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Synthesis and characterization of novel octa-arm star-block thermoplastic elastomers consisting of poly (*p*-chlorostyrene-*b*-isobutylene) arms radiating from a calix[8]arene core*

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Abstract

The synthesis and characterization of novel octa-arm star-blocks consisting of poly(*p*-chlorostyrene-*b*-isobutylene) (P*p*ClSt-*b*-PIB) arms radiating from a calix[8]arene (C8) core are described. The synthesis was accomplished by living isobutylene (IB) polymerization induced by a novel octafunctional calix[8]arene derived initiator **1**, followed by addition and living polymerization of *p*-chlorostyrene (*p*ClSt). This sequential block copolymerization method allowed for precise molecular weight control of both polymeric blocks and thus gave rise to star-block thermoplastic elastomers (TPE) with an outstanding combination of mechanical and thermal properties, i.e., high tensile strengths (22 - 27 MPa) and elongations (~500 %). Differential scanning calorimetry (DSC) indicated microphase separation into glassy P*p*ClSt (T_g = 129°C) and rubbery PIB (T_g = -66°C) domains, and transmission electron microscopy (TEM) indicated that the P*p*ClSt domains are dispersed in the PIB matrix.

Introduction

The synthesis and properties of linear PIB-*b*-P*p*ClSt-*b*-PIB triblocks and three-arm star-blocks with P*p*ClSt-*b*-PIB arms have been investigated earlier (1). The use of the octafunctional calix[8]arene derivative **1** as the initiator for the synthesis of various PIB-based stars has also been demonstrated (2-8). We have now extended these studies and used *p*ClSt to provide star-block TPEs with superior properties. Advantages offered by P*p*ClSt are high T_g (~129°C), flame resistance, adhesion to polar substrates due to the Cl substituent, good optical properties, etc. Also the *p*-Cl substituent eliminates intermolecular aromatic alkylation [a minor side reaction observed during the carbocationic polymerization of styrene (St)] which leads to branchy stars and undesirably high molecular weight products (5, 6).

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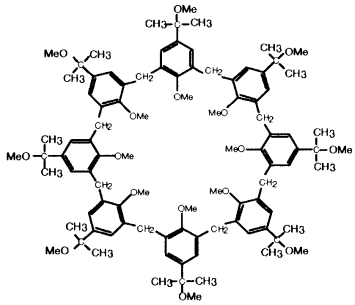
Here we report the first synthesis, characterization, and select mechanical properties of novel octa-arm star-block copolymers comprised of eight P*p*ClSt-*b*-PIB arms radiating from a C8 core. The synthesis strategy, shown in Scheme 1, involved the preparation of living octa-arm PIB-stars by initiator **1**, followed by blocking of *p*ClSt to the target star-block.



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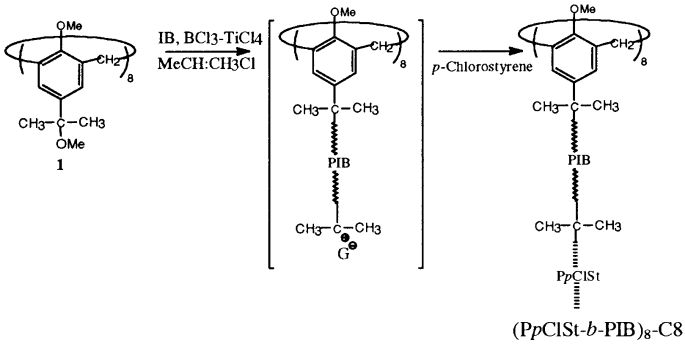

Experimental

A. Materials

The materials used together with the synthesis and characterization of initiator **1** have been described (2). Methylcyclohexane, MeCH, (Aldrich) was refluxed over night in presence of CaH_2 and distilled before use. *p*ClSt (Lancaster) was purified by passing the monomer through an inhibitor-removing column before use.

