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Quasiliving Carbocationic Polymerization.
XIV. Synthesis of Poly(styrene-b-Isobutylene)

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ABSTRACT

The synthesis of poly(styrene-b-isobutylenes) by the sequential addition of styrene and isobutylene has been accomplished. First a stream of styrene was added to a cumyl chloride/$TiCl_4$ in n-hexane/methylene chloride charge at -50°C under quasiliving conditions. After the polystyrene block has reached a desirable sequence-length (molecular weight), gaseous isobutylene was continuously introduced to the quasiliving polystyrene carbocation until the polyisobutylene block also reached a desirable molecular weight. The $\overline{M}_n$ versus monomer input plot was uninterrupted and linear over both monomer introduction phases, indicating quasiliving conditions over the entire regime of block copolymer synthesis. The block copolymers have been characterized by selective solvent extraction and GPC, and their compositions determined by ^{1}H-NMR spectroscopy.

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INTRODUCTION

Quasiliving carbocationic polymerization is a unique technique for the synthesis of polymers and copolymers, both random and block, with "tailored" compositions, molecular weights, and narrow molecular weight distributions [1]. This technique has already been used for the sequential synthesis of various block copolymers of α-methylstyrene/isobutyl vinyl ether [2] and methyl vinyl ether/isobutyl vinyl ether [3].

In the course of our continued investigations in this field, we became interested in the synthesis of block copolymers of styrene and isobutylene. Both polystyrene and polyisobutylene are well-known inexpensive materials exhibiting desirable properties, and a combination of these properties in block copolymers promised to lead to interesting new materials.

The quasiliving homopolymerization of styrene and isobutylene has been developed in our laboratories [4, 5]. Thus it was decided to initiate a project whose aim was to combine these syntheses and to prepare diblock copolymers of styrene and isobutylene by the sequential quasiliving technique, i.e., to start the synthesis by the continuous quasiliving addition of one of the monomers and after reaching a desirable polymer sequence length, to switch to the second monomer and maintain quasiliving addition until a sufficient sequence length is attained with the second monomer as well.

EXPERIMENTAL

Materials

Styrene was washed with 10 wt% NaOH solution and with distilled water, dried over molecular sieves (4 Å) overnight, then distilled from CaH_2 under vacuum at 35°C. Isobutylene was dried by passing the gas over molecular sieves and BaO. n-Hexane and methylene chloride were purified by standard methods used in our laboratories [1, 6]. Cumyl chloride (2-chloro-2-phenyl-propane) was synthesized from α-methylstyrene by passing HCl gas through a cooled α-methylstyrene/CH_2Cl_2 mixture followed by repeated freeze-drying. $TiCl_4$ was distilled from P_2O_5 under moisture-free nitrogen.

Procedures

Polymerizations were carried out in a stainless stell enclosure under dry N_2 at -50°C in 250 cm^3 three-neck round-bottom flasks equipped with mechanical stirrer, Teflon plug for monomer addition, and outlet for sampling. A continuous stream of styrene/CH_2Cl_2 mixtures were introduced into charges of 100 mL solvent (60 mL n-hexane + 40 mL methylene chloride) containing the cumyl chloride/$TiCl_4$ initiating system by a precision solvent-metering pump (Beckman Model 110 A) and a glass capillary outlet. The flow rate was 2 g St/min. The initial concentration of cymyl chloride initiator was 1×10^{-2} M and that of $TiCl_4$ coinitiator was 2×10^{-2} M. During the styrene polymerization small aliquots (0.1 cm^3) were withdrawn with a syringe from the reaction mixture and were injected into capped vials containing excess methanol. After the necessary amount of styrene was introduced, the addition of gaseous isobutylene started immediately. The latter was introduced as a gas directly above the surface of the charge at a constant flow rate (0.35 g/min) from a reservoir whose temperature could be controlled. At the end of the second polymerization period, methanol was added to the charge. Conversions were determined gravimetrically and were 100% or very close to it in every run. Molecular weights of PSt samples were measured by gel permeation chromatography on a Waters Associates 6000 A High Pressure GPC equipped with five Microstyragel columns (10^5, 10^4, 10^3, 5×10^2 Å) and dual UV/RI detectors. Molecular weights were calculated from GPC traces using polystyrene calibration. Number-average molecular weights of block copolymers were determined by using a Mechrolab Model 503 High-Speed Membrane Osmometer (equipped with S S 08 membranes conditioned in toluene) at 37°C.

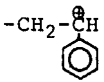
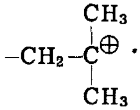
The crude products of block copolymer syntheses were precipitated by methanol, then washed and dried to constant weight. For selective solvent separation n-pentane and methyl ethyl ketone (MEK) were used. The soluble and insoluble fractions were separated by centrifugation.

The composition of crude products and that of the fractions were determined by using a Varian T-60 NMR spectrometer and CCl_4 solutions. The molar ratio of PSt and PIB sequences in the block copolymers were calculated according to

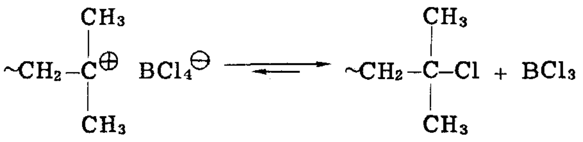
$$\frac{St}{IB} = \frac{8}{5R - 3}$$

where R is the ratio of integrated areas reflecting the aliphatic and aromatic protons.

RESULTS AND DISCUSSION

First we had to decide which monomer to use for the synthesis of the first block; styrene or isobutylene. In theory, either monomer could be used since the relative stabilities of the two carbocations involved, i.e.,  $-CH_2-\overset{\oplus}{C}H(C_6H_5)$ and  $-CH_2-\overset{\oplus}{C}(CH_3)_2$ · are similar, so that crossover for block formation appeared to be achievable from either species. Important practical considerations, however, led us to choose styrene as the first monomer and isobutylene as the second: First of all, our ultimate goal was the sequential synthesis of poly(styrene-b-isobutylene-b-styrene) glassy-rubbery-glassy thermoplastic elastomers, and thus the first block had to be the polystyrene sequence [7]. Second, the initiation of quasiliving polymerization of styrene is readily controllable and rather less sensitive to the presence of unavoidable traces of moisture impurities [4]; in contrast, initiation of quasiliving isobutylene polymerization is often plagued by run-away or "flash" reactions under the same conditions [5]. (The effect of moisture is further discussed below.)

The quasiliving polymerization of styrene has been studied by Puskás et al. [4] who showed that polystyrene sequences with $\overline{M}_n$ up to 30,000 g/mol can be readily obtained under readily achievable conditions (cumyl chloride/BCl_3 initiating system, CH_2Cl_2, -50°C). We have built upon this information and adapted these conditions with the important difference that we substituted $TiCl_4$ for BCl_3 as the coinitiator. Changing the coinitiator was necessary because according to previous research with isobutylene this monomer cannot be efficiently polymerized by the quasiliving technique BCl_3 [5]. Evidently the $BCl_4^{\ominus}$ counteranion is rather unstable and the equilibrium between the growing polyisobutyl carbocation and the chlorine-terminated polymer chain is strongly shifted toward the latter:



$$\sim CH_2-\overset{\oplus}{C}(CH_3)_2\ BCl_4^{\ominus} \rightleftharpoons \sim CH_2-C(CH_3)_2-Cl + BCl_3$$

Thus we started our investigations by demonstrating that quasiliving polymerization of styrene can also be achieved by the use of $TiCl_4$ coinitiator. Having done this, we proceeded by introducing gaseous isobutylene into stirred quasiliving polystyrene charges. The technique of condensing a steady stream of isobutylene gas onto the surface of stirred quasiliving polystyrene charges was adapted from Puskás et al. [5].

The considerable practical advantages of adding the isobutylene as the second monomer is that the sudden flash polymerization of isobutylene is avoided. Workers in this field are well familiar with the phenomenon of strongly exothermic flash polymerization of isobutylene when this monomer is added to strong Friedel-Crafts acids, e.g., $TiCl_4$, BF_3, and $AlCl_3$, in the presence of moisture impurities [8]. Subanalytical quantities of moisture (e.g., $<10^{-3}$ M) are present on the walls of the equipment used and most likely on the polar CH_2Cl_2 solvent used. Such flash initiation has also been observed in the quasiliving polymerization of isobutylene [5]. In the absence of moisture, isobutylene can be added to these acids without significant polymerization occurring (these matters are discussed in depth elsewhere, Ref. 8). For some reason the rate of polymerization of styrene is less sensitive toward moisture impurities, and flash initiation can be easily avoided [4].

Efforts were made to render the initiation of styrene polymerization controllable. Thus the concentration of the cumyl chloride initiator was 1×10^{-2} M, i.e., about at least one order of magnitude higher than that of suspected "H_2O" impurities. However, even if "H_2O" would have initiated styrene polymerization, the only difference would have been in the head-groups, i.e., the head-group of the polystyrene block initiated by "H_2O" would have been a CH_3 group, whereas that initiated by cumyl chloride would have been capped by a $C_6H_5C(CH_3)_2$ group.

When isobutylene was added to quasiliving polystyrene cations, there was no trace of a flash reaction: evidently the moisture impurities in the system were consumed during the styrene polymerization phase ("self-cleaning") and by the time the gaseous isobutylene introduction started, the system was virtually devoid of moisture. It is assumed that the hydrocarbon monomers were essentially dry. That the amount of moisture in the system must have been very low to start with, is indicated by the kinetics of the experiments (see later), by the fact that homopolystyrene was absent among the products, and by the uniformly monomodal GPC traces of all fractions obtained.

Figures 1, 2, and 3 show $\overline{M}_n$ versus monomer input plots reflecting the results of three experiments. The horizontal axis is divided into two parts, indicating the grams of styrene added followed by the grams of isobutylene introduced. The $\overline{M}_n$'s were determined by GPC during the quasiliving polystyrene growth phase. After the introduction of isobutylene has started, block copolymer starts to form and GPC cannot be used for $\overline{M}_n$ determination. Thus the last $\overline{M}_n$ was determined by osmometry. The fact that the $\overline{M}_n$ versus monomer input plot connecting the data obtained during the first phase of the experiment (i.e., quasiliving homopolymerization of styrene) can be smoothly extrapolated by a straight line to the last $\overline{M}_n$ obtained at the cessation of isobutylene introduction, indicates quasiliving kinetics throughout the entire experiment. (Attempts were made to obtain samples for osmometry during the second phase of the experiments; however, faced with

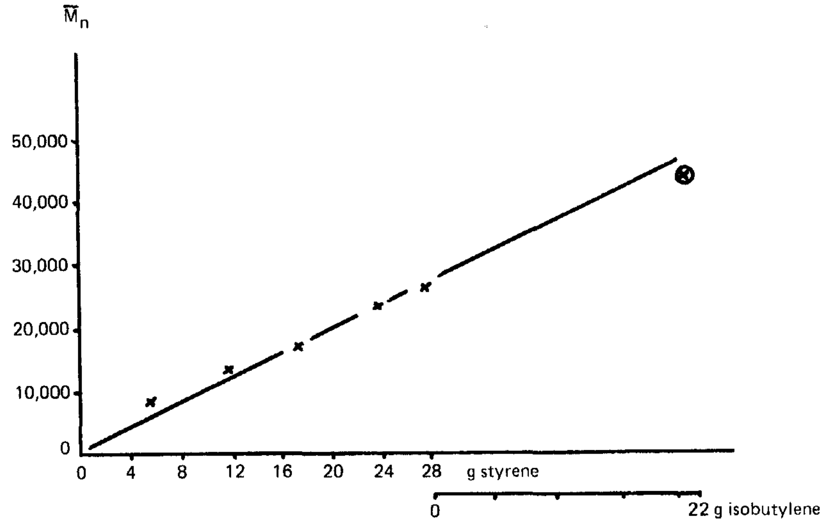


FIG. 1. Sequential synthesis of poly(styrene-b-isobutylene) by the quasiliving technique. (Initial charge: [CC] = 1×10^{-2} $\underline{M}$, [$TiCl_4$] = 2×10^{-2} $\underline{M}$ in 60/40 v/v n-C_6H_{14}/CH_2Cl_2, 100 mL, -50°C. Input rates: styrene = 2 mL/min, then isobutylene = 0.5 mL/min. (×) $\overline{M}_n$'s by GPC, ⊗ = $\overline{M}_n$ by osmometry.)

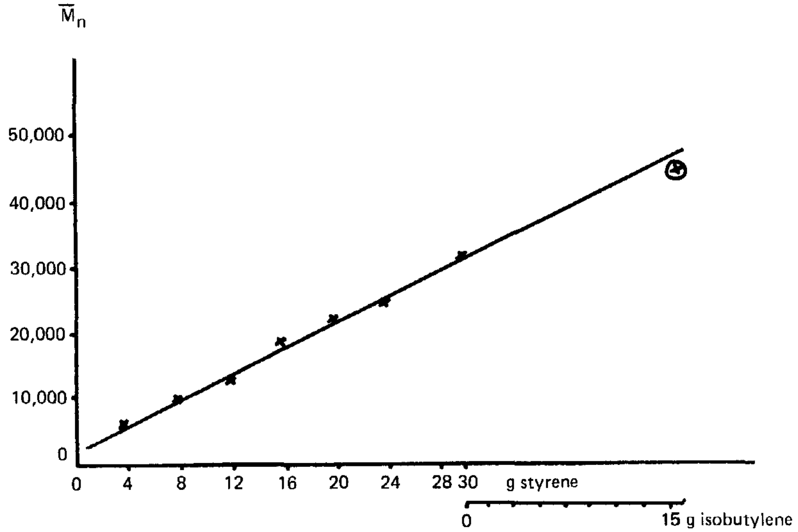


FIG. 2. See legend to Fig. 1.

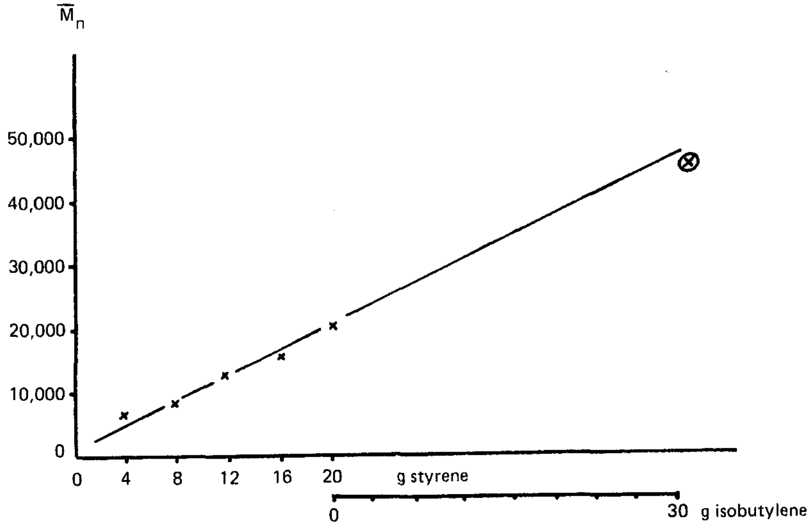
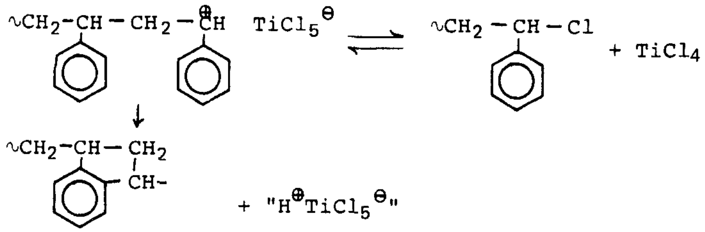


FIG. 3. See legend to Fig. 1.

the necessity of withdrawing relatively large quantities of aliquots, i.e., samples containing ~0.5 g solids, we chose to concentrate on obtaining larger final quantities for further characterization studies.)

After the polystyrene growth phase the addition of isobutylene should be started without delay. In the absence of olefin the quasiliving equilibrium may yield undesirable indanyl structures:



Thus in several experiments when there was a lag in the addition of the isobutylene, homopolymers have formed. Indeed, it is advisable to start the isobutylene addition before the complete disappearance of styrene, i.e., to have a brief overlap period. This overlap probably gives rise to a random or tapered styrene-isobutylene copolymer at the PSt/PIB junction; however, we have ignored this minor perturbation. ^{1}H-NMR spectroscopy did not show St-IB dyads in any of our products.

TABLE 1. Composition of Poly(styrene-b-isobutylene) Block Copolymers Synthesized by QL Technique

Styrene added (g)	Isobutylene added (g)	$\frac{\text{Moles of styrene added}}{\text{Moles of isobutylene added}}$	$\overline{M}_n$ of PSt-block[a]	$\overline{M}_n$ of diblock[d]	$R^{b,c}$	$\frac{\text{Number of St units}^c}{\text{Number of IB units}}$
19.6	40.0	0.46	18,600	47,300	5.60	0.32
28.0	21.7	0.69	28,800	45,900	2.95	0.68
13.3	9.8	0.72		32,400	2.92	0.69
28.7	18.9	0.81		43,300	2.58	0.81
28.0	15.5	0.97		42,500	2.27	0.96
30.0	15.7	1.03	29,700	45,200	2.12	1.05
15.3	7.4	1.12		23,600	2.00	1.14
22.0	10.3	1.27		37,900	1.86	1.27

[a] By GPC.

[b] $R = \frac{\text{Integrated area of aliphatic protons}}{\text{Integrated area of aromatic protons}}$

[c] By ^{1}H-NMR spectroscopy.

[d] By osmometry.

Composition and molecular weight data are shown in Table 1. In particular, Fig. 1 reflects the results of an experiment where the objective was to produce a diblock copolymer containing about equal amounts of polystyrene and polyisobutylene. The sequential feeding of 28 g styrene followed by 22 g isobutylene yielded a diblock of $\overline{M}_n$ = 45,900 comprising a polystyrene block of $\overline{M}_n$ = 25,800 and a polyisobutylene block of $\overline{M}_n$ = 20,100. Figure 2 reflects the data of an experiment aiming at the formation of a diblock with a long polystyrene and short polyisobutylene sequence, $\overline{M}_n$ total = 45,200, $\overline{M}_{n,PSt}$ = 29,700, $\overline{M}_{n,PIB}$ = 15,500. Conversely, Fig. 3 shows the data consistent with the formation of a relatively short polystyrene connected to a longer polyisobutylene block, $\overline{M}_n$ total = 47,300, $\overline{M}_{n,PSt}$ = 18,600, $\overline{M}_{n,PIB}$ = 28,700. Figure 4 summarizes the characterization data of a representative experiment (final product of Experiment 1, see Fig. 1). As detailed in the Experimental Section, the product of a sequential block copolymerization (crude product) was first extracted with n-pentane to remove the PIB or PIB-rich block copolymer, and the n-pentane-insoluble fraction was further extracted with methyl ethyl ketone (MEK)

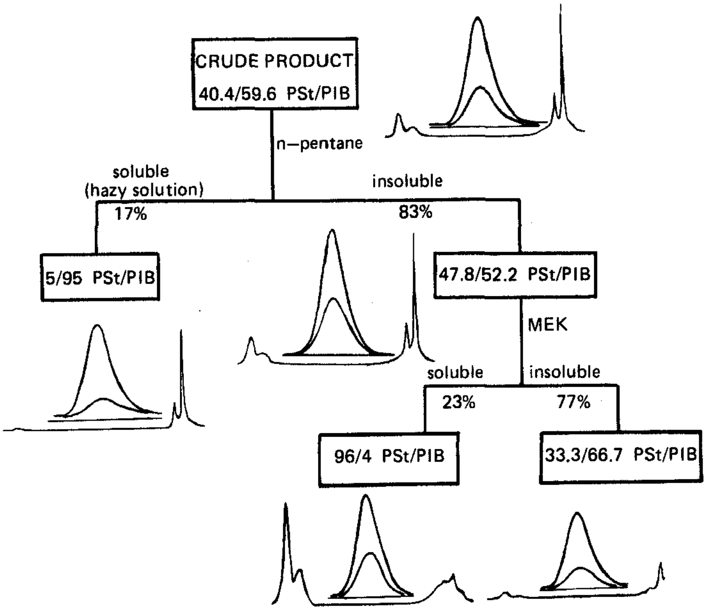


FIG. 4. Scheme of fractionation and characterization of fractions by GPC and ^{1}H-NMR spectroscopy (integrating traces not shown).

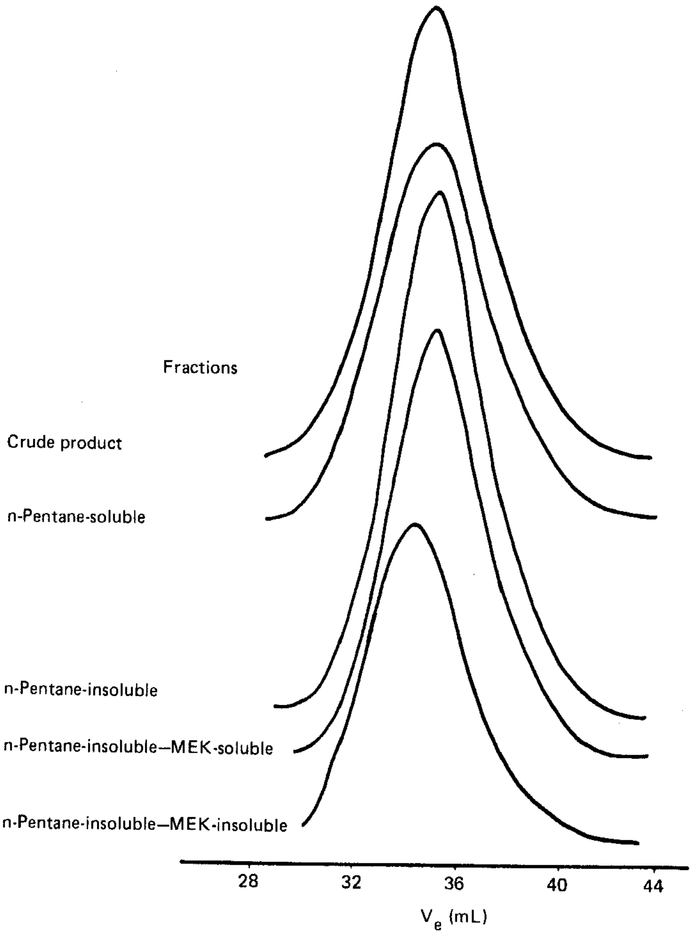


FIG. 5. GPC traces of the five products shown in Fig. 4.

to remove the PSt or PSt-rich block copolymer. The n-pentane-MEK-insoluble fraction is considered pure poly(styrene-b-isobutylene). In none of the experiments did we find PSt or PIB homopolymers, and every fraction contained both components. This is strong indication for block copolymerization with 100% blocking efficiency. The fractions, however, were not compositionally homogeneous. For example, according to the results summarized in Fig. 4, the composition of the n-pentane-soluble fraction was 5/95 PSt/PIB, and that of the n-pentane-insoluble MEK-insoluble block copolymer fraction 33.3/66.7 PSt/PIB was not much different from that of the "crude product" with 40.4/59.6 PSt/PIB.

Figure 5 is a summary and comparison of the GPC traces of the various fractions. Interestingly, there is very little difference in the position of the traces suggesting that the hydrodynamic volumes of the various block copolymer fractions are very similar. Furthermore, none of the fractions show strong evidence for bi- or multimodality. These observations can be rationalized by assuming that the blocking efficiency of isobutylene from PSt chains, be these in the form of PSt-Cl or PSt , is independent of the PSt chain length, and that the molecular weight distribution of the PSt sequence does not affect that of the attached PIB sequence.

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