizations,² a basic initiator-coinitiator-electron pair donor-proton trap-solvent-temperature system was selected to effect orienting living copolymerization experiments with the IB-pMeSt monomer pair. Relative monomer compositions were set at $[IB]/[pMeSt] = 97:3$ and $90:10$ mol/mol, i.e. close to the industrially important feed compositions. Table 1 shows the reagents selected together with concentrations and temperatures explored for further optimization studies.

We agree with earlier authors⁴⁻⁶ that chain transfer to monomer cannot be completely eliminated by merely manipulating experimental conditions; however, we submit that conditions may be found under which the rate of chain transfer is sufficiently depressed relative to that of propagation so that technologically meaningful molecular weights can be obtained.^{2,4,30} The presence of chain transfer may be undetectable at low molecular weights,¹¹ but will become increasingly noticeable at

Table 1. Experimental conditions selected to study the copolymerization of IB and pMeSt

[IB]/[pMeSt]	97:3 and 90:10 mol/mol
Initiator and its concentration	5-tBu-1,3-DiCumOMe, $2.5 \times 10^{-3} \text{ mol l}^{-1}$
Coinitiator and its concentration	TiCl ₄ , $8.0 \times 10^{-2} \text{ mol l}^{-1}$
Electron pair donor and its concentration	TEA, (0, 2.5, 7.5, 12.5) $\times 10^{-3} \text{ mol l}^{-1}$
Proton trap and its concentration	DtBP, (0, 2.5, 5.0, 12.5) $\times 10^{-3} \text{ mol l}^{-1}$
Solvent	Ethyl chloride
Temperature	-20, -40, -52, -65 and -85 °C

higher molecular weight levels, say above $10,000 \text{ g mol}^{-1}$.

In order to produce high molecular weight copolymers, $([M_1] + [M_2])/[I]_0$ must be large while maintaining the validity of

$$\overline{DP}_n = \frac{[M_1] + [M_2]}{[I]_0} \quad (10)$$

However, experimentally such conditions are difficult to achieve because, on the one hand, $[I]_0$ cannot be decreased to or below $5 \times 10^{-4} - 1 \times 10^{-3} \text{ mol l}^{-1}$, i.e. to the level of protic impurities even in well purified charges, because at such low $[I]_0$ levels controlled initiation will not occur,³¹ and, on the other hand, $([M_1] + [M_2])$ cannot be increased to too high concentrations because the danger of excessive viscosities and/or heterogeneity at high conversions. The next section concerns the presentation and analysis of a large number of representative results, and demonstrates the

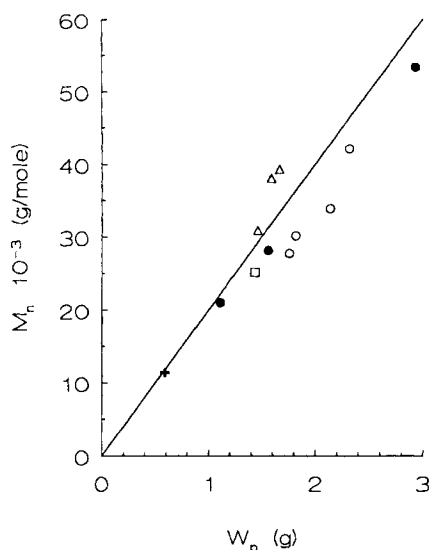


Figure 1. \overline{M}_n vs W_p diagnostic plot for the 'most promising living systems,' for [IB]/[pMeSt]=97:3 at (●) -52, (Δ) -65 and (○) -85 °C, and for [IB]/[pMeSt]=90:10 at (+) -52 and (□) -85 °C. For details, see Table 2

synthesis of high molecular weight IB-pMeSt copolymers by living copolymerization.

Conditions for living copolymerization of IB-pMeSt charges

Based on orienting experiments (outlined in the previous section), we proceeded to develop a strategy for achieving living copolymerizations and for the synthesis of high molecular weight copolymers. The results of a very large number of orienting experiments have been examined and Table 2 shows those which held the greatest promise for the synthesis of the sought copoly-

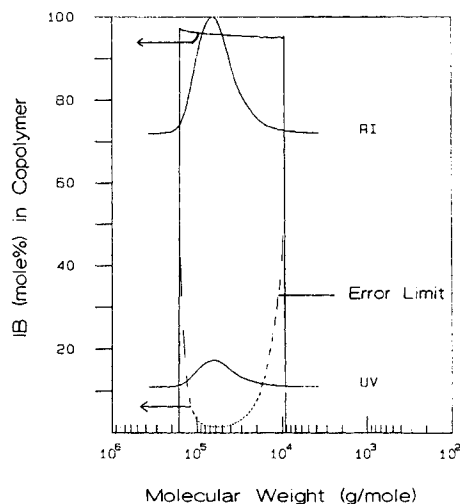


Figure 2. Overall copolymer composition and with RI and UV traces as a function of molecular weight (the broken line indicates error limits). The heights and vertical placements of the RI and UV traces are arbitrary. Synthesis conditions: [IB]/[pMeSt]=97:3; $[I]_0 = 2.5 \times 10^{-3} \text{ mol l}^{-1}$; $[TiCl_4] = 8 \times 10^{-2} \text{ mol l}^{-1}$; $[TEA] = 7.5 \times 10^{-3} \text{ mol l}^{-1}$; $[DtBP] = 5.0 \times 10^{-3} \text{ mol l}^{-1}$; solvent, ethyl chloride; $T = -85 \text{ °C}$; volume of monomers, 9 ml; total volume, 20 ml; time, 3 min. Results: conversion = 35.5%; $[IB]/[pMeSt]_{\text{in copolymer}} = 96.0:4.0$ by GPC and 95.2:4.8 by ¹³C NMR,³³ $\overline{M}_n = 42,150 \text{ g mol}^{-1}$ (by GPC); $\overline{M}_w/\overline{M}_n = 1.34$; $I_{eff} = 106\%$. Triad analysis by ¹³C NMR:³³ IB-pMeSt-IB $\approx 56\%$; IB-pMeSt-pMeSt + pMeSt-pMeSt-IB $\approx 43\%$; pMeSt-pMeSt-pMeSt $\approx 1\%$

Table 2. Promising conditions and results of living IB-pMeSt copolymerization (5-tBu-1,3-DiCumOMe-TiCl₄-TEA + DiBP-EtCl system, [TiCl₄] = 8 × 10⁻² mol l⁻¹, volume of monomers = 3 ml, total charge = 20 ml)

CONDITIONS				RESULTS							
IB/pMeSt (mol/mol)	T (°C)	[I] ₀ (10 ⁻³ mol l ⁻¹)	[TEA] (10 ⁻³ mol l ⁻¹)	[DiBP] (10 ⁻³ mol l ⁻¹)	IB/pMeSt in polymer (mol/mol)		I _{eff} (%)	Conversion (%)	W _p (g)	M _n (g mol ⁻¹)	M _w /M _n
					By GPC	By NMR					
97:3	-52	2.5	5.0	5.0	96:3: 3.7	—	106	53.9	1.1105	21,050	1.39
97:3	-52	2.5	7.5	5.0	96:6: 3.4	—	110	75.8	1.5621	28,150	1.42
97:3 ^a	-52	2.5	7.5	5.0	95:9: 4.1	95:5: 4.5	109	47.6	2.9329	53,350	1.43
97:3	-65	2.5	7.5	2.5	96:3: 3.7	95:7: 4.3	95	69.4	1.4633	30,900	1.49
97:3	-65	2.5	7.5	5.0	96:3: 3.7	—	84	75.4	1.5910	38,100	1.41
97:3	-65	2.5	7.5	12.5	96:4: 3.6	—	85	79.0	1.6675	39,350	1.44
97:3	-85	2.5	7.5	5.0	96:8: 3.2	—	122	80.8	1.7596	27,750	1.38
97:3	-85	2.5	7.5	5.0	96:9: 3.1	—	115	83.6	1.8201	30,150	1.38
97:3	-85	2.5	7.5	5.0	96:8: 3.1	—	122	98.3	2.1410	33,900	1.38
97:3 ^a	-85	2.5	7.5	5.0	96:0: 4.0	95:2: 4.8	106	35.5	2.3185	42,150 ^b	1.34
90:10	-52	2.5	5.0	5.0	83:3: 16.7	83:0: 17.0	103	27.3	0.5876	11,400	1.45
90:10	-85	2.5	7.5	5.0	84:0: 16.0	—	110	63.2	1.4369	25,150	1.56

^a Volume of monomers 9 ml.

^b By LS and RI detectors. M_n = 41,800 ± 1700 and M_w/M_n = 1.24

mers. The effects of experimental variables on conversion, copolymer molecular weight, molecular weight distribution (MWD) and composition were determined, and are presented in the following sections. According to the data in Table 2, living copolymerizations yielded copolymers with up to $\bar{M}_n \approx 50,000 \text{ g mol}^{-1}$ and $\bar{M}_w/\bar{M}_n \approx 1.4$ with $[\text{IB}]/[\text{pMeSt}] = 97:3$ mol/mol initial feed ratios.

Figure 1 demonstrates that under the conditions specified in Table 2 the extent of chain transfer is negligible. Interestingly, the effect of temperature on \bar{M}_n is within experimental error in the range -85 to -52°C . Composition analysis by GPC and NMR spectroscopy indicated the formation of true copolymers. Detailed structural and compositional analyses are described in the accompanying paper³² and further

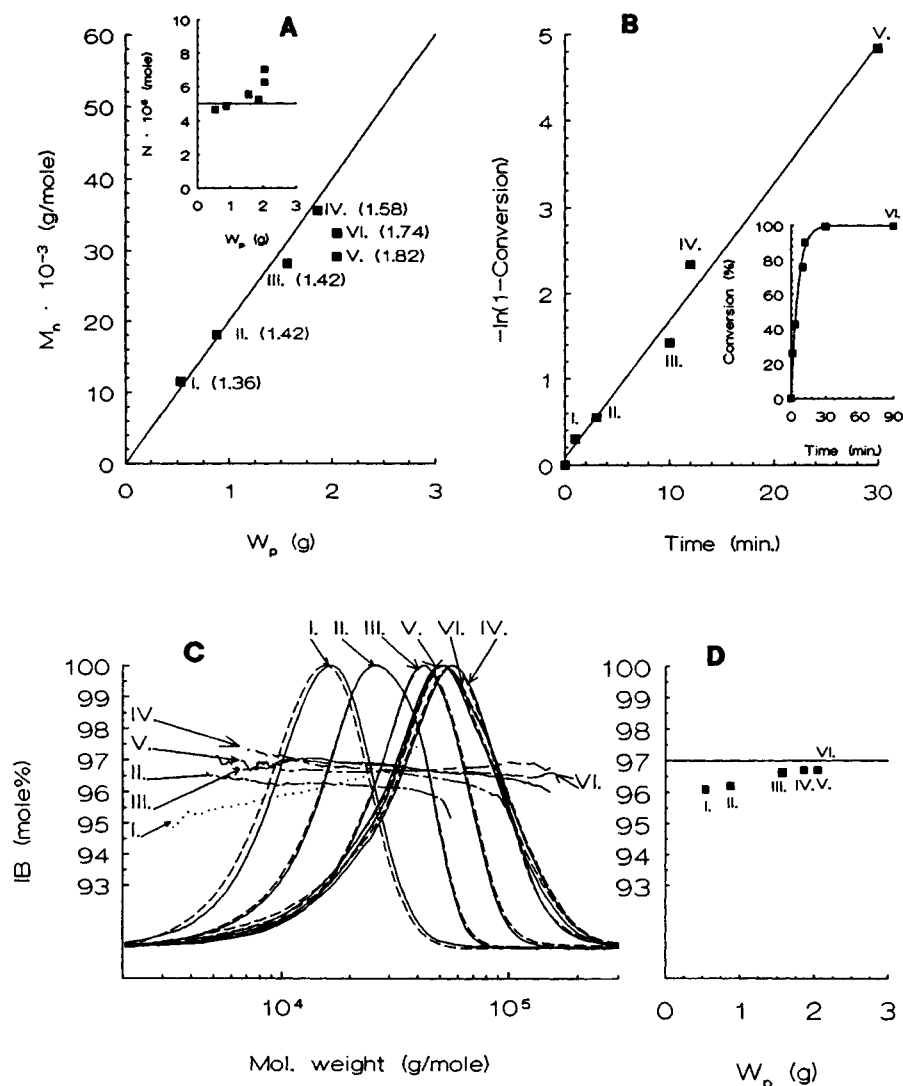


Figure 3. Diagnostic plots for the living copolymerization of IB-pMeSt charges (samples identified by roman numerals). (A) \bar{M}_n (and N) vs W_p (the solid lines indicate $I_{\text{eff}} = 100\%$, 'theoretical lines'); (B) rate (conversion) vs time; (C) IB content vs molecular weight; bell-shaped curves show GPC RI and UV traces (solid and broken lines, respectively), and the close to horizontal lines show overall IB contents obtained by Fodor's method (see text); (D) cumulative IB content vs W_p (horizontal line shows initial monomer composition). Experimental conditions: $[\text{IB}]/[\text{pMeSt}] = 97:3$; $[\text{I}]_0 = 2.5 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{TiCl}_4] = 80.0 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{TEA}] = 7.5 \times 10^{-3} \text{ mol l}^{-1}$, $[\text{DtBP}] = 5.0 \times 10^{-3} \text{ mol l}^{-1}$; solvent, ethyl chloride; $T = -52^\circ\text{C}$

information will be published later.³³ Figure 2 shows data obtained in a representative experiment aimed at the determination of overall copolymer composition by Fodor's algorithm.²⁹ Information generated by the RI and UV detectors of the GPC instrument in conjunction with Fodor's method provides copolymer compositions at every vertical slice and the overall composition of the total sample over the entire molecular weight axis.

Figures 3–6 summarize the results of four series of experiments and Table 3 facilitates the rapid overview of the experimental design (concentrations normalized

with respect to initiator concentration). Comparison of Figures 3–5 shows the effect of temperature in the range from -52 to -85°C , and a comparison of Figure 4 with Figure 6 shows the effect of two proton trap concentrations.

The diagnostic plots (see earlier) for the living copolymerization are shown in Figure 3(A)–(D). According to the data in Figure 3(A) and (B), living copolymerization prevails up to *ca* 90% conversion (i.e. the data points are within experimental error of the theoretical line). However, as the monomer concentration decreases (close to 100% conversions), zero-order chain transfer (see, e.g.,

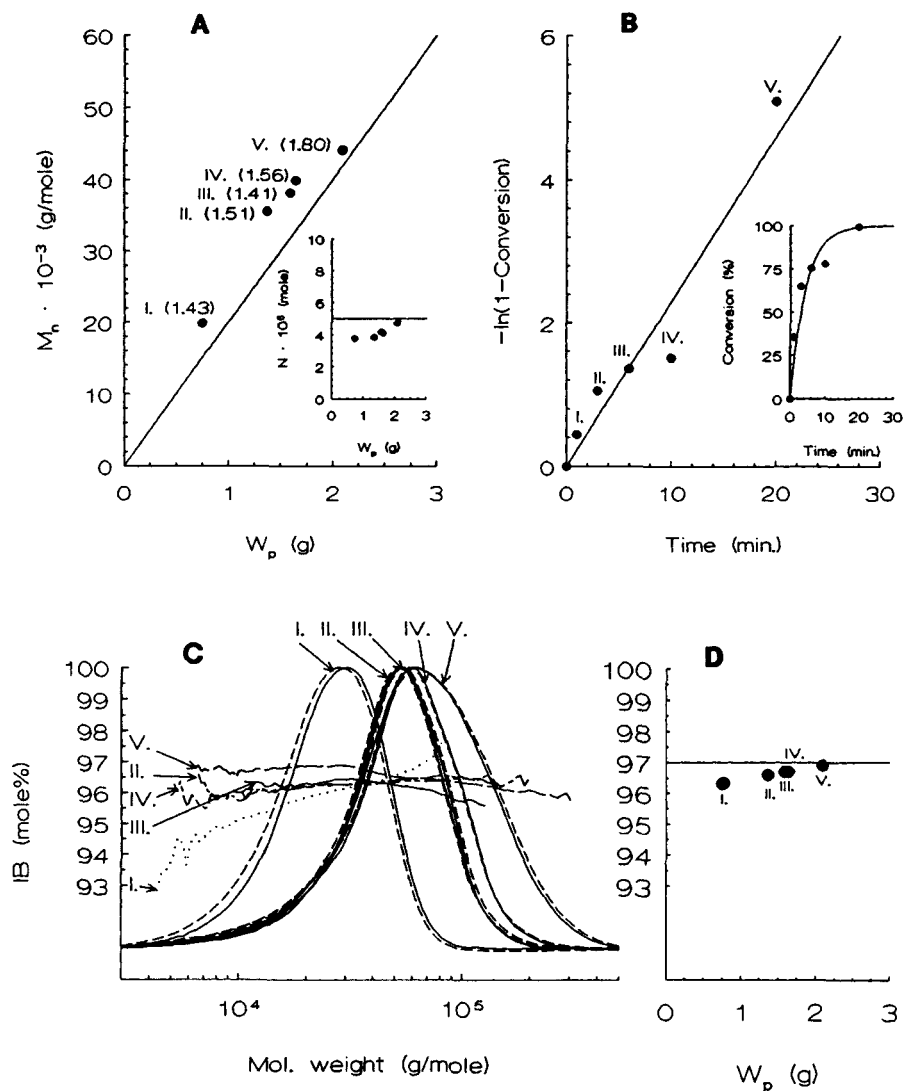


Figure 4. Diagnostic plots for the living copolymerization of IB-pMeSt charges. Details as in Figure 3 except $T = -65^\circ\text{C}$

Ref. 8) becomes operational, which causes a drastic depression of molecular weight, an increase of N and a broadening of MWD [see numbers in parentheses in Figure 3(A)]. Figure 3(C) shows RI and UV traces (solid and broken lines, respectively) obtained by GPC. Sample I exhibits a relatively high UV absorbance at low molecular weights, suggesting that its pMeSt content is higher at low molecular weights [cf. broken composition line for sample I in Figure 3(C)] most likely because of chain transfer by pMeSt. Although the \bar{M}_n vs W_p plot [Figure 3(A)] does not show noticeable chain transfer, slow initiation and chain transfer may be compensatory (cf. Ref. 8). The amount of low molecular weight polymers,

however, is insignificant and becomes negligible with increasing conversions. Samples II–VI exhibit nearly identical RI and UV traces, indicating that the composition of the copolymers is independent of molecular weight. This is further substantiated by the essentially horizontal overall composition curves in Figure 3(C). [The confidence limits of these composition curves are lowest at the two ends; a typical error curve is displayed in Figure 2; however, error curves are not shown in Figure 3(C) because of the congestion in the figure]. Figure 3(D) shows the cumulative composition of Samples I–VI. Samples V and VI were obtained at close to 100% conversions, and therefore exhibit identical IB

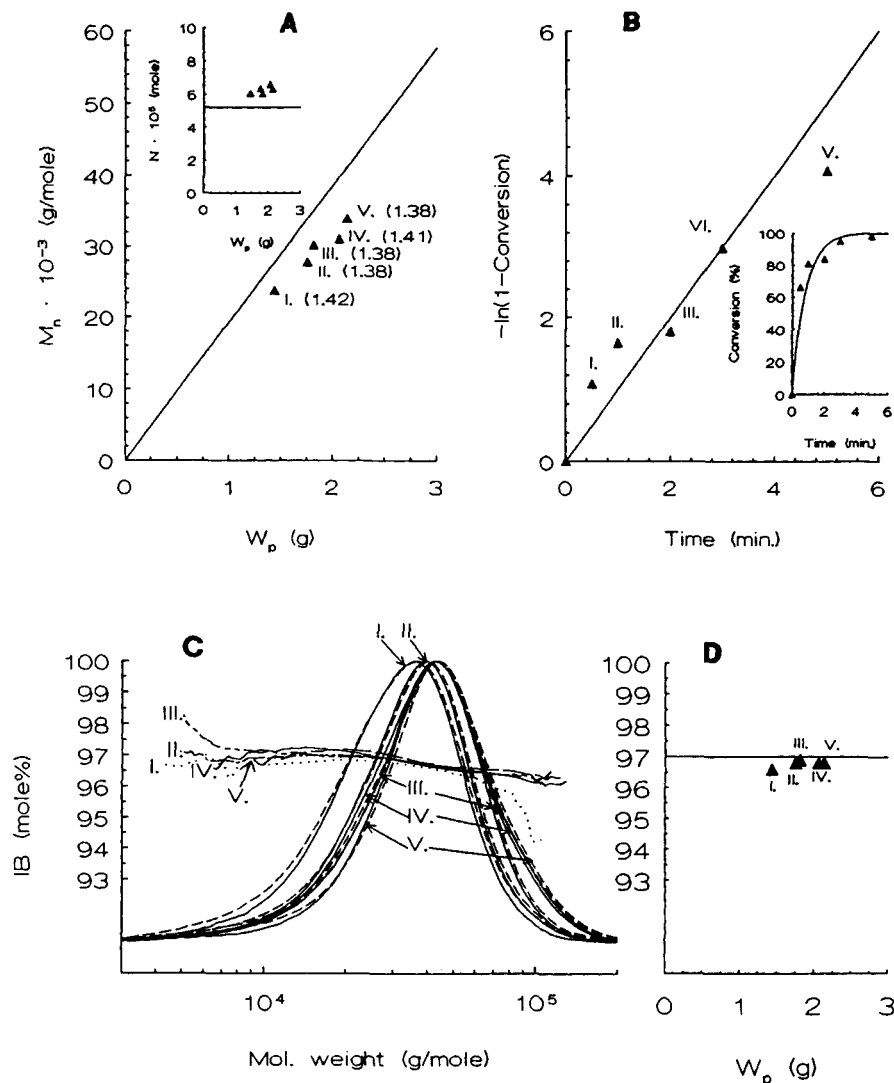


Figure 5. Diagnostic plots for the living copolymerization of IB-pMeSt charges. Details as in Figure 3 except $T = -85^\circ\text{C}$

contents. The horizontal line at $[IB] = 97$ mol% indicates the composition of the initial monomer mixture ('feed composition'). At 100% monomer conversion, i.e. when both monomers disappear because they become incorporated into the copolymer, the initial feed composition and the copolymer composition must be the same.

Obviously, sample I contains less IB (or more pMeSt) than the other samples because pMeSt is more reactive than IB and will therefore preferentially enter the copolymer. As a result, the feed composition will drift with increasing conversion toward the less reactive

monomer, IB, and this drift will give rise to compositional heterogeneity in every macromolecule. That part of a macromolecule which arose at lower conversions will be richer in the more reactive monomer, pMeSt, than that formed later. It should be emphasized, however, that horizontal composition curves, such as in Figure 2 or 3(C), indicates only that every slice of the chromatogram (i.e. both short and long chains in the distribution) is of the same average composition, but it does not mean that the composition of the individual copolymer molecules is random. To prove randomness,

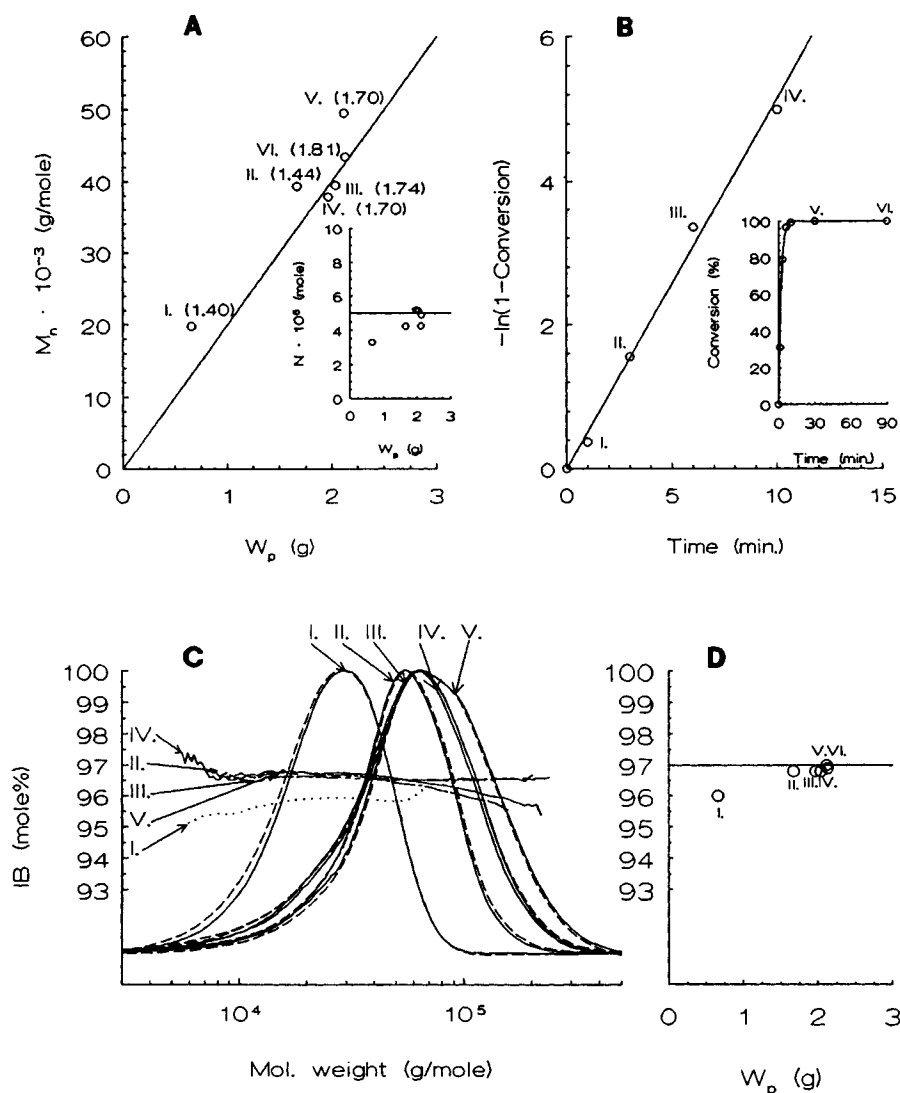


Figure 6. Diagnostic plots for the living copolymerization of IB-pMeSt charges. Details as in Figure 4 except with $[DtBP] = 12.5 \times 10^{-3} \text{ mol l}^{-1}$

Table 3. Design of experiments shown in Figures 3–6

Figure No.	[IB]/[pMeSt] (mol/mol)	[I] ₀ : [TEA] : [DtBP] : [TiCl ₄]	T (°C)
3	97:3	1 : 3 : 2 : 32	-52
4	97:3	1 : 3 : 2 : 32	-65
5	97:3	1 : 3 : 2 : 32	-85
6	97:3	1 : 3 : 5 : 32	-65

the exact arrangement (sequence length distribution) of the two monomers in the copolymer must be determined, for example, by NMR spectroscopy (see, e.g., Ref. 26).

Figure 3(C) and (D) indicate that true copolymers formed and that the product is not a mixture of two homopolymers or a diblock. If a mixture of homopolymers or a diblock had been formed, the more reactive pMeSt would have been used up first, which means that sample I obtained with 3 mol% pMeSt at *ca* 25% overall conversion would have given a copolymer containing $(3/25) \times 100 = 12$ mol% pMeSt and 88 mol% IB, which is different from the experimental value of 96.1 mol% IB.

Figure 4(A)–(D) show the results of a series of experiments at -65°C. Apparently the extent of chain transfer [Figure 4(A)] and termination are insignificant in samples I–IV, but chain transfer becomes noticeable at close to 100% conversion ($\bar{M}_w/\bar{M}_n \approx 1.8$, sample V). As indicated by the data in Figure 4(A), the rate of initiation is low relative to propagation and the molecular weights are higher than the theoretical values. Figure 4(C) and (D) carry similar messages to Figure 3(C) and (D): true copolymerization has been achieved and copolymers with close to constant average compositions (except for sample I) as a function of molecular weight have been formed. By lowering the temperature, the rate of chain transfer relative to propagation was suppressed and higher molecular weights than at -52°C were obtained. By lowering the temperature further to -85°C, the diagnostic plots for the chain transfer and termination [Figure 5(A) and (B)] indicate lower than theoretical molecular weights and declining copolymerization rates, although the initial copolymerization rate is much higher than at -52 and -65°C [cf. insets in Figures 3(B) and 4(B)]. The GPC RI and UV traces show no significant differences, indicating true copolymer formation with close to constant macrocomposition, irrespective of molecular weights [Figure 5(C)]. Since the samples are within the 80–100% conversion range [see inset in Figure 5(B)], their cumulative compositions do not show an observable drift [Figure 5(D)].

Figures 6(A)–(D) and 4(A)–(D) reflect similar experimental conditions except at [DtBP] was increased by a factor of 2.5. Evidently an increase in [DtBP] 2–5

times over that of [I]₀ did not significantly improve livingness.

Effect of temperature on molecular weights, molecular weight distributions, number of chains and copolymer composition

Figures 7–9 show the effect of temperature on copolymer \bar{M}_n s, MWDs, number of chains and composition with [IB]/[pMeSt]=97:3 and 90:10 feed compositions. The molecular weights are higher than the theoretical values at relatively higher temperatures (> -52°C) and lower conversions, which suggests slow initiation (Figure 7). With decreasing temperature (i.e. at and below -52°C) the system shifts toward fast initiation (Figures 8 and 9). Chain transfer, however, is operational because the \bar{M}_n s are lower than theoretical values and MWD broadening is evident [Figure 9(A), -52°C]. Chain transfer is less significant at higher IB/pMeSt ratios because, evidently, pMeSt is a chain-transfer agent. Chain transfer becomes negligible at lower temperatures and at low [pMeSt]. Copolymer composition is mainly affected by conversion and is independent of temperature in the range -85 to -20°C [Figures 7(B), 8(B) and 9(B)].

Effect of [DtBP] on molecular weights, molecular weight distributions, number of chains and copolymer composition

Figures 10 and 11 illustrate the effect of [DtBP] on copolymer \bar{M}_n s, MWDs, number of chains and composition at -65 and -20°C. In the absence of DtBP and at higher conversions, the molecular weights are lower than the theoretical values, indicating chain transfer [Figure 10(A)]. Above [DtBP] = 5×10^{-3} mole l⁻¹ an increase in [DtBP] has no additional effect. The effect of [DtBP] at higher temperatures is more significant (Figure 11). At -20°C in the absence of DtBP, fast propagation yields low molecular weights and high conversions, whereas in the presence of DtBP relatively slow propagation and low conversion were observed.

In the presence of proton trap, protons arising from impurities and/or chain transfer are captured by DtBP and the entire TEA input is available for complexation

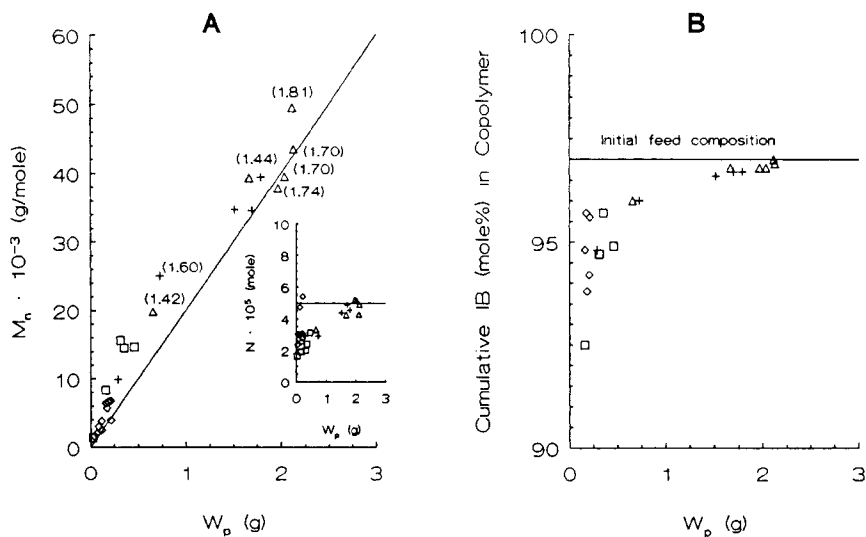


Figure 7. (A) \bar{M}_n (and N) vs W_p (the solid lines indicate $I_{eff} = 100\%$, 'theoretical lines') and (B) cumulative IB content vs W_p plots for IB-pMeSt copolymers at (\diamond) -20, (\square) -40, ($+$) -52 and (Δ) -65 °C. Synthesis conditions: $[IB]/[pMeSt] = 97:3$; $[I]_0 = 2.5 \times 10^{-3} \text{ mol l}^{-1}$; $[TiCl_4] = 80.0 \times 10^{-3} \text{ mol l}^{-1}$; $[TEA] = 7.5 \times 10^{-3} \text{ mol l}^{-1}$; $[DtBP] = 12.5 \times 10^{-3} \text{ mol l}^{-1}$; solvent, ethyl chloride. 100% conversion was reached only at -65 °C ($W_p = 2.11$ g); at -20, -40 and -52 °C 100% conversion would occur at $W_p = 1.94, 2.02$ and 2.06 g, respectively

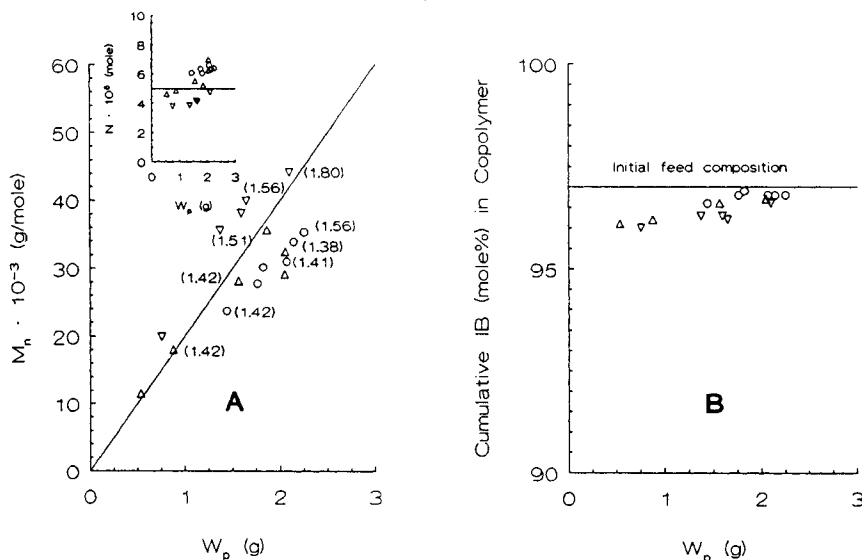


Figure 8. \bar{M}_n (and N) vs W_p (the solid lines indicate $I_{eff} = 100\%$, 'theoretical lines') and (B) cumulative IB content vs W_p plots for IB-pMeSt copolymers at (Δ) -52, (∇) -65 and (\circ) -85 °C. Synthesis conditions as in Figure 7 except with $[DtBP] = 5.0 \times 10^{-3} \text{ mol l}^{-1}$. 100% conversion was reached at $W_p = 2.06$ g (-52 °C), $W_p = 2.11$ g (-65 °C) and $W_p = 2.18$ g (-85 °C)

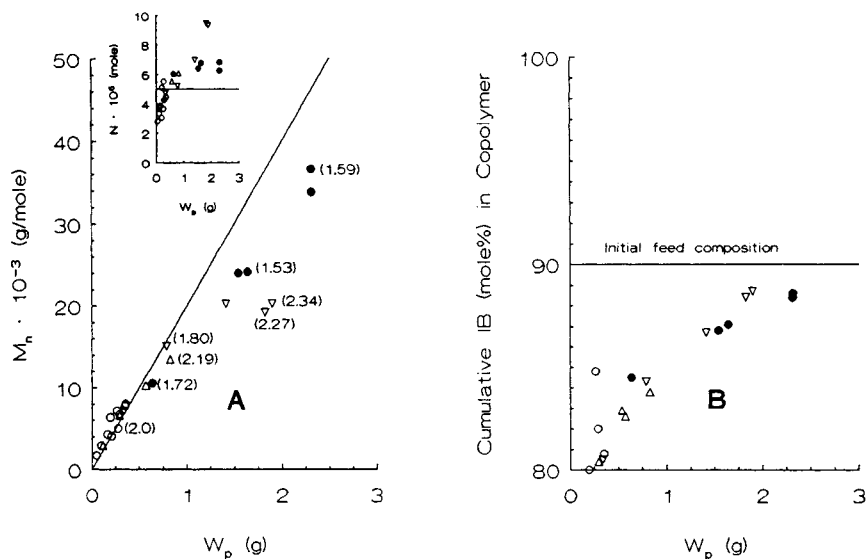


Figure 9. \bar{M}_n (and N) vs W_p (the solid lines indicate $I_{\text{eff}} = 100\%$, 'theoretical lines') and (B) cumulative IB content vs W_p plots for IB-pMeSt copolymers at (O) -20 , (Δ) -40 , (∇) -52 and (\bullet) -85°C . Synthesis conditions as in Figure 7 except with $[\text{IB}]/[\text{pMeSt}] = 90:10$ and at -85°C $[\text{TEA}] = 7.5 \times 10^{-3} \text{ mol l}^{-1}$, $[\text{DtBP}] = 12.5 \times 10^{-3} \text{ mol l}^{-1}$. 100% conversion was reached only at -85°C ($W_p = 2.27 \text{ g}$); at -20 , -40 and -52°C 100% conversion would occur at $W_p = 1.97, 2.06$ and 2.15 g , respectively

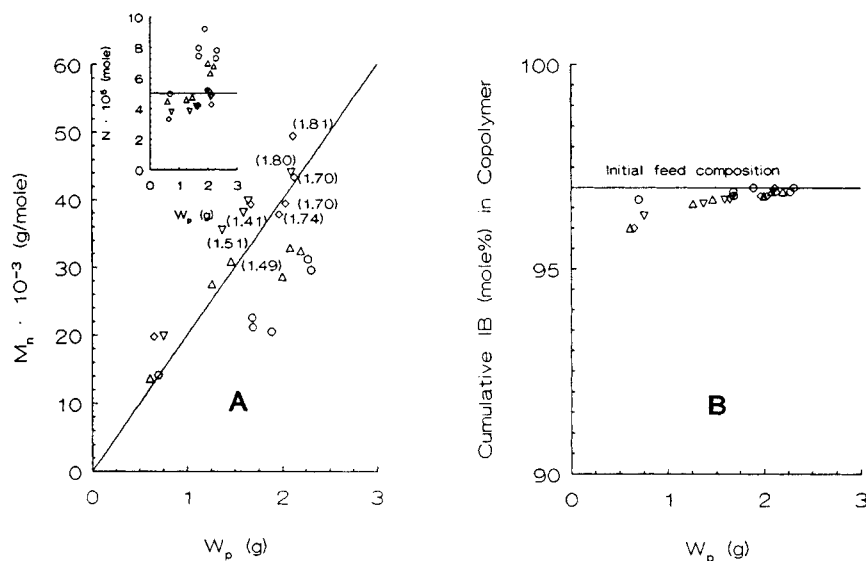


Figure 10. \bar{M}_n (and N) vs W_p (the solid lines indicate $I_{\text{eff}} = 100\%$, 'theoretical lines') and (B) cumulative IB content vs W_p plots for IB-pMeSt copolymers at -65°C with $[\text{DtBP}] =$ (O) 0, (Δ) 2.5×10^{-3} , (∇) 5.0×10^{-3} and (\circ) $12.5 \times 10^{-3} \text{ mol l}^{-1}$. Synthesis conditions: $[\text{IB}]/[\text{pMeSt}] = 97:3$; $[\text{I}] = 2.5 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{TiCl}_4] = 80.0 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{TEA}] = 7.5 \times 10^{-3} \text{ mol l}^{-1}$; solvent, ethyl chloride. 100% conversion was reached at $W_p = 2.11 \text{ g}$

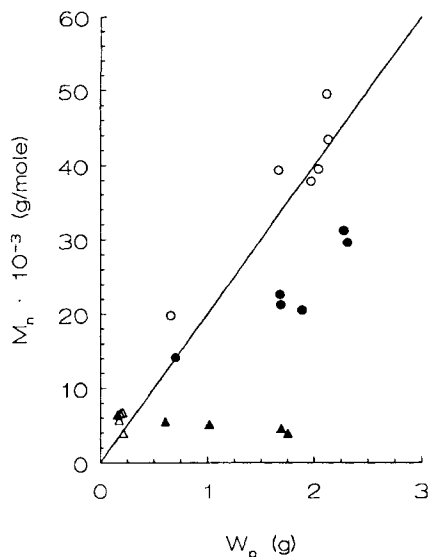


Figure 11. \bar{M}_n vs W_p plot (the solid line indicates $I_{\text{eff}} = 100\%$, 'theoretical line') for IB-pMeSt copolymers at ($\blacktriangle, \triangle$) -20°C and (\bullet, \circ) -65°C and with (\blacktriangle, \bullet) DtBP absent and (\triangle, \circ) [DtBP] = $12.5 \times 10^{-3} \text{ mol l}^{-1}$. Synthesis conditions as in Figure 7 except [DtBP]. 100% conversion was reached only at -65°C ($W_p = 2.11 \text{ g}$); at -20°C 100% conversion would occur at $W_p = 1.94 \text{ g}$

with TiCl_4 ; this results in slow propagation and close to theoretical molecular weights. In the absence of the proton trap, the protons, arising mainly by chain transfer, particularly at higher temperatures, preferentially react with TEA, whose concentration is thus reduced; a reduced [TEA] leads to diminished complexation with TiCl_4 , which in turn leads to reduced living copolymerization, enhanced conventional propagation and reduced \bar{M}_n relative to theoretical values. The composition of copolymers is independent of [DtBP] [Figure 10(B)].

Effect of [ED] on molecular weights, molecular weight distributions, number of chains and copolymer composition

Figure 12 illustrates the effect of [TEA] on copolymer \bar{M}_n s, MWDs and number of chains at [IB]/[pMeSt] = 97:3 and 90:10 feed compositions at -52°C . At higher [TEA] the experimental molecular weights are closer to the theoretical values, indicating the extended living nature of the system. The copolymer composition is independent of [TEA].

Comparison of the IMA and AMI techniques and their effect on molecular weights, molecular weight distributions and number of chains

Figure 13 compares the effect of the IMA and AMI techniques³⁴ on copolymer \bar{M}_n s, MWDs and number of

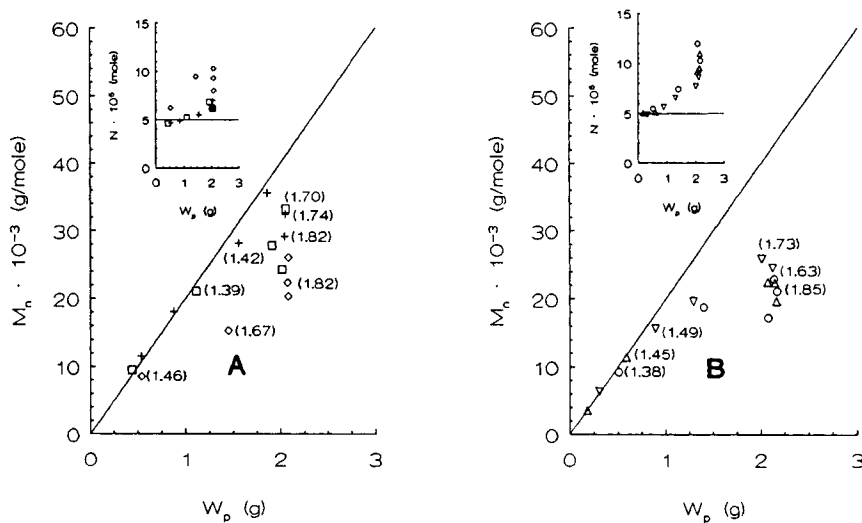


Figure 12. \bar{M}_n (and N) vs W_p plots (the solid lines indicate $I_{\text{eff}} = 100\%$, 'theoretical lines') for IB-pMeSt copolymers at -52°C (A) [IB]/[pMeSt] = 97:3 with [TEA] = (\circ) 2.5×10^{-3} , (\square) 5.0×10^{-3} and ($+$) $7.5 \times 10^{-3} \text{ mol l}^{-1}$; (B) [IB]/[pMeSt] = 90:10 with [TEA] = (\circ) 2.5×10^{-3} , (\triangle) 5.0×10^{-3} and (∇) $7.5 \times 10^{-3} \text{ mol l}^{-1}$. Synthesis conditions: $[I]_0 = 2.5 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{TiCl}_4] = 80.0 \times 10^{-3} \text{ mol l}^{-1}$; [DtBP] = $5.0 \times 10^{-3} \text{ mol l}^{-1}$; solvent, ethyl chloride. 100% conversion was reached at $W_p = 2.06 \text{ g}$ ([IB]/[pMeSt] = 97:3) and $W_p = 2.15 \text{ g}$ ([IB]/[pMeSt] = 90:10)

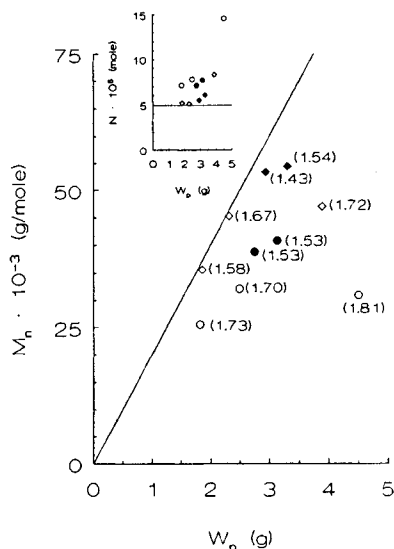


Figure 13. \bar{M}_n (and N) vs W_p plot (the solid lines indicate $I_{eff} = 100\%$, 'theoretical lines') for IB-pMeSt copolymers produced by the (\circ , \diamond) IMA and (\bullet , \blacklozenge) AMI techniques with $[IB]/[pMeSt] = (\diamond, \blacklozenge)$ 97:3 and (\circ, \bullet) 90:10 ($t = 10$ min in AMI experiments; $\Delta t = 10$ min in IMA experiments). Synthesis conditions as in Figure 3 except $[IB]/[pMeSt]$

chains at $[IB]/[pMeSt] = 97:3$ feed composition at -52 and -85 °C. As expected, the AMI technique is superior to the IMA technique in producing close to theoretical \bar{M}_n s. Specifically, in the present experiments we obtained IB-pMeSt copolymers with up to $\bar{M}_n \approx 50,000$ g mol $^{-1}$ by the AMI technique.

CONCLUSIONS

The living carbocationic copolymerization of the IB-pMeSt monomer pair has been achieved by the use of $[IB]/[pMeSt] = 97:3$ and the 5-tBu-1,3-DiCumOMe-TiCl $_4$ -ethyl chloride-TEA-DtBP (< -52 °C) system. The copolymer composition depends mainly on feed composition and total monomer conversion. While chain transfer is operational, its effect can be minimized and copolymers with up to $\bar{M}_n \approx 50,000$ g mol $^{-1}$ and $\bar{M}_w/\bar{M}_n \approx 1.4$ can readily be obtained.

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