B. Polymerizations

Living octa-arm $PIB^{\oplus}$ stars with predetermined arm molecular weights were prepared by a two-stage procedure (2). A representative block-polymerization was carried out as follows: Initiator **1**, (0.0491 g, 3.19×10^{-5} mol) was dissolved in CH_3Cl (10 mL), then, in sequence, IB (1 mL), dimethylacetamide, DMA (0.04 mL, 5.0×10^{-4} mol), and di-*tert*-butylpyridine, DtBP (0.07 mL, 3.0×10^{-4} mol) were added, and the polymerization was induced by the addition of BCl_3 (0.05 mL, 7.65×10^{-4} mol) at -80 °C. After 60 minutes MeCH (15 mL) and IB (3.2 mL) were added and the polymerization was continued by the addition of $TiCl_4$ (0.22 mL, 2.04×10^{-3} mol). After 80 and 110 minutes of total reaction time a mixture of MeCH (9 mL), CH_3Cl (6 mL) and IB (4.2 mL) was added followed by $TiCl_4$ (0.13 mL, 1.22×10^{-3} mol). After 140 minutes a mixture of MeCH (36 mL) and CH_3Cl (24 mL), and *p*ClSt (5.0 mL) was added and a further amount of $TiCl_4$ (0.32 mL, 3.06×10^{-3} mol) was introduced. After 290 minutes the polymerization was quenched by prechilled methanol. The product was washed with 5% HCl, water, and methanol, and the volatiles removed by evaporation. It was purified

by dissolving in THF, precipitating by adding methanol and drying in vacuum at room temperature.

C. Characterization

Molecular weights were determined by GPC (Waters Associates) equipped with a laser light scattering (LLS) detector (Wyatt Technology). The procedure has been described (2, 6). ^{1}H NMR spectra (~10 mg star-blocks in ~0.7 mL $CDCl_3$) were recorded by a Varian Gemini-200 spectrometer and 64 FIDs were collected. A differential scanning calorimeter (DSC), Dupont Instrument, Model DSC2910, was used to determine the glass transition temperatures. Thermogravimetric analyses were carried on a thermogravimetric analyzer (TGA), TA Instruments, Model Hi- Res TGA 2950. Stress-strain measurements were carried out on compression molded samples by a described procedure (6, 7). The morphology of the star-blocks was investigated by a JOEL (JEM-1200EX II) transmission electron microscope. Films were cast from toluene and annealed for 2 days at 120 °C. Ultra thin sections (~ 50 nm) of unstained samples were cut by a cryogenic microtome.

Results and Discussion

A. Synthesis and Molecular Characterization

The objective of this research was the preparation by a core-first strategy of novel octa-arm star-block polymers [(P*p*ClSt-*b*-PIB)$_8$-C8] consisting of eight *P*pClSt-*b*-PIB arms radiating from a C8 core by the strategy outlined in Scheme 1. Octa-arm stars with living PIB$^{\oplus}$ arms were prepared by the use of initiator **1** in conjunction with BCl_3-$TiCl_4$ coinitiators by a two-stage procedure (2, 3). P*p*ClSt blocks were obtained by the sequential *p*ClSt addition to the living charge at ~ 95 % IB conversions. Earlier studies showed that CH_3Cl:MeCH solvent mixtures are suitable for the living polymerization of *p*ClSt (1, 9). The *p*ClSt conversions and the molecular weights of the *P*pClSt blocks depend on solvent polarity, $TiCl_4$ concentration, and blocking time (7). Star-blocks with high *P*pClSt contents (> 22%) were prepared under relatively polar conditions and high $TiCl_4$ concentrations (see footnote below Table 1).

Molecular weight build-up was followed by withdrawing samples from the living charges and analyzing them by GPC. Figure 1 shows the results of a representative experiment. During IB polymerization in the presence of BCl_3, only a few IB units are added to the initiator (Stage 1); however, after the introduction of $TiCl_4$ the molecular weights rapidly increases to the predetermined value (Stage II). After crossover to *P*ClSt (i.e., PIB$^{\oplus}$ + *p*ClSt $\longrightarrow$ PIB-*p*ClSt$^{\oplus}$) the molecular weight increases relatively slowly (Stage III). Evidently, the rate of *p*ClSt polymerization is lower than that of IB. Similar studies during the preparation of (PSt-*b*-PIB)$_8$-C8 star-blocks showed that the rate of styrene polymerization is higher than that of IB (5, 6). The lower reactivity of *p*ClSt relative to St is due to the electron withdrawing *p*-Cl substituent which destabilizes the carbenium ion and hence lowers its reactivity.

