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QUASILIVING CARBOCATIONIC POLYMERIZATION. XVII. SYNTHESIS OF POLY(STYRENE-β-ISOBUTYLENE-β-STYRENE)

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ABSTRACT

Poly(styrene-*b*-isobutylene-*b*-styrene) has been synthesized by sequential carbocationic polymerization under quasiliving conditions at -90°C. The quasiliving synthesis was effected by first continuously and slowly condensing gaseous isobutylene (IB) to a bifunctional initiating system (*p*-dicumyl chloride/$TiCl_4$) dissolved in a hexane-methylene chloride (60:40 v/v) mixture. After the quasiliving polyisobutylene (PIB) sequence had reached a desired molecular weight, styrene (St) was continuously and slowly added to produce the polystyrene (PSt) sequence. The products consisted of the target triblock. However, due to initiation by impurities and possibly to chain transfer to both IB and St, it also contained diblocks and small amounts of homopolymers. While the latter could be removed by selective fractionation, the triblocks and diblocks could not be separated. The mechanism of quasiliving polymerization leading to PIB/PSt blocks is discussed.

INTRODUCTION

Earlier publications in this series concerned the quasiliving carbocationic polymerization of styrene (St) [1] and isobutylene (IB) [2], and forced ideal copolymerization of these monomers [3]. In the course of these investigations, the sequential synthesis of poly(St-*b*-IB) diblock copolymers (PSt-*b*-PIB) was accomplished [1]. As a continuation of this work, the sequential synthesis of poly(St-*b*-IB-*b*-St) has now been explored.

A similar glassy/rubbery/glassy triblock, i.e., poly(α-methylstyrene-*b*-IB-*b*-α-methylstyrene) has already been prepared by first synthesizing an α,ω-di-*t*-chloro-terminated PIB (^{t}Cl-PIB-Cl^t) by the BCl_3-based inifer technique and, after purification and recovery, using this prepolymer in conjunction with $(C_2H_5)_2AlCl$ [4] or $SnCl_4$ [5] to initiate the polymerization of α-methylstyrene. The disadvantages of this synthesis route are the necessity of using two different initiating systems (i.e., (1) binifer/BCl_3 to prepare the ^{t}Cl-PIB-Cl^t prepolymer and (2) subsequently $(C_2H_5)_2AlCl$ to prepare the target triblock), and the fact that the ^{t}Cl-PIB-Cl^t prepolymer has to be purified, recovered, and redissolved prior to the second block polymerization step.

Two possible synthetic routes have been considered:

1. Coupling of two poly(St-*b*-IB) diblocks at the PIB end.
2. Sequential monomer addition, i.e., initiating the quasiliving polymer-

> ization of IB by a bifunctional initiating system and, after having reached a suitable molecular weight of PIB, switching to the polymerization of St.

A third possibility, i.e., sequential monomer addition starting with a monofunctional initiating system that initiates the polymerization of St, then switching to IB and finally switching back to St, was discarded at the onset since this route would have been similar to Route 2 with one additional monomer switching step.

A thorough evaluation of the advantages/disadvantages of these options led to the conclusion that, on balance, Route 2 was more promising. In regard to the first option, the preparation of the quasiliving PSt-*b*-PIB$^{\oplus}$ diblock has already been described [1]. However, the quantitative functionalization of the quasiliving PIB$^{\oplus}$ terminus has not been accomplished, and the quantitative coupling of a PSt-*b*-PIB$^{\oplus}$ or of a suitably functionalized PSt-*b*-PIB diblock at the PIB terminus remains to be accomplished. In contrast, in regard to Route 2, the only synthetic step that has not yet been demonstrated is the sequential quasiliving polymerization of St by the quasiliving PIB$^{\oplus}$:

$$\text{PIB}^{\oplus} + \text{St} \longrightarrow\longrightarrow \text{PIB-}b\text{-PSt}^{\oplus}. \qquad \text{(I)}$$

In view of earlier experience with copolymerizing St and IB [3], this blocking step did not seem to represent an insurmountable obstacle.

This paper concerns the synthesis of poly(St-*b*-IB-*b*-St) by sequential monomer addition, and the characterization of the products by GPC and other techniques.

EXPERIMENTAL

Materials

The purification of IB [2] and St [6] has been described. The preparation and characterization of the 1,4-(2-chloro-2-propyl)benzene or *p*-dicumyl chloride (DCC) initiator have been published [7]. $TiCl_4$ coinitiator (Aldrich 99.8%) was used as received. The purification of hexane [2] and methylene chloride [3] has been described.

Procedures

Polymerizations were carried out in a stainless steel enclosure under dry N_2 at -50 or -90°C. Figure 1 shows the reactor used. It consisted of a four-neck

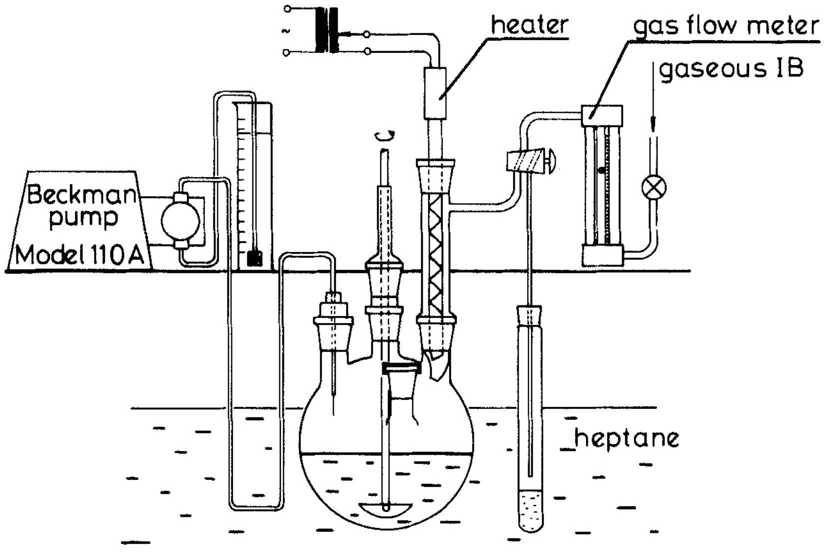


FIG. 1. Equipment used for triblock synthesis.

round-bottom flask (250-500 mL) equipped with a stirrer, a heated inlet for gaseous IB, and a glass capillary for the introduction of St; the fourth neck was capped with a rubber septum. To insure the continuously controlled addition of St (i.e., to completely eliminate pulsation during monomer delivery), the outlet of the glass capillary was further restricted by drawing it out to a fine tip.

The experiments were carried out by first placing into the reactor a hexane-methylene chloride 60:40 (v/v) solvent mixture and dissolving in it, in sequence, DCC and $TiCl_4$ under stirring at room temperature. Then the flask was immersed in the bath, and when the desired temperature was reached, the polymerizations were started by the introduction of a stream of gaseous IB, controlled by means of a calibrated flow meter. Subsequent to IB introduction, the controlled addition of St was effected. To prevent freezing of this monomer, the St stream was diluted with CH_2Cl_2 (1:1, v/v). A precision pump (Beckman, Model 110A) was used to insure the continuous introduction of St.

The progress of the reaction was followed by withdrawing aliquots (~0.2 mL) at desired time intervals by a syringe through the rubber septum and injecting them into capped vials containing a few milliliters of methanol. Polymerizations were stopped by adding the active charge to excess methanol outside the dry box. After evaporating the volatiles, conversions were determined gravimetrically; conversions were essentially 100%.

Molecular weights of homopolymers were determined by GPC (Waters Associates equipment including dual RI and UV detectors). Details of the methodology have been described previously [10]. Molecular weights of copolymers were obtained by a Hewlett-Packard (Model 503) membrane osmometer, using toluene solvent at 25°C [1].

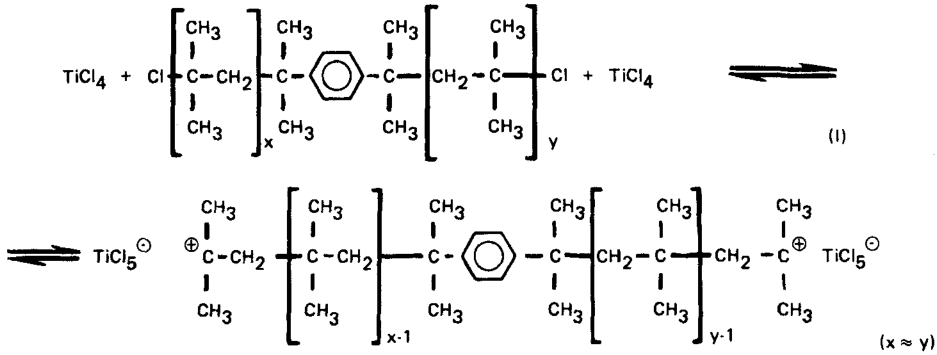
Copolymer compositions were determined by integration of ^{1}H-NMR resonances observed with a Varian T-60 NMR spectrometer from CCl_4 solutions at 25°C [1].

Some samples were fractionated by the process described previously [1].

RESULTS AND DISCUSSION

(a) Orienting Experiments

A large number of orienting experiments was conducted to work out the essential experimental parameters for the sequential monomer addition synthesis route. Specifically, the task was first to prepare an α,ω-bi-quasiliving PIB by use of the DCC/$TiCl_4$ system:



(I)

and, second, to find conditions for the switching from the quasiliving prepolymer dication $^{\oplus}$PIB$^{\oplus}$ to the quasiliving polymerization of St:

$$({}^{t}\text{Cl-PIB-Cl}^{t} \rightleftharpoons {}^{\oplus}\text{PIB}^{\oplus}) + \text{St} \rightleftharpoons {}^{\oplus}\text{PSt-PIB-PSt}^{\oplus}. \qquad \text{(II)}$$

In regard to the first step, earlier investigators showed that the cumyl chloride/$TiCl_4$ combination efficiently indicates the quasiliving polymerization of IB [2]. Also, ^{t}Cl-PIB-Cl^t has been prepared and characterized by Kennedy and Smith [4] and Kennedy et al. [5]; and according to Kaszás et al. [3], 2-chloro-2,4,4-trimethylpentane (which models the end groups of this prepolymer) in conjunction with $TiCl_4$ readily initiates the polymerization of IB.

In view of these findings, the quasiliving equilibrium

$$ {}^t\text{Cl-PIB-Cl}^t + 2\text{TiCl}_4 \rightleftharpoons \text{TiCl}_5^{\ominus}\ {}^{\oplus}\text{PIB}^{\oplus}\ \text{TiCl}_5^{\ominus} \qquad \text{(III)} $$

was anticipated to exist.

In regard to the pertinent references for the second step, i.e., the addition of St to quasiliving $PIB^{\oplus}$, the forced ideal copolymerization of IB/St charges under quasiliving conditions was demonstrated [3].

Taking Puskás et al.'s data [2] into consideration, we selected the DCC/$TiCl_4$ system for the preparation of ^{t}Cl-PIB-Cl^t. According to these results, other Lewis acids, e.g., $SnCl_4$, or other carbenium ion generating species, e.g., $AgSbF_6$, are unsuitable for the generation of quasiliving PIB.

Orienting experiments have consistently yielded better results (100% conversion) at -90 than at -50°C. Thus, it was decided to perform all runs at -90°C.

Our possibilities were also restricted by the choice of the solvent system. To maintain homogeneous conditions throughout, we had to use 60:40 (v/v) hexane-methylene chloride mixtures. Increasing the CH_2Cl_2 content would have caused precipitation of PIB, whereas increasing the hexane content would have caused PSt to come out of solution and the degree of dissociation of the quasiliving ion pair would have been reduced.

(b) Block Copolymerizations

The results of a representative experiment are shown in Figs. 2-4).

Specifically, Fig. 2 shows representative RI and UV traces of samples withdrawn in the course of a run carried out for a total of 50 min. Figure 3 is a plot of $\overline{M}_n$ as a function of the monomers added, and Fig. 4 shows the number of polymer molecules formed as a function of IB added, i.e., during the first "IB phase" of the experiment.

In line with the observations with the cumyl chloride/$TiCl_4$ system [2], the DCC/$TiCl_4$ combination was found to be an efficient initiating system for the polymerization of IB. Also, similar to Puskás et al.'s findings [2],

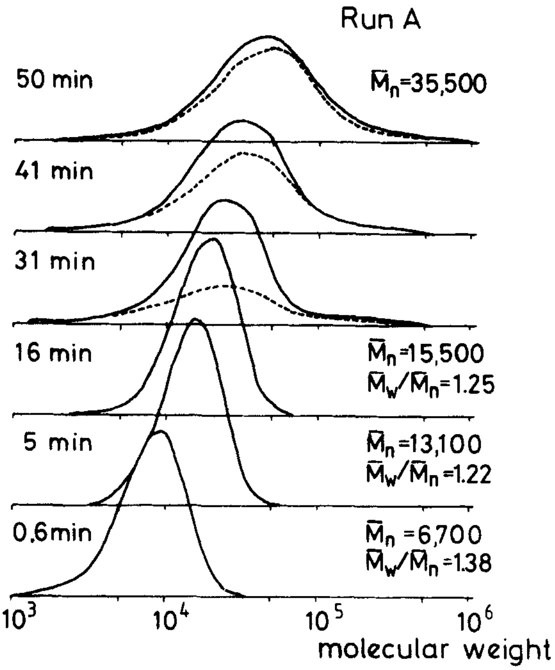


FIG. 2. Select GPC traces obtained during triblock synthesis for Run A. V_0 = 100 mL; $[DCC]_0$ = 11 mmol/L; $[TiCl_4]_0$ = 55.8 mmol/L; 90°C; IB phase, 10 mmol/min, 20 min; St phase, 11.7 mmol/min, 29.5 min. Areas under the RI traces have been normalized. (—) RI trace; (--) UV trace.

the $\bar{M}_n$ of PIB was found to jump to 10 000 right at the start and to increase at a lower rate thereafter (cf. Fig. 3). The earlier workers [1, 2] attributed this jump increase in $\bar{M}_n$ to unavoidable traces of moisture.

The molecular weight distributions were unimodal and narrow ($\bar{M}_w/\bar{M}_n$ = 1.38-1.22 during the IB phase, see Fig. 2). Disturbingly, however, the number of molecules increased linearly with the amount of IB added, indicating quite extensive chain transfer to monomer (see Fig. 4). In this plot [2]

$$[P] = I_0 + \frac{k_{tr}}{\eta k_p} At, \qquad (1)$$

where [P] is the concentration of polymer molecules at time t, I_0 is the effective initiator concentration at time $t = 0$, k_{tr} and k_p are the rate constants

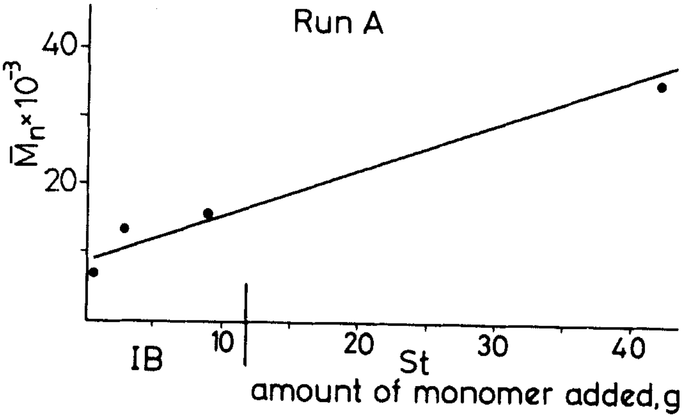


FIG. 3. Number-average molecular weight of the polymers, $\bar{M}_n$, as a function of the amount of monomer added.

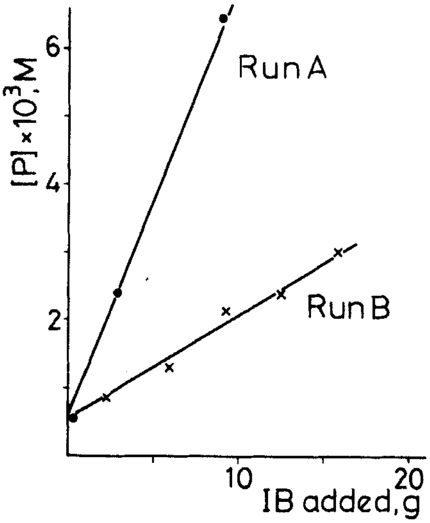


FIG. 4. Polymer concentration as a function of monomer added during the IB phase. Run A: $I_0 = 0.6$ mmol/L, $k_{tr}/k_p = 6.4 \times 10^{-3}$; Run B: $I_0 = 0.0566$ mmol/L, $k_{tr}/k_p = 3.1 \times 10^{-3}$; calculated by plotting Eq. (1).

for chain transfer and propagation, respectively, and $1 \leq \eta \leq 2$ (if the macrocations grow at both ends $\eta \doteq 2$; if at only one end, $\eta = 1$; in the present case we assumed $\eta = 2$), while A is the rate of monomer addition.

The intercept obtained by plotting Eq. (1) gives $I_0 = 0.4$ mmol/L. This value is close to the moisture content in conventional well-dried systems [10, 11], and may be an indication that unscavengeable water may function as an initiating impurity in conjunction with $TiCl_4$ coinitiator under our experimental conditions.

The simultaneous examination of the RI and UV traces shown in Fig. 2 provides evidence for block polymerization of St to quasiliving $PIB^{\oplus}$. The IB phase in this experiment lasted 20 min. The UV trace of the sample withdrawn at 31 min, i.e., 11 min after the start of the St phase, indicates the presence of UV-active PSt in the product. Importantly, the position of the RI and UV traces are almost identical, which suggests that each quasiliving $PIB^{\oplus}$ in the product distribution has incorporated a PSt moiety. Upon continued St addition, the amount of PSt incorporation increases in the expected manner (cf. RI and UV traces in Fig. 2 of product obtained at 41 and 50 min).

The $\overline{M}_n$ of the final block polymer product harvested from the reactor was 35 500 (by osmometry). It is of interest that this $\overline{M}_n$ and the $\overline{M}_n$'s of the samples taken during the IB period are situated along the same straight line if they are plotted against the amount of monomer added (Fig. 3).

Solvent fractionation coupled with compositional analysis of the final product is further evidence for successful block polymer synthesis. Thus the product was selectively fractionated first with *n*-pentane and subsequently with methyl ethyl ketone (MEK), and the relative amounts and compositions of the individual fractions were determined (see Table 1). The two main fractions were hazy solutions. The bulk of the product (87.2 mol%) appears in the *n*-pentane-soluble/MEK-soluble fraction, and it contains 55/45 mol/mol PSt/PIB. Since PSt is insoluble in *n*-pentane and PIB is insoluble in MEK, this *n*-pentane-soluble/MEK-soluble fraction must contain the target block polymer.

Further evidence for block polymerization is the fact that the second largest fraction (i.e., the *n*-pentane-insoluble/MEK-soluble fraction, 10.3%) contains a large amount of PIB (31 mol%). PIB would appear in the MEK-soluble fraction only by being pulled into solution by the readily MEK-soluble PSt moiety. Thus the overwhelming proportion of the product, a total of 97.5 mol/, consists of block polymers.

A very small amount (1.5 mol%) of relatively high molecular weight PIB ($\overline{M}_n \approx 70\ 000$) could not be detected by our GPC instrument. In view of its rather high $\overline{M}_n$, this PIB was most likely formed by direct initiation by the

TABLE 1. Product Fractions Obtained in Run A

Soluble[a] in		Amount, mol%	$\overline{M}_n$	Composition, mol%	
n-Pentane	MEK			St	IB
Unfractionated			35 500[b]	56	44
+	+	87.2	34 000[b]	55	45
-	+	10.3	42 900[b]	79	31
+	-	1.5	69 900[c]	0	100
-	-	0.4		TiO$_2$	

[a] + = soluble, – = insoluble.
[b] By membrane osmometry.
[c] By GPC.

$\sim CH_2C^{\oplus}(CH_3)_2TiCl_4OH^{\ominus}$ ion pair which had arisen from the inevitable water impurities in the system. Puskás et al. [2] found that water (i.e., the $TiCl_4OH^{\ominus}$ counteranion) leads to very high $\overline{M}_n$ PIB in similar systems (cf. Fig. 2 in Ref. 2; see also below).

The balance of the product (~0.4 mol%) was TiO_2 which formed from $TiCl_4$ upon quenching the reaction with excess methanol and drying.

We were unable to find a method to separate possible PIB/St diblocks from the target triblock.

Attempts were made to investigate the mechanical properties of cast films, but in spite of repeated efforts, we could not obtain a homogeneous film for characterization. All the films were hazy, wrinkled, inhomogeneous, and unsuitable for stress-strain analysis. Similarly, cast films of the pentane-soluble-MEK-soluble and pentane-insoluble/MEK-soluble fractions were inhomogeneous. On manual stretching, these films appeared to be rather brittle and weak. The lack of the thermoplastic elastomer characteristics is most likely due to the higher than desirable overall PSt content and the relatively low molecular weight of the PIB segment. Since very low molecular weight ($\overline{M}_n < 10^3$) PIB and PSt are soluble in MEK and *n*-pentane, respectively, these films might have been contaminated with these by-products which could have contributed to the poor mechanical properties.

Another series of experiments was carried out to increase the molecular

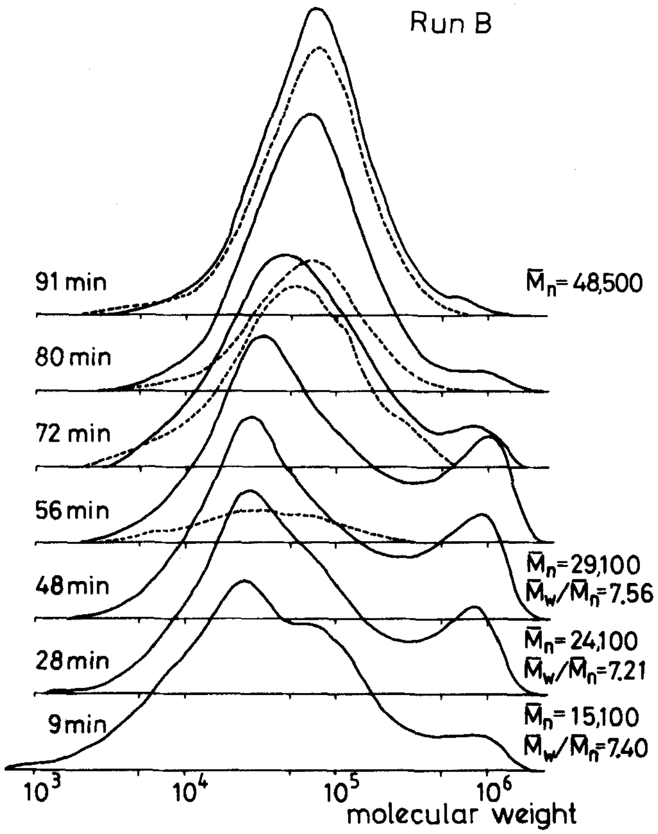


FIG. 5. Select GPC traces for Run B. V_0 = 200 mL; $[DCC]_0$ = 2.79 mmol/L; $[TiCl_4]$ = 10 mmol/L; -90°C; IB phase, 5.89 mmol/min, 53 min; St phase, 9.29 mmol/min, 39 min. *Areas under the RI traces have been normalized.* (—) RI trace; (--) UV trace).

weight of the triblock and thus to obtain a thermoplastic elastomer. In designing the experimental conditions, we aimed to work with a final charge concentration of less than 18-20%. We found that the stirring of solutions whose concentration exceeds ~20% becomes virtually impossible on account of the high viscosity of the system, particularly at lower temperatures. To achieve these objectives we reduced the initiator concentration to [DCC] = 2.79 mmol/L. The legend of Fig. 5 gives other pertinent conditions, while the figure shows select RI and UV traces obtained in the course of a representative experiment.

According to the RI trace, the molecular weights obtained during the IB phase were indeed higher, but the molecular weight distributions were multimodal, particularly during the early stages of the polymerization.

In line with the findings of Puskás et al. [2], the peak at $\overline{M}_n \approx 10^6$ is assigned to macromolecules formed due to adventitious moisture ("H_2O"). The growing species responsible for this high molecular weight product is most likely the dissociated $\sim CH_2C^{\oplus}(CH_3)_2TiCl_4OH^{\ominus}$ ion pair, and the rate constant of propagation is very high [2]. The other peak ($\overline{M}_n \approx 2 \times 10^4$) must be due to propagation by the $\sim CH_2C(CH_3)_2{}^{\oplus}TiCl_5{}^{\ominus}$ ion pair. The propagation rate constant of the latter ion pair is smaller, but its concentration is higher than those of the former one (since ["H_2O"] < [DCC]). Thus, it is not surprising that the ratio of the peaks remains approximately the same during the IB period.

The duration of the IB phase was 53 min in this experiment. The sample withdrawn 3 min after the start of St introduction shows significant St incorporation in the lower molecular weight species; however, the $\overline{M}_n \approx 10^6$ peak is characterized by the absence of UV absorption. Evidently the growing centers that produce the higher molecular weight PIB are unable to start the block polymerization of St.

It can be assumed [12] that chain transfer to monomer occurs only via the counteranion. We postulate that the hypothetical acid $HTiCl_4OH$ exists at least momentarily in the system and that it very rapidly initiates the homopolymerization of St. Due to the rapid homopolymerization of St by $HTiCl_4OH$, block polymerization to the high-$\overline{M}_n$ cation is prevented.

In Fig. 4, Curve B shows the number of polymer molecules [P] as a function of the IB added (see Eq. 1). Evidently the I_0 values were quite similar in the two experiments. However, the k_{tr}/k_p ratio was somewhat smaller than in the previous run.

Repeated attempts were made to prepare cast sheets for mechanical testing, but without success. The sheets obtained were opaque and visibly inhomogeneous. Efforts were also made to separate manually (cutting out, using forceps) homogeneous islands from the less homogeneous areas in the product and casting films from these manually separated fractions. However, even these measures failed to yield homogeneous casts for testing. It is postulated that much "cleaner" products could be obtained in the complete absence of moisture, i.e., under high-vacuum conditions.

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