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Living Carbocationic Copolymerizations. V. Synthesis of Isobutylene/p-Methylstyrene Copolymers with the Constant Copolymer Composition Technique in the Leidenfrost Reactor

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LIVING CARBOCATIONIC COPOLYMERIZATIONS. V. SYNTHESIS OF ISOBUTYLENE/*p*-METHYLSTYRENE COPOLYMERS WITH THE CONSTANT COPOLYMER COMPOSITION TECHNIQUE IN THE LEIDENFROST REACTOR

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ABSTRACT

Living copolymerization of the isobutylene (IB)-*p*-methylstyrene (*p*MeSt) monomer pair in combination with the constant copolymer composition (CCC) technique produces high molecular weight ($\overline{M}_n \approx$ 100,000 g·mol^{-1}) and narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n \approx$ 1.45) compositionally uniform IB/*p*MeSt copolymer molecules in the industrially important IB/*p*MeSt = 97–99/3–1 mol% composition range. Syntheses were carried out with $TiCl_4$ coinitiator in *n*-butyl chloride homogeneous solution at −85°C by the use of the Leidenfrost reactor (i.e., by direct cooling of the charge with liquid nitrogen). In order to carry out the CCC technique it was necessary to obtain reliable copolymerization reactivity ratios. These investigations led to $r_{IB} = 0.5 \pm 0.1$ and $r_{p\text{MeSt}} = 10 \pm 4$. The attainment of CCC and living copolymerization conditions has been quantitatively demonstrated by dedicated diagnostic plots. Specifically, the attainment of CCC conditions was

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proven by the analysis of composite rate plots (comonomers input *and* corresponding copolymer formed versus time) and composition plots (comonomer composition in feed *and* copolymer formed versus weight of copolymer formed, W_p), and living copolymerization was proven by linearly ascending number-average molecular weight of copolymer ($\overline{M}_n$) versus W_p plots starting at the origin.

I. INTRODUCTION

We recently developed a novel technique, the constant copolymer composition (CCC) technique, for the laboratory synthesis of compositionally uniform copolymers from isobutylene (IB) and *p*-methylstyrene (*p*MeSt), i.e., a comonomer pair whose reactivity ratios differ by close to an order of magnitude [1]. We also showed that it is possible to achieve living copolymerization of this monomer pair, at least over the industrially important IB/*p*MeSt = 97–99/3–1 mol% copolymerization range. And, finally, we demonstrated that the CCC and living copolymerization techniques can be combined and thus have prepared IB/*p*MeSt copolymers of uniform structures (i.e., CCC) with reasonably high molecular weights ($\overline{M}_n \approx 65{,}000$ g·mol^{-1}) and molecular weight distribution ($\overline{M}_w/\overline{M}_n \approx 1.5$) [2].

In the course of these investigations we have gained increased insight into the mechanism of copolymerization of monomer pairs having quite different structures (i.e., aliphatic and aromatic olefins) and found that in such cases the reactivity ratios (*r* values) are valid only over a very limited composition range [3, 4]. For example, for the IB/*p*MeSt monomer pair in the IB/*p*MeSt = 97–98/3–2 mol% range, the feed-copolymer composition values needed to calculate the *r* values must also be close to this narrow range, say IB/*p*MeSt = 90–99/10–1 mol% [4]. We have carried out additional investigations to elucidate the microstructure of IB/*p*MeSt compolymers by NMR spectroscopy over the entire comonomer composition range [5].

An analysis of our experiments showed that while CCC conditions have been attained and compositionally uniform copolymers were on hand, the molecular weight of copolymers was below our target ($\overline{M}_n \approx 65{,}000$ g·mol^{-1} versus our target of $\approx 100{,}000$ g·mol^{-1}), most likely due to insufficient temperature control in the reactor. Evidently, our 2-L round-bottom flask reactor equipped with an efficient stirrer immersed in a cooling bath at −60 or −64°C was unable to remove completely the rapidly evolving heat of copolymerization and the charge temperature was ≈10°C higher than that of the cooling bath [2]. To increase the accuracy of our temperature control and thus to obtain copolymer molecular weights closer to our target, we decided to employ a Leidenfrost reactor. The operational principle of this reactor has been described in detail [6]. Briefly, in this reactor efficient and highly accurate temperature control and mixing are maintained by the measured direct injection of liquid nitrogen into the charge.

This paper concerns a demonstration of the synthesis of high molecular weight, narrow molecular weight distribution, compositionally uniform IB/*p*MeSt copolymers by a combination of living copolymerization and CCC techniques in the Leidenfrost reactor, and the determination of reactivity ratios of IB and *p*MeSt valid over the industrially important copolymer composition range under the conditions employed.

II. EXPERIMENTAL

II.1. Materials

The following combination of chemicals was used in copolymerization experiments at −85°C. Charge: IB/*p*MeSt = 98–99/2–1 mol%. Feed: IB/*p*MeSt = 97–98/3–2 mol%/5-*tert*-butyl-1,3-dicumyl methyl ether (5-*t*Bu-1,3-DiCumOMe) initiator/$TiCl_4$ coinitiator/*n*-butyl chloride (*n*-BuCl) solvent/triethylamine (TEA) electron pair donor/2,6-di-*tert*-butylpyridine (D*t*BP) proton trap.

The source and purification of the chemicals have been described [2].

II.2. Procedures

Copolymerizations were carried out in a Leidenfrost reactor under a dry nitrogen atmosphere at −85°C (Fig. 1). A 3-L cylindrical reactor equipped with stirrer, jacketed inlet tube for liquid N_2 introduction and a feed inlet capillary was charged

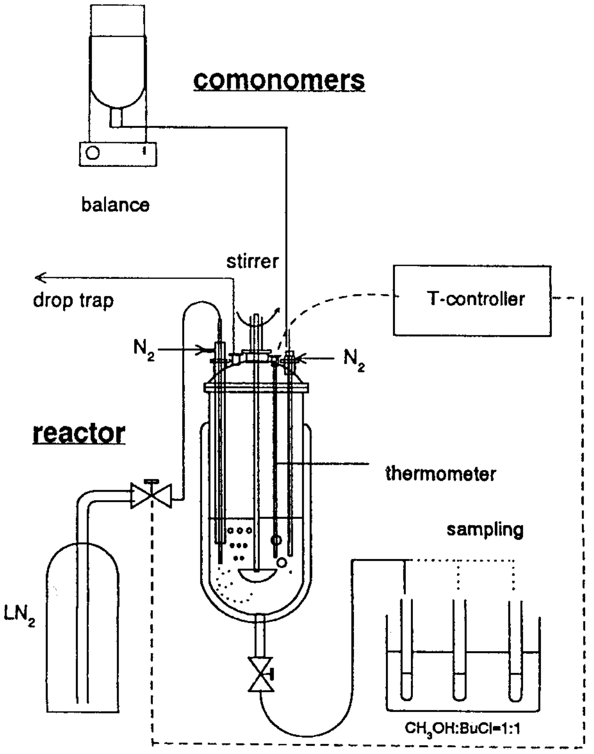

FIG. 1. Scheme of equipment used for constant copolymer composition experiments in a Leidenfrost reactor directly cooled by liquid nitrogen.

with monomers, solvent, initiator, and additivies (see Table 1, "Initial charge," except $TiCl_4$) and maintained at −85°C by the measured direct injection of liquid N_2. The total initial charge was 1400 mL. Copolymerization was triggered by the addition of prechilled $TiCl_4$ solution. After the copolymerization started, the valve of the cylinder containing the mixture of comonomers (see Fig. 1 and Table 1, "IB/*p*MeSt in feed") was opened and the comonomers feed was continuously added into the reactor at a predetermined rate and composition (see Section III for details). The total amount of comonomers added was continuously monitored by an electronic balance. During the copolymerization, samples were taken and quenched with prechilled CH_3OH:*n*-BuCl = 1:1 (see Fig. 1). The temperature was continuously monitored and controlled in the reactor by a Pt-resistance thermometer and controller (Omega CN 7000). Molecular weights were determined by a Waters high pressure GPC instrument. Details of the copolymerizations, CCC conditions, and characterization methods have been described [1-3, 7, 8].

III. RESULTS AND DISCUSSION

III.1. Design of CCC Experiments

Under CCC conditions the rate of comonomers addition and that of conversion of monomers into copolymer must be equal for both comonomers [1, 2]. To achieve these goals: a) the comonomer composition in the charge has to be determined and b) the comonomer's input rate has to be known.

These two prerequisites can be achieved as follows. a) The composition of the comonomers in the charge (*p*MeSt/IB, where *p*MeSt and IB are relative amounts of comonomers in mol% in the charge) must be such that it should produce the target copolymer composition ($p\mathrm{MeSt}_{\mathrm{in\ copol.}}/\mathrm{IB}_{\mathrm{in\ copol.}}$, where $p\mathrm{MeSt}_{\mathrm{in\ copol.}}$ and $\mathrm{IB}_{\mathrm{in\ copol.}}$ are the relative amounts of comonomers in mol% in the copolymer) [1, 4]. Thus the initial charge composition can be calculated from the instantaneous copolymer composition equation [9]:

TABLE 1. Experimental Conditions

Experiments	I	II
T(°C)	−85 ± 2	−85 ± 2
Initial charge, V_0 = 1400 mL		
Solvent	BuCl	BuCl
10^3 $[I]_0$ (mol/L)	0.90	0.72
10^3 [TEA] (mol/L)	3.6	3.6
10^3 [DtBP] (mol/L)	8.9	8.9
IB + *p*MeSt (mol)	1.75 + 0.029	2.37 + 0.024
(IB/*p*MeSt)[a]	(98.4/1.6)	(99/1)
10^3 $[TiCl_4]$ (mol/L)	36	36
Comonomers feed (bulk), IB/*p*MeSt[a]	97/3	98/2
Average feed rate (g/min)	4.7	4.7

[a] IB/*p*MeSt is in mol%/mol%.

$$\frac{p\mathrm{MeSt}}{\mathrm{IB}} = -\frac{1-\dfrac{p\mathrm{MeSt}_{\text{in copol.}}}{\mathrm{IB}_{\text{in copol.}}}}{2r_{p\mathrm{MeSt}}} + \sqrt{\left(\frac{1-\dfrac{p\mathrm{MeSt}_{\text{in copol.}}}{\mathrm{IB}_{\text{in copol.}}}}{2r_{p\mathrm{MeSt}}}\right)^2 + \frac{p\mathrm{MeSt}_{\text{in copol.}}}{\mathrm{IB}_{\text{in copol.}}}\,\frac{r_{\mathrm{IB}}}{r_{p\mathrm{MeSt}}}} \tag{1}$$

where $r_{p\mathrm{MeSt}}$ and r_{IB} are the reactivity ratios. The reactivity ratios were determined from experiments carried out over the same comonomer concentration range and under conditions similar to CCC experiments (see Section III.2). b) The input rate of the comonomers was estimated on the basis of earlier findings [1] and numerous preliminary experiments, and further fine tuned by additional experiments.

III.2. Determination of Reactivity Ratios in *n*-Butyl Chloride Solvent

Based on our earlier investigations with the IB/*p*MeSt system [4] the monomer reactivities are markedly different (*p*MeSt is much more reactive than IB) and the composition of the feed will rapidly change even at very low conversions. This drift in feed composition will result in a significant drift in copolymer composition and must be taken into account to calculate meaningful reactivity ratios. In the course of our studies aimed to develop suitable experimental conditions for homogeneous living copolymerization, a large amount of compositional data were gathered over a very narrow composion range. These experiments included conversion vs time experiments, AMI (all monomer in) experiments with less than 100% monomer conversion, IMA (incremental monomer addition) experiments with less than 100% monomer conversion, and preliminary CCC experiments. These data provided the needed instantaneous comonomer and copolymer composition information for the determination of the reactivity ratios [4]. The cumulative and instantaneous polymer compositions, f_c and f_i, and conversion C are interrelated by

$$\frac{\int_0^C f_i \cdot dC}{C} = f_c \tag{2}$$

To calculate r_{IB} and $r_{p\mathrm{MeSt}}$ by the differential copolymer composition equation, we need the instantaneous copolymer composition (f_i) and the instantaneous feed composition (F_i). We have obtained f_i by computer fitting f_c (in mol%) as a function of conversion, and expressed as

$$f_i = \frac{d}{dC} \cdot (f_c \cdot C) \tag{3}$$

The instantaneous comonomer compositions were calculated from the material balance equations and from the cumulative composition data. These F_i and f_i are true instantaneous values and can be used without any assumptions to calculate r_{IB} and $r_{p\mathrm{MeSt}}$ by the differential copolymer composition equation.

Figure 2 shows all the calculated instantaneous composition data (F_i and f_i). Since the composition information was gathered over a very narrow composition range, neither linearization methods for the determination of reactivity ratios (Fineman-Ross [10], Kelen-Tüdös [11]) could be used. Instead of the linearization methods we have iterated the primary data and the best fit was obtained with $r_{\mathrm{IB}} = 0.5$

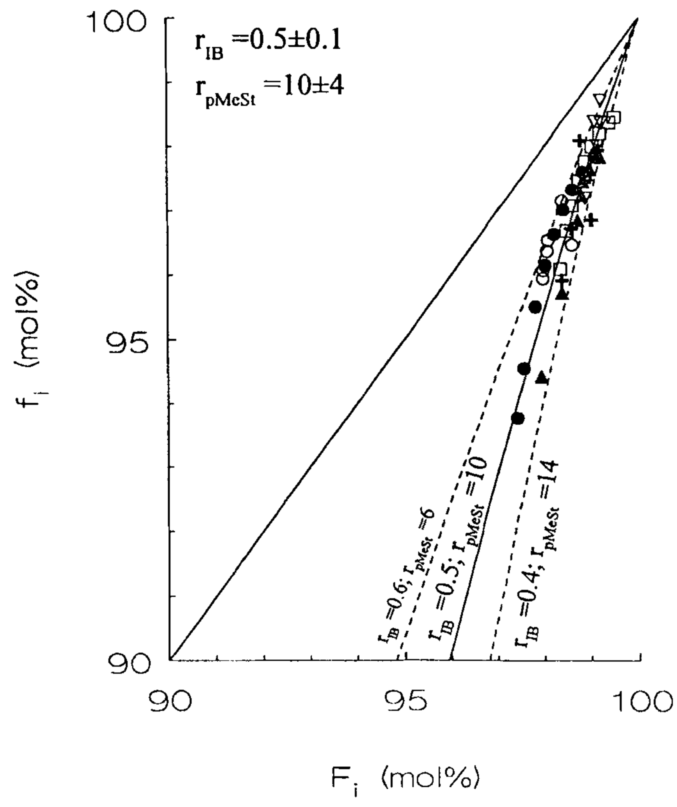

FIG. 2. Instantaneous copolymer composition (f_i) as a function of instantaneous comonomer composition (F_i) in the IB/*p*MeSt/BuCl copolymerization system. −90°C. Conversion vs time, AMI and IMA experiments, carried out in large test tubes: (●) charge, 97/3; (□) charge, 98/2. Preliminary CCC experiments: −90°C, charge, 99/1; feed, 97/3; (▽) initial comonomer concentration in charge = 1.8 mol/L; (+) initial comonomer concentration in charge = 0.6 mol/L; −85°C, initial comonomer concentration in charge = 1.2 mol/L; (○) charge, 98/2; feed, 97/3; (▲) charge, 98/5/1.5; feed, 97/3.

± 0.1 and r_{pMeSt} = 10 ± 4. The error limits (also shown in Fig. 2) are obviously higher for *p*MeSt since its concentration is much less than that of IB. These sets of values, on account of the wider error limits, also embrace the values generated earlier for EtCl solvent (r_{IB} = 0.74 ± 0.11 and r_{pMeSt} = 7.99 ± 3.34) [4].

III.3. Synthesis of Uniform High Molecular Weight IB-*p*MeSt Copolymers under CCC and LC$^+$ Copolymerization Conditions in the Leidenfrost Reactor

This section concerns two representative experiments that demonstrate the synthesis of compositionally uniform high molecular weight relatively narrow molecular weight distribution IB/*p*MeSt copolymers under CCC and living copolymerization conditions in the Leidenfrost reactor.

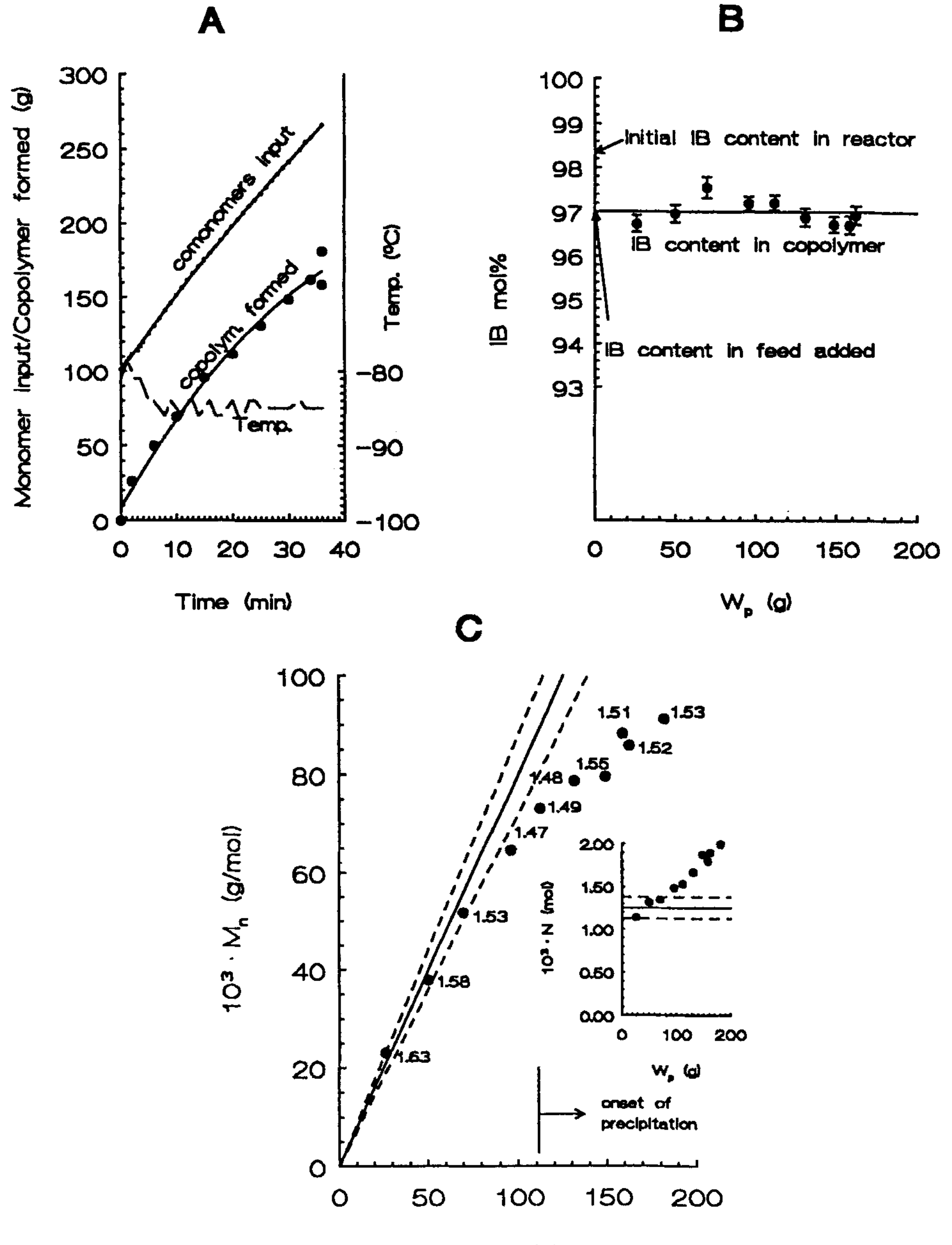

FIG. 3. Diagnostic plots for the constant copolymer composition condition and the living copolymerization of IB-*p*MeSt charges in Experiment I. (A) Comonomers input and corresponding copolymer formed vs time, showing that the rate of comonomers input and that of copolymer formation are practically identical. (B) Comonomer composition in feed and copolymer composition vs W_p, showing that the IB content in the feed is equal to the IB content in the copolymer. (C) $\overline{M}_n$ vs W_p indicates significant chain transfer above $\overline{M}_n \approx$ 70,000 g·mol^{-1}; the numbers indicate $\overline{M}_w/\overline{M}_n$; the broken lines show ±10% error limits in the molecular weight determination. Experimental conditions: see Table 1, Column I.

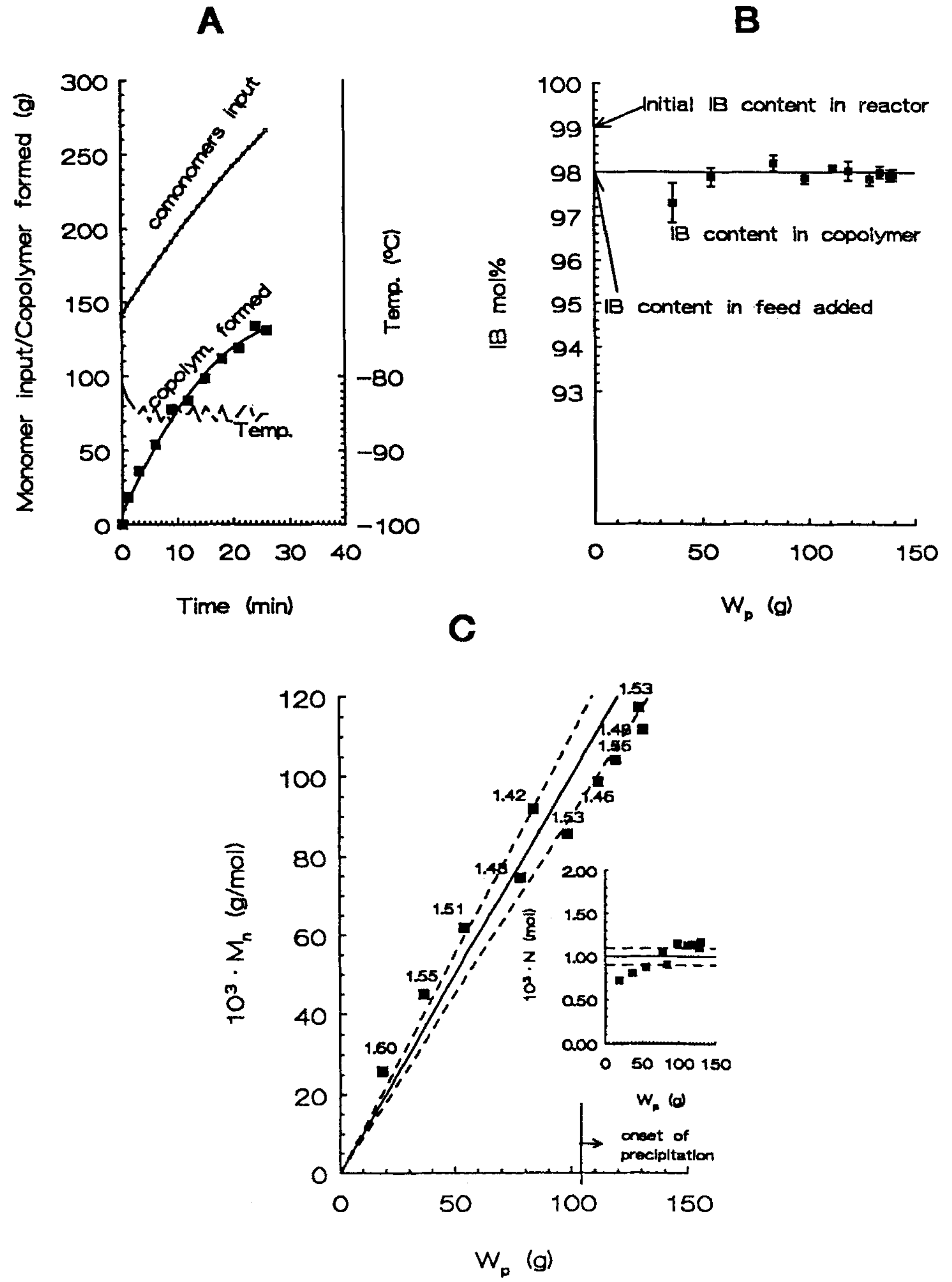

FIG. 4. Diagnostic plots for the constant copolymer composition condition and the living copolymerization of IB-*p*MeSt charges in Experiment II. (A) Comonomers input and corresponding copolymer formed vs time, showing that the rate of comonomers input and that of copolymer formation are practically identical. (B) Comonomer composition in feed and copolymer composition vs W_p, showing that the IB content in the feed is equal to the IB content in the copolymer. (C) $\overline{M}_n$ vs W_p indicates slight chain transfer above $\overline{M}_n \approx 100{,}000$ g·mol^{-1}; the numbers indicate $\overline{M}_w/\overline{M}_n$; the broken lines show ±10% error limits in the molecular weight determination. Experimental conditions: see Table 1, Column II.

Experiment I. Table 1 shows the ingredients and conditions used, and the diagnostic plots in Fig. 3 summarize the results obtained. According to the first diagnostic plot, Fig. 3(A), the input rate of the comonomers feed was close to the rate of the copolymerization. According to the second diagnostic plot, Fig. 3(B), the IB content in the copolymer was practically equal to that in the feed. The composition of the charge remained the same, the compositions of the copolymer and feed, and the rates of copolymerization and comonomers input were identical within experimental error during the entire experiment. Evidently the cumulative copolymer composition did not change. According to the sum total of these evidences, CCC conditions have been achieved.

The third diagnostic plot, Fig. 3(C), shows that the copolymerization exhibited living character up to $\overline{M}_n \approx 70{,}000\ \mathrm{g \cdot mol^{-1}}$. The charge was homogeneous up to $\overline{M}_n \approx 80{,}000\ \mathrm{g \cdot mol^{-1}}$. Chain transfer became noticeable above $\overline{M}_n \approx 60{,}000\ \mathrm{g \cdot mol^{-1}}$, i.e., the molecular weights started to deviate from the theoretical line and the MWDs started to broaden.

Experiment II. Table 1 shows the ingredients and conditions used, and the diagnostic plots shown in Fig. 4 summarize the results obtained. According to the first diagnostic plot, Figure 4(A), the input rate of comonomers was close to the rate of the copolymerization. According to the second diagnostic plot, Fig. 4(B), the IB content in the copolymer was essentially equal to that in the feed. The composition of the charge did not change, the compositions of the copolymer and the feed, and the rates of copolymerization and comonomers input were identical within experimental error during the entire experiment. The cumulative composition of the copolymer did not change. This evidence shows that CCC conditions have been achieved.

The third diagnostic plot, Figure 4(C), shows that the copolymerization exhibited living character during the entire experiment. The charge was homogeneous up to $\overline{M}_n \approx 100{,}000\ \mathrm{g \cdot mol^{-1}}$ and the molecular weights followed the theoretical line (i.e., insignificant chain transfer activity) within experimental error and the MWDs did not broaden.

These representative experiments proved that, under CCC and living copolymerization conditions in the Leidenfrost reactor, the IB/*p*MeSt monomer pair readily produces compositionally uniform copolymers with up to $\overline{M}_n \approx 100{,}000\ \mathrm{g \cdot mol^{-1}}$ and $\overline{M}_w/\overline{M}_n \approx 1.45$.

IV. CONCLUSIONS

High molecular weight ($\overline{M}_n \approx 100{,}000\ \mathrm{g \cdot mol^{-1}}$) IB-*p*MeSt copolymers have been prepared by the use of the constant copolymer composition technique under living copolymerization conditions at −85°C in the Leidenfrost reactor. Reactivity ratios of $r_{IB} = 0.5 \pm 0.1$ and $r_{pMeSt} = 10 \pm 4$ were determined. The targeted copolymer compositions of IB/*p*MeSt = 97/3 and 98/2 mol% have been attained in spite of the large reactivity difference between the comonomers.

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