Figure 2 shows representative GPC (RI) traces of products obtained before and after *p*ClSt addition. Each trace shows the presence of two products. The major peaks (~30 and ~29 mL, respectively) correspond to the precursor PIB star and the final P*p*ClSt-*b*-PIB star-block. The minor peaks are due to side products and their origin has been discussed and explained (2, 6). The small peak at ~33 mL (trace b) is due to a mixture of linear diblocks (P*p*ClSt-*b*-PIB) formed by the crossover of linear living PIB$^{\oplus}$ to *p*ClSt (~12%, by RI peak area, after extracting the P*p*ClSt with MEK) and P*p*ClSt (4-6%). The

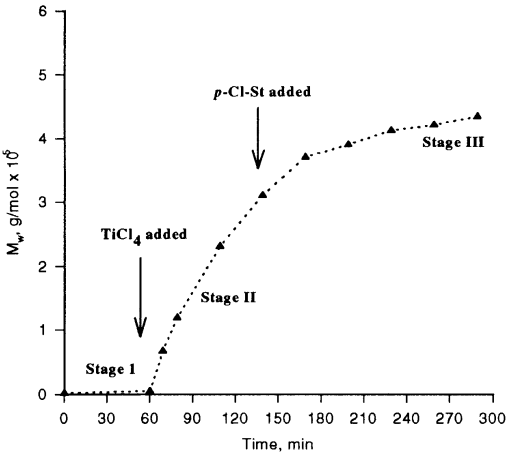

Figure 1. Molecular weight build-up during star-block formation. For conditions see Experimental.

peak corresponding to the star-block at ~29 mL shows narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ 1.13) and the absence of shoulders in the high molecular weight region even after long blocking times. These results are significantly different from those observed during the blocking of St (5, 6). The dispersity of the star-block did not increase after *p*ClSt addition, whereas in the case of blocking with St, the star-blocks always showed broader dispersities than the precursor PIB stars (5, 6). These results indicate the absence of intermolecular alkylation during blocking of *p*ClSt.

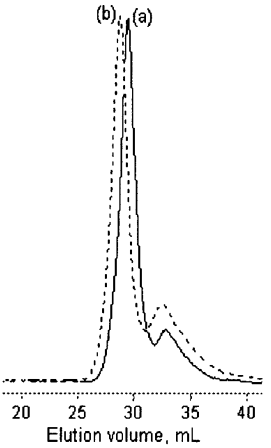

Figure 2. GPC (RI) trace of products (a) before and (b) after *p*ClSt addition.

Figure 3 shows the GPC(RI) traces of a star-block before and after MEK extraction (which removes P*p*ClSt). Attempts to remove diblock contaminants by extraction with *n*-pentane were unsuccessful. Products with low P*p*ClSt contents were soluble in *n*-pentane (both star-block and diblock), whereas those with high P*p*ClSt contents did not show any change in the amount of diblock contaminant upon extraction with *n*-pentane.

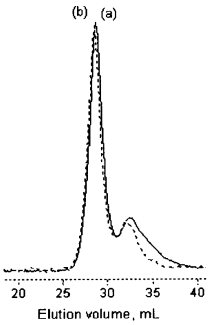

Figure 3. GPC (RI) traces of (P*p*ClSt-*b*-PIB)$_8$-C8 (a) before (solid line) and (b) after (dotted line) MEK extraction.

Molecular characteristics of select star-blocks are summarized in Table 1. To calculate molecular weights, the dn/dc values of the MEK extracted star-blocks were determined by a differential refractive index detector (Optilab 903). The dn/dc of diblocks and star-blocks were assumed to be the same because the core contribution to the dn/dc of star is negligible. The P*p*ClSt content was also determined by ^{1}H NMR spectroscopy and by total conversions assuming 100% IB conversion. The molecular weights and P*p*ClSt contents determined by GPC (LLS) were in good agreement with those obtained by ^{1}H NMR spectroscopy and calculated from conversions.

B. Properties of (PpClSt-b-PIB)$_8$-C8 Stars

As shown by Figure 4, DSC thermogram of a representative star-block indicates two T_gs corresponding to the PIB (at -66 °C) and P*p*ClSt (at 127 °C segments.

