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# Polyisobutylene-Containing Block Copolymers by Sequential Monomer Addition. 5. Synthesis, Characterization, and Select Properties of Poly(*p*-*tert*-butylstyrene-*b*-isobutylene-*b*-*p*-*tert*-butylstyrene)[†]

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ABSTRACT: Novel triblock copolymers poly(*p*-*tert*-butylstyrene-*b*-isobutylene-*b*-*p*-*tert*-butylstyrene) (P*pt*-BuSt–PIB–P*pt*BuSt) have been synthesized by the addition of *p*-*tert*-butylstyrene (*pt*BuSt) to biliving polyisobutylene carbocations ($^+$PIB$^+$). Triblocks containing PIB midblocks in the range of 50 000–70 000 ($\bar{M}_w/\bar{M}_n$ = 1.13–1.27) and 27–44 wt % P*pt*BuSt outer blocks were prepared. The molecular weights of the respective blocks (i.e., overall composition of triblocks) were controlled by living carbocationic polymerization techniques. The products were characterized by fractional precipitation, GPC, DSC, $^1$H NMR spectroscopy, and osmometry, and their select physical properties were investigated by Instron testing and penetrometry. The triblocks exhibited interesting thermoplastic elastomer (TPE) properties.

## Introduction

We have recently developed convenient methods for the synthesis of a series of novel triblock copolymers[1] consisting of a soft PIB midsegment flanked by two hard outer segments, such as polystyrene,[2] poly(*p*-chlorostyrene),[3] polyindene,[4] cyclized *trans*-1,4-polyisoprene,[5] and poly(methyl methacrylate).[6] All these products were found to exhibit interesting TPE properties. In the course of these investigations we have recently prepared the new triblock P*pt*BuSt–PIB–P*pt*BuSt. Incentive for this work arose because of the relatively high $T_g$ (126–131 °C) of P*pt*BuSt,[7] the hard segment of this new TPE. This paper concerns the synthesis by carbocationic sequential monomer addition of this triblock, its characterization, and an investigation of some of its physical properties.

## Experimental Section

1. **Materials.** The synthesis and purification of 2-chloro-2,4,4-trimethylpentane (TMPCl), 1,4-bis(2-methoxy-2-propyl)benzene (or *p*-dicumyl methyl ether, DiCumOMe), and the sources and purification of $CH_3Cl$, isobutylene (IB), and $TiCl_4$ have been described.[8-11] Methylcyclohexane (MeCHx; Lancaster Synthesis) was purified by chromatography over F-20 alumina (Fisher) and distilled over $CaH_2$ in vacuum and chromatographed over alumina (neutral; Brockman activity-1, Fisher) in a drybox under nitrogen gas. 2,6-Di-*tert*-butylpyridine (D*t*BP; Aldrich), dimethylacetamide (DMA; Aldrich), hexamethylphosphoramide (HMPA; Aldrich), and deuterated chloroform ($CDCl_3$; Aldrich) were used as received. Methanol, benzene, toluene (Fisher), and *n*-pentane (Kodak) solvents were used without additional purification.

2. **Polymerization.** Polymerizations were carried out in a stainless steel drybox under a dry-nitrogen atmosphere in large (75-mL) test tubes or in 500-mL round-bottomed flasks equipped with a mechanical stirrer using MeCl/MeCHx (40/60, v/v) solvent mixtures at −80 °C. The moisture level in the charges was estimated by control experiments carried out in the absence of purposely added initiator. Details of the AMI (*a*ll *m*onomer *i*n) and IMA (*i*ncremental *m*onomer *a*ddition) techniques have been described.[10]

2.1. **Homopolymerization.** Model blocking experiments, i.e., *pt*BuSt homopolymerizations initiated by the TMPCl/$TiCl_4$ system, were carried out by adding $TiCl_4$ to premixed TMPCl/*pt*BuSt/solvent charges in the absence or presence of D*t*BP and/or DMA. Unless specified otherwise, the total volume of the charge, $V_0$, was 25 mL, and a fraction of the nonpolar component of the solvent system (McCHx) was replaced by the equivalent volume of *pt*BuSt. Polymerizations were usually run for 6 min, unless otherwise noted, and stopped by the addition of prechilled methanol.

The synthesis of biliving polyisobutylene, $^+$PIB$^+$, by the bifunctional DiCumOMe/$TiCl_4$ initiating system has been described.[9] The PIB center blocks of the triblocks were synthesized under essentially identical conditions.

2.2. **Block Copolymerization.** A 500-mL three-neck round-bottomed flask equipped with a mechanical stirrer was charged with a MeCl/MeCHx (40/60, v/v) mixture followed by the addition of the initiator (40/60, v/v) mixture followed by the addition of the initiator (I = DiCumOMe), then D*t*BP and DMA, if specified, and thermostated at −80 °C. The calculated quantity of IB was added under constant stirring, and finally the coinitiator $TiCl_4$ (I/$TiCl_4$ = 1/16) was introduced to start the polymerization. At 15-min intervals fresh aliquots of IB were added to the stirred light yellow charges. Samples were withdrawn for molecular weight and conversion analyses by using a cooled pipet. Details of this so-called IMA technique have been described.[10] Prior to the blocking step, additional $TiCl_4$ was added to augment the I/$TiCl_4$ to 1/20. Blocking was started by the introduction of a prechilled dilute *pt*BuSt solution (diluted with the solvent mixture to prevent freezing) to the charge. The orange charges were stirred at −80 °C for specific times, and the reactions were quenched with prechilled methanol. The polymers were precipitated by pouring the charges into a large excess of methanol; the products were dissolved in THF, slowly reprecipitated into methanol, and dried in a vacuum oven at room temperature. Yields were determined gravimetrically.

3. **Characterization.** Molecular weights and molecular weight distributions, that is, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values for PIB, and $\bar{A}_n$ and $\bar{A}_w/\bar{A}_n$ (apparent molecular weights by GPC using polystyrene standards) values for triblocks were obtained by a Waters high-pressure GPC assembly (Model 6000A pump, $\mu$-Styragel columns of $10^5$, $10^4$, $10^3$, 500, and 100 Å; UV and RI detectors). The flow rate of THF was 1 mL/min. Calibration curves were obtained with narrow molecular weight polyisobutylene and polystyrene standards. Absolute molecular weights of the block polymers were determined by membrane osmometry using a HP503 high-speed instrument and toluene solvent at 37 °C. $^1$H NMR spectra were taken on a Varian Gemini 200-MHz spectrometer using $CDCl_3$ as solvent. Block polymer compositions were calculated by comparing the relative magnitudes of resonance intensities corresponding to the aromatic and aliphatic protons. The weight percent of P*pt*BuSt was

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[†] Part XLVII of Living Carbocationic Polymerization. Part XLVI: Pernecker, T.; Kennedy, J. P. *Polym. Bull.* **1991**, *26* (3), 305.

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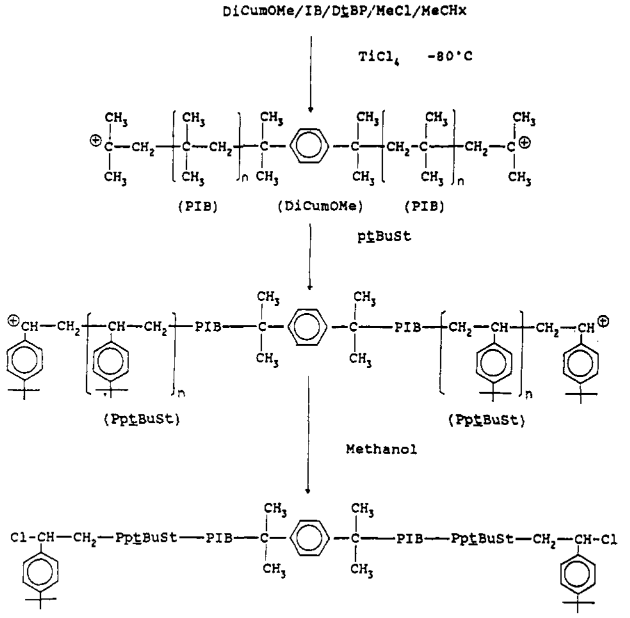
**Scheme I**
**Strategy for Triblock Synthesis**



calculated by the equation

$$\mathrm{Ppt}\text{BuSt (wt \%)} = \frac{160.3 \times 2A}{160.3 \times 2A + 56.1(B - 3A)} \times 100$$

where $A$ and $B$ are, respectively, the area of aromatic and aliphatic protons in the spectrum, 160.3 = molecular weight of p*t*BuSt, and 56.1 = molecular weight of isobutylene.

Optically clear bubble-free homogeneous films were cast from THF solutions and vacuum dried at 65 °C for 7–10 days, and microdumbells were cut for physical property analyses by an Instron tester. The crosshead rate was 5 cm/min. Shore A hardness was measured by a Shore Durometer, according to ASTM D2204. DSC measurements were performed with a Du Pont 9900 instrument, at a heating rate of 10 °C/min under $N_2$.

4. **Fractional Precipitation.** Fractional precipitation[12,13] was carried out by the dropwise addition of methanol as the nonsolvent to a solution of 5.00 g of block polymer in 900 mL of benzene ($d$ = 0.874) plus 450 mL of *n*-pentane ($d$ = 0.626) in a separatory funnel. *n*-Pentane was used to reduce the density of the system and thus to prevent the ascending of the precipitate during the precipitation. Rapid stirring and slow precipitant addition prevented local precipitation. At the onset of precipitation, i.e., after the turbidity remained permanent, stirring was discontinued and the system stored until precipitation was complete (at least 24 h). The final fraction was obtained by evaporating the remaining solvents. The precipitated fractions were separated and collected and dried to constant weight in vacuum; their molecular weights and molecular weight distributions were analyzed by GPC using PIB calibration, and compositions were determined by $^1$H NMR spectroscopy.

## Results and Discussion

1. **Overall Strategy and Pp*t*BuSt Homopolymerization.** Scheme I summarizes the strategy used for the synthesis of Pp*t*BuSt-PIB-Pp*t*BuSt. To guide us in the synthesis and to aid in the definition of conditions required for the individual steps, model experiments were carried out to demonstrate (1) the attainment of living carbocationic homopolymerization of Pp*t*BuSt (a fact that has not yet been described in the scientific literature) and (2) the crossover from the first living polyisobutylene segment to the second living p*t*BuSt segment; i.e., $\mathrm{PIB}^+ + \mathrm{p}t\mathrm{BuSt} \rightarrow \mathrm{PIB{-}Pp}t\mathrm{BuSt}^+$. Efforts were made to reach these objectives with a single series of model experiments.

Thus, model studies were carried out with the TMPCl/$TiCl_4$/IB system. The TMPCl/$TiCl_4$ combination was viewed to mimic the terminal unit of a living $\mathrm{PIB}^+\mathrm{TiCl_5}^-$ chain, and initiation of p*t*BuSt polymerization by the $\mathrm{TMP}^+\mathrm{TiCl_5}^-$ system was to simulate the critical crossover from the first living block ($\mathrm{PIB}^+$) to the second living block (i.e., $\mathrm{PIB{-}Pp}t\mathrm{BuSt}^+$).

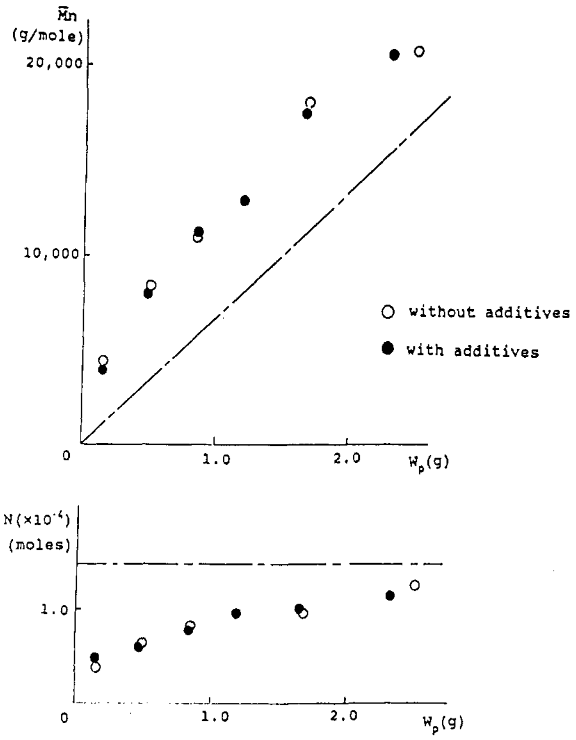


**Figure 1.** p*t*BuSt homopolymerization. TMPCl (I) = 1.5 × $10^{-4}$ mol, $TiCl_4$ = 1.8 × $10^{-3}$ mol (=12 × I), MeCl/MeCHx (40/60), $V_0$ = 25 mL, 6 min, −80 °C. AMI technique (in moles × $10^{-3}$ of p*t*uBuSt): 1.1, 3.3, 5.6, 7.8, 11.1, and 16.7. Additives: DMA = 1.5 × $10^{-4}$ mol, D*t*BP = 1.0 × $10^{-4}$ mol.

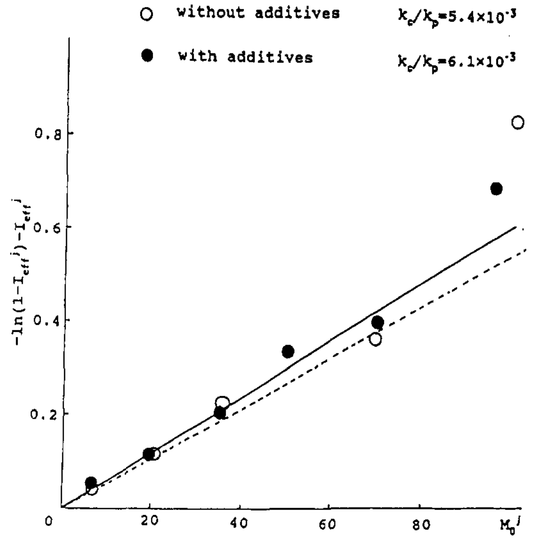


**Figure 2.** Analysis of slow initiation of p*t*BuSt polymerization (conditions in Figure 1).

Figure 1 shows the results of a series of experiments carried out under the conditions detailed in the legend. According to the $\bar{M}_n$ versus $W_p$ (grams of Pp*t*BuSt formed) and corresponding $N$ (number of moles of Pp*t*BuSt obtained (i.e., $(W_p/\bar{M}_n)/\mathrm{I})$) versus $W_p$ plots, the experimental $\bar{M}_n$'s are higher and the $N$'s lower than the theoretical value, calculated by assuming 100% initiation efficiency ($I_{eff}$). The shapes of the curves are characteristic of systems in which initiation is slow relative to propagation.[14]

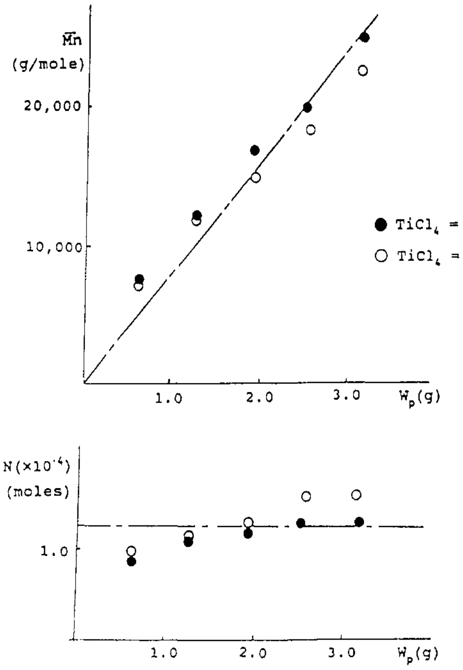


**Figure 3.** p*t*BuSt homopolymerization. TMPCl (I) = 1.25 × $10^{-4}$ mol, D*t*BP = 1.25 × $10^{-4}$ mol, MeCl/MeCHx (40/60), $V_0$ = 25 mL, 6 min, −80 °C. AMI technique (in moles × $10^{-3}$ of p*t*-BuSt): 3.9, 7.8, 11.7, 15.5, and 19.4.

**Table I**
**Effect of $TiCl_4$ Concentration on PptBuSt Homopolymerization**[a]

| $TiCl_4$, $10^{-3}$ mol | *w*, g | conv, % | $\overline{M}_n$(GPC) | $N \times 10^5$ |
|---|---|---|---|---|
| 1.8 | 0.471 | 66.2 | 15 093 | 3.1 |
| 2.4 | 0.512 | 72.0 | 15 438 | 3.3 |
| 3.0 | 0.642 | 90.3 | 21 319 | 3.0 |
| 4.5 | 0.699 | 98.3 | 19 523 | 3.6 |

[a] p*t*BuSt = 0.8 mL (0.711 g), vol. = 25 mL (MeCl/MeCHx = 40/60), 6 min, −80 °C.

A series of companion experiments were carried out in which an electron donor (DMA) and the proton trap (D*t*BP) were present in the charge. The beneficial effect of these additives in mediating living polymerizations has been discussed in detail.[2,11,15] However, as shown by the data in Figure 1, these ingredients did not seem to affect the overall results. Similar results were also obtained by use of the very strong electron donor HMPA or by tripling the concentration of DMA (i.e., DMA/I = 3).

In line with the analysis of relatively slowly initiating living carbocationic polymerizations,[14] the data in Figure 1 have been replotted in Figure 2 according to $-\ln(1 - I_{\text{eff}}^j) - I_{\text{eff}}^j$ versus $M_0^j/I_0$, where $I_{\text{eff}}^j$ and $M_0^j$ are the initiation efficiency of the *j*th reaction and initial monomer concentration of the *j*th reaction, respectively. As indicated by the rectilinear plot obtained, the polymerization of p*t*-BuSt induced by the TMPCl/$TiCl_4$ system, in the absence or presence of DMA and D*t*BP, is living and proceeds by slow initiation relative to propagation. The slopes of the plots in Figure 2 yield $k_c/k_p$ (rate constants of cationation and propagation) = 5.4 × $10^{-3}$ and 6.2 × $10^{-3}$ for the polymerization in the absence and presence of additives, respectively. These values are within experimental variation. Evidently the TMPCl/$TiCl_4$/p*t*BuSt system is a relatively slowly initiating living polymerization whose $k_c/k_p$ ratio is unaffected by the presence of DMA or D*t*BP. Slow cationation of p*t*BuSt is probably due to the relatively low reactivity of the TMPCl/$TiCl_4$ combination.

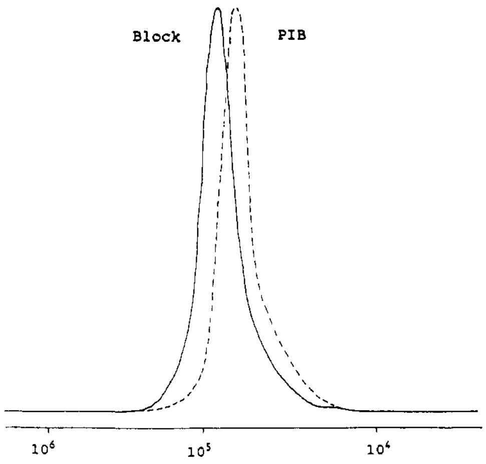


**Figure 4.** GPC(RI) traces of the PIB precursor and the Pp*t*BuSt–PIB–Pp*t*BuSt triblock polymer (sample B8 in Table II).

An effort has also been made to examine the living nature of the TMPCl/$TiCl_4$/p*t*BuSt system by the IMA method (TMPCl = 2.4 × $10^{-4}$ mol, $TiCl_4$ = 3.0 × $10^{-3}$ mol, D*t*BP = DMA = 2.5 × $10^{-4}$ mol, 25 mL of MeCl/MeCHx = 40/60, p*t*BuSt = 00.3 mL × 6, 6 min between aliquots, −80 °C); however, for some unknown reason the product exhibited a bimodal molecular weight distribution after the second monomer addition. Since the conventional AMI technique is quite satisfactory for designed block copolymer synthesis, which was the overall objective of these studies, additional efforts have not been made to prove livingness with the more laborious IMA technique.

To further prove livingness and to accelerate initiation relative to propagation, experiments were carried out by

**Table II**
**Synthesis and Select Properties of PptBuSt–PIB–PptBuSt Triblocks**

| | PIB | | | triblock[b] | | | | properties | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $\overline{M}_n$ | | | | | | | |
| sample | $M_n$ | $M_w/M_n$ | $I_{\text{eff}}$, % | osmometry | NMR | $\overline{A}_w/\overline{A}_n$ | pp*t*BuSt, wt % | tensile strength, MPa | modulus at 300%, MPa | elongation, % | hardness, Shore A |
| B1 | 46 900 | 1.23 | 117 | 92 300 | 89 000 | 1.36 | 42 | 13 | 11.2 | 370 | 77 |
| B2 | 50 900 | 1.25 | 111 | 91 000 | 88 000 | 1.39 | 42 | 9 | 6.8 | 460 | 73 |
| B3 | 49 400 | 1.21 | 111 | 72 100 | 73 000 | 1.32 | 30 | 9 | 3.7 | 590 | 69 |
| B4 | 65 500 | 1.22 | 97 | 97 700 | 108 000 | 1.40 | 40 | 16 | 5.0 | 550 | 76 |
| B5 | 67 300 | 1.27 | 90 | | 119 000 | 1.52 | 44 | 16 | 8.7 | 470 | 83 |
| B6 | 76 600 | 1.13 | 83 | | 102 000 | 1.25 | 27 | 11 | 1.6 | 720 | 48 |
| B7 | 74 800 | 1.17 | 83 | | 100 000 | 1.43 | 34 | 13 | 3.8 | 590 | 68 |

[a] IB phase: [DiCumOMe] = 4.0 × $10^{-4}$ mol, [D*t*BP] = 8.8 × $10^{-5}$ mol, [$TiCl_4$] = 6.4 × $10^{-3}$ mol, 4 × (7 mL of IB/15 min), $V_0$ = 250 mL of MeCl/MeCHx (40/60, v/v), 1 h, −80 °C. p*t*BuSt blocking phase: [$TiCl_4$] = 1.6 × $10^{-3}$ mol, 20 of mL p*t*BuSt in 20 mL of MeCl/MeCHx, 1 h, −80 °C. [b] Both monomers (IB and p*t*BuSt) were completely (~100%) converted. B1: single IB addition (22.2 g). B3: 17.5 mL of ptBuSt in 17.5 mL of MeCl/MeCHx. B4–B7: [D*t*BP] = 4.0 × $10^{-4}$ mol. B5: [DMA] = 2.0 × $10^{-4}$ mol, 22.5 mL of p*t*BuSt in 22.5 mL of MeCl/MeCHx; blocking time = 2 h. B6: 15 mL of p*t*BuSt in 15 mL of MeCl/MeCHx. B7: [DMA] = 1.3 × $10^{-4}$ mol. 17.5 mL of p*t*BuSt in 17.5 mL of MeCl/MeCHx; blocking time = 1.5 h.

**Table III**
**Fractional Precipitation of Pp*t*BuSt-PIB-Pp*t*BuSt**

| fraction | weight g | weight % | $\bar{A}_n$ (GPC) | $\bar{A}_w/\bar{A}_n$ | Pp*t*BuSt,[a] wt % |
|---|---|---|---|---|---|
| 0 | 5.00 | 100.0 | 80 200 | 1.35 | 41.5 |
| 1 | 0.53 | 10.6 | 88 500 | 1.28 | 15.5 |
| 2 | 0.19 | 3.8 | 89 300 | 1.27 | 25.2 |
| 3 | 1.10 | 22.0 | 89 700 | 1.26 | 39.8 |
| 4 | 1.79 | 35.8 | 90 000 | 1.24 | 40.7 |
| 5 | 0.88 | 17.6 | 89 900 | 1.27 | 41.1 |
| 6 | 0.21 | 4.2 | 88 700 | 1.29 | 42.7 |
| 7 | 0.18 | 3.6 | 77 100 | 1.34 | 49.3 |
| residue | 0.22 | 4.4 | 30 800 | 2.16 | 64.5 |

[a] Calculated from $^1$H NMR data.

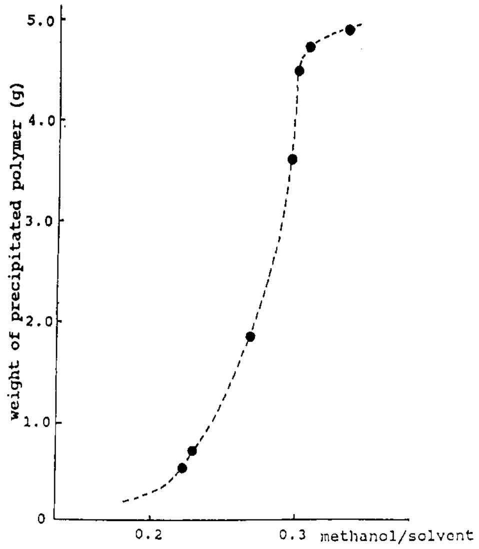


**Figure 5.** Fractional precipitation of Pp*t*BuSt-PIB-Pp*t*BuSt (sample B2 in Table II).

increasing the molar concentration of the coinitiator from $[I]/[TiCl_4] = 1/12$ to 1/20 and 1/30. Figure 3 shows the results. With $[I]/[TiCl_4] = 1/20$ the experimental data are very close to the theoretical $\bar{M}_n$ versus $W_p$ and $N$ versus $W_p$ lines. A close inspection of the data still shows relatively slow initiation; however, deviation from the theoretical line is much smaller than in the $[I]/[TiCl_4] = 1/12$ experiment (cf. Figure 1). In the $[I]/[TiCl_4] = 1/30$ experiment the first three samples at low $W_p$'s were practically identical to those of the $[I]/[TiCl_4] = 1/20$ set; however, the higher $W_p$ samples may indicate the onset of chain transfer to monomer. Due to the very high moisture sensitivity of $TiCl_4$ coinitiator, there is a possibility that the increase in $N$ with increasing $TiCl_4$ concentration in the above experiments is due to increased initiation by moisture. To investigate this possibility, a series of control experiments (absence of initiator) with various $TiCl_4$ concentrations were carried out. Results are shown in Table I. As indicated by the values of $N$, initiation by moisture is negligible in the homopolymerization of p*t*BuSt in the range examined.

**2. Block Polymerization.** Led by the results of model experiments described in the previous section, a series of blocking experiments were carried out by introducing p*t*BuSt to living $^+$PIB$^+$ charges (see Scheme I). Table II summarizes the conditions used and results obtained. In all instances blocking of p*t*BuSt was evidenced by the shift of the GPC(RI) trace toward higher molecular weights. Figure 4 shows a representative results: the GPC(RI) trace of the $^+$PIB$^+$ precursor (obtained by removing an aliquot from the charge just prior to the addition of p*t*BuSt) appears at lower molecular weights than that of the blocked product obtained 1 h after p*t*BuSt addition to the living $^+$PIB$^+$.

The molecular weights of the midsegments obtained in B1, B2, and B3 are lower than those obtained in the other experiments because of the relatively high initiation efficiencies. $I_{eff} > 100\%$ indicates side reactions, such as initiation by adventitious moisture and/or chain transfer to the monomer, which might produce a homopolymer and/or diblock. To suppress these side reactions, increased amounts of D*t*BP (equal to the initiator input) were used; under those conditions, $I_{eff}$ decreased to essentially the theoretical level (see samples B4–B7). In experiments B5 and B7 DMA was added (DMA/I = 1/2 and 1/3); however, this electron donor did not show a discernible effect. Similar to earlier observation with

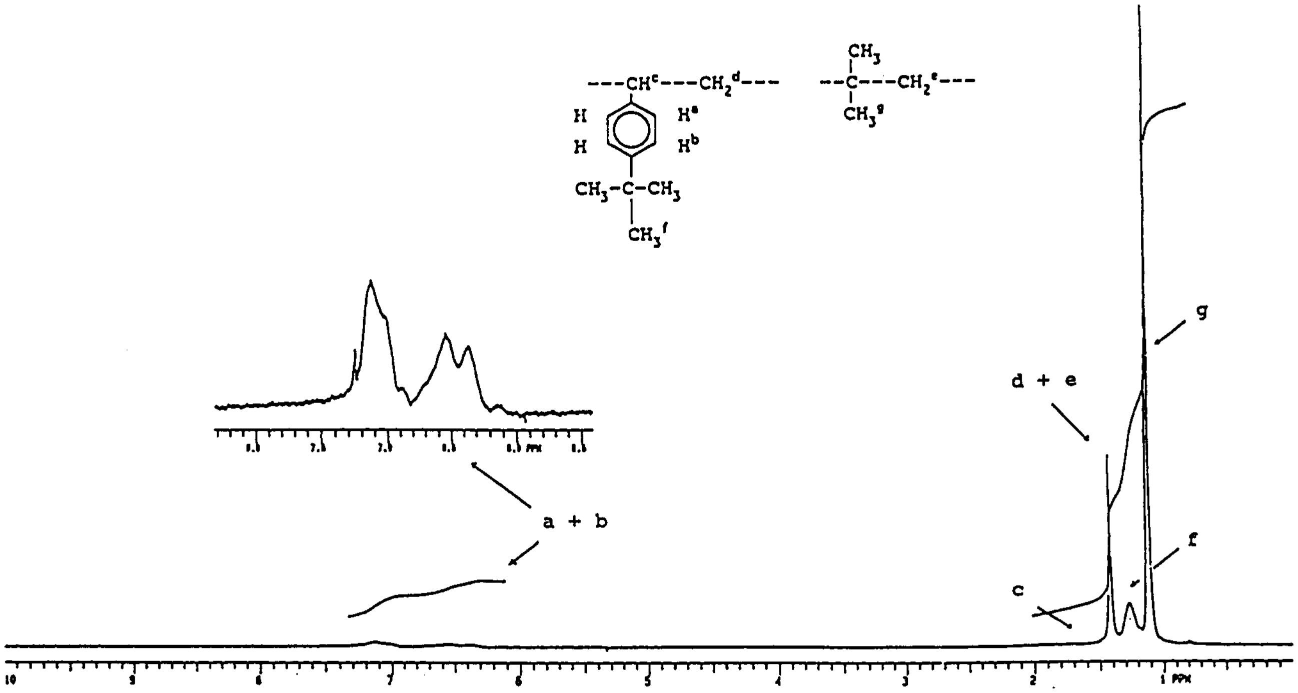


**Figure 6.** $^1$H NMR spectrum of Pp*t*BuSt-PIB-Pp*t*BuSt (sample B3 in Table II).

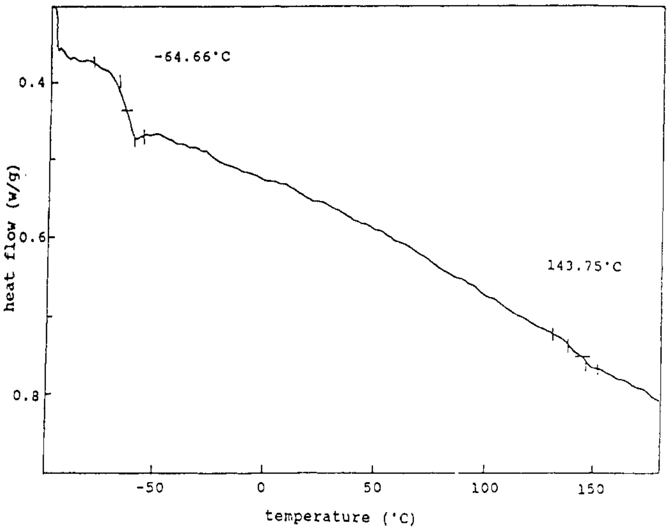


**Figure 7.** DSC scan of P*pt*BuSt-PIB-P*pt*BuSt (sample B1 in Table II).

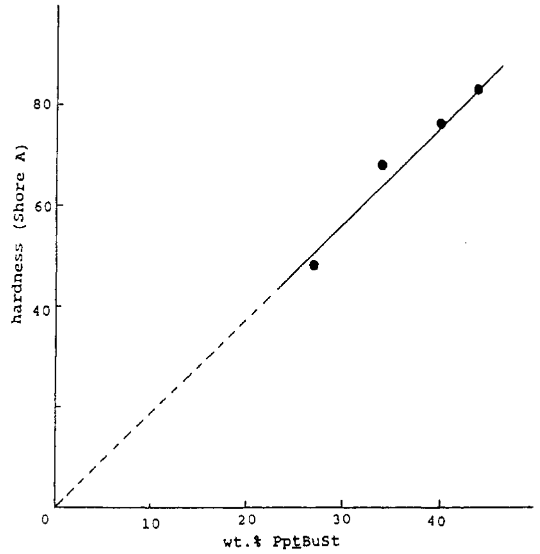


**Figure 8.** Effect of P*pt*BuSt content in P*pt*BuSt-PIB-P*pt*BuSt triblocks on hardness.

styrene as the second monomer,[2] the supplemental addition of $TiCl_4$ to the living charge just before *pt*BuSt introduction, i.e., increasing $I/TiCl_4$ to 1/20, was found to be beneficial: When a second aliquot of $TiCl_4$ was not added, *pt*BuSt conversions tended to be lower than complete (~85%).

**3. Homogeneity Analysis by Fractional Precipitation.** Efforts were made to analyze the homogeneity of the products, particularly in regard to PIB homopolymer and PIB-P*pt*BuSt diblock contents. Since the solubility characteristics of PIB and P*pt*BuSt are similar (both polymers are soluble in aliphatic hydrocarbons, e.g., *n*-pentane, *n*-hexane), selective solvent separation could not be effected, and fractional precipitation was carried out. Thus, the crude product was dissolved in a benzene/*n*-pentane mixture, and fractions were collected by the addition of increasing amounts of methanol precipitant (see the Experimental Section). The results of an experiment are summarized in Table III and Figure 5. The original solution was optically clear and homogeneous, the bulk of the product precipitated between fractions 3 and 6 (79.6%), and the composition of the fractions remained essentially unchanged with 42.3 ± 1.5% P*pt*BuSt. Evidently fractionation occurred by composition and not by molecular weights. Even the first and the last fractions contained both polymers. The molecular weight distributions of the fractions also remained unchanged (except for the last fraction) and were somewhat narrower than those of the unfractionated material. According to these fractionation data together with GPC information (see Figure 4), significant quantities of diblocks and/or homopolymer cannot be present.

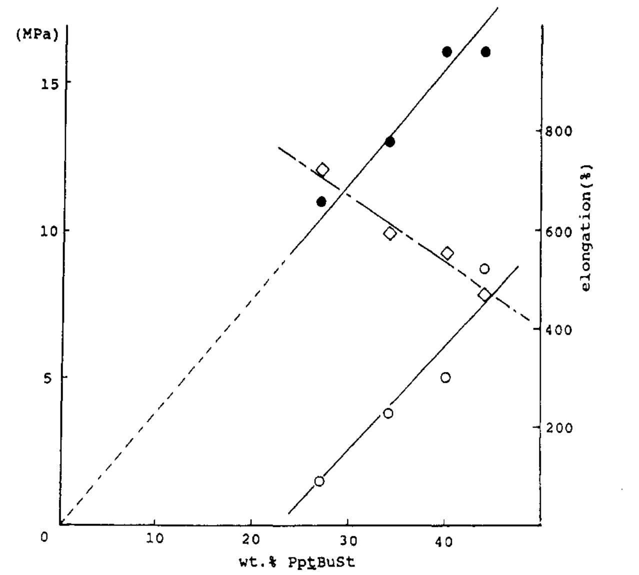


**Figure 9.** Mechanical properties (tensile strength, 300% modulus, elongation) versus P*pt*BuSt content in triblocks: (●) tensile strength, (○) modulus at 300%, (◇) elongation.

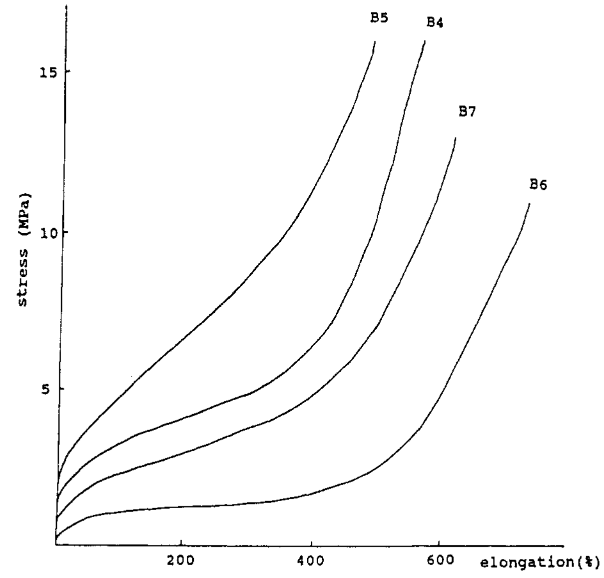


**Figure 10.** Stress–strain traces of P*pt*BuSt-PIB-P*pt*BuSt.

**4. Characterization and Select Properties.** The overall composition of P*pt*BuSt-PIB-P*pt*BuSt triblocks was investigated by $^1$H NMR spectroscopy. Figure 6 shows the spectrum of a representative unfractionated sample (B3 in Table II) together with resonance assignments. According to this evidence, the proudct contains elements of both constituents, P*pt*BuSt and PIB.

The micromorphology of P*pt*BuSt-PIB-P*pt*BuSt has been investigated by DSC. Figure 7 shows a DSC trace of a representative sample (B1 of Table II). The two $T_g$'s, at ~ −65 and ~144 °C, characteristic of PIB and P*pt*BuSt domains, respectively, indicate the existence of two largely immiscible phases. The average sizes of these domain diameters must be smaller than ~4000 Å (i.e., the lowest wavelength of visible light) and the dispersions intimate because cast sheets of these triblocks were optically clear.

Select physical properties of the triblocks have been investigated by penetrometry (hardness) and Instron testing (tensile, modulus, elongation). The data obtained are given in Table II and Figures 8–10. Figure 8 shows the effect of Pp*t*BuSt content on Shore A values of samples B4–B7, i.e., of samples with $I_{\mathrm{eff}}$ = 83–97% ($I_{\mathrm{eff}} > 100\%$ suggests homopolymer and/or diblock contamination). Evidently the hardness of the triblocks increases with increasing weight percent of Pp*t*BuSt. Not too surprisingly, the PIB segments in these blocks lead to desirably soft TPEs. Comparable poly(styrene-*b*-butadiene-*b*-styrene) and similar triblocks are much harder materials.

The Pp*t*BuSt content also strongly affects the other mechanical properties. Figures 9 and 10 summarize the data obtained with the triblocks, the synthesis of which gave close to theoretical $I_{\mathrm{eff}}$s (B4–B7 in Table II). As expected the tensile strengths and moduli increase whereas the elongations decrease with increasing weight percent of Pp*t*BuSt in the triblocks. Interestingly, linear back-extrapolation of tensile strength, and the hardness values (see Figure 8), versus % Pp*t*BuSt content relationship, reaches the origin. The shapes of the stress–strain traces shown in Figure 10 are typical of strong elastomers. The steeply rising strengths with elongation are most likely due to the crystallization of PIB midsegments.

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## References and Notes

(1) Kaszas, G.; Hager, W.; Kennedy, J. P. U.S. Patent 4,946,899, 1990.
(2) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Hager, W. G. *J. Polym. Sci.* **1991**, *A29*, 427.
(3) Kennedy, J. P.; Kurian, J. *J. Polym. Sci.* **1990**, *A28*, 3725.
(4) Kennedy, J. P.; Keszler, B.; Tsunogae, Y.; Midha, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 310.
(5) Kaszas, G.; Puskas, J.; Kennedy, J. P. *J. Appl. Polym. Sci.* **1990**, *39*, 119.
(6) Kennedy, J. P.; Price, J. L. *Mater. Sci. Eng.* **1991**, *64*, 40.
(7) Brandrup, J.; Immergut, E. H. *Polymer Handbook*; John Wiley & Sons: Chichester, U.K., 1989; Chapter 4, p 224.
(8) Kaszas, G.; Gyor, M.; Kennedy, J. P.; Tudos, F. *J. Macromol. Sci., Polym. Chem. Ed.* **1982–83**, *A18* (9), 1367.
(9) Kaszas, G.; Puskas, J.; Kennedy, J. P. *Polym. Bull.* **1987**, *18*, 123.
(10) Faust, R.; Kennedy, J. P. *J. Polym. Sci.* **1987**, *A25*, 1847.
(11) Kaszas, G.; Puskas, J.; Kennedy, J. P. *Makromol. Chem., Makromol. Symp.* **1988**, *13/14*, 473.
(12) Rabek, J. F. *Experimental Methods in Polymer Chemistry*; John Wiley & Sons: Chichester, U.K., 1980; Chapter 4 and references therein.
(13) Ceresa, R. J. *Block and Graft Copolymers*; Butterworths: London, 1962; Chapter 9.
(14) Zsuga, M.; Kennedy, J. P.; Kelen, T. *J. Macromol. Sci., Chem.* **1989**, *A26* (9), 1305.
(15) Zsuga, M.; Kennedy, J. P. *Polym. Bull.* **1989**, *21*, 5.

**Registry No.** Pp*t*BuSt–PIB (block copolymer), 130547-48-7.