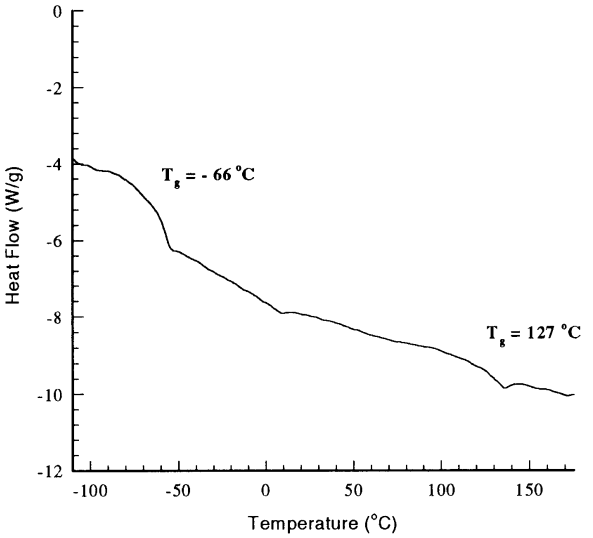

Figure 4. DSC thermogram of a representative octa-arm star-block (sample 21-2, Table 1). Heating rate 10 °C/min in N_2 atmosphere.

Table 1. Molecular characteristics and compostion of some select octa-arm P*p*ClSt-*b*-PIB star copolymers[a].

	IB polymerization			Blocking				P*p*ClSt wt %			
Sample	PIB star $\overline{M}_w$ x10^{-5} g/mol	PIB arm[b] $\overline{M}_w$ x10^{-3} g/mol	$\overline{M}_w/\overline{M}_n$	dn/dc cm^3/g	Star-block $\overline{M}_w$ x10^{-5} g/mol	$\overline{M}_w/\overline{M}_n$	P*p*ClSt arm[b] $\overline{M}_w$ x10^{-3} g/mol	GPC	^{1}H NMR[c]	Conv.	Composition[d]
18-3	3.10	38	1.12	0.130	3.99	1.13	11	22	23	21	(P*p*ClSt/11-*b*-PIB/38)$_8$-C8
21-1	1.42	18	1.09	0.141	2.90	1.14	19	51	52	52	(P*p*ClSt/19-*b*-PIB/18)$_8$-C8
21-2	3.15	39	1.13	0.135	4.45	1.13	16	29	31	30	(P*p*ClSt/16-*b*-PIB/39)$_8$-C8
21-3	3.66	46	1.12	0.132	4.86	1.12	15	25	27	23	(P*p*ClSt/15-*b*-PIB/46)$_8$-C8

[a] molecular weights and dispersities determined by LLS. Astra 4.0.
[b] calculated from homo PIB star based on theoretical number of arms, 8.
[c] ^{1}H NMR spectroscopy measurements were made on MEK extracted samples. The contribution of the core to the aromatic region has been neglected.
[d] first digit = $\overline{M}_w$ x 1000 of P*p*ClSt; second digit = $\overline{M}_w$ x 1000 of PIB.

Synthesis conditions:

18-3: Stage I; **1** = 3.19 x10^{-5} mol, CH_3Cl = 10 mL, IB = 1 mL, DMA = 5.0 x 10^{-4} mol, D*t*BP = 3.0 x 10^{-4} mol, BCl_3 = 7.65 x 10^{-4} mol, 60 min; Stage II; MeCH = 15 mL, IB = 3.2 mL, $TiCl_4$ = 2.04 x 10^{-3} mol, 20 min; two incremental additions of (IB = 4.2 mL + CH_3Cl = 6 mL + MeCH = 9 mL followed by $TiCl_4$ = 1.22 x 10^{-3}mol; 30 min each); blocking of *p*ClSt = 5.0 mL, CH_3Cl = 24 mL, MeCH = 36 mL, $TiCl_4$ = 3.06 x 10^{-3}, 150 min.

21-1: Stage I; **1** = 3.19 x10^{-5} mol, CH_3Cl = 10 mL, IB = 1 mL, DMA = 5.0 x 10^{-4} mol, D*t*BP = 3.0 x 10^{-4} mol, BCl_3 = 7.65 x 10^{-4} mol, 60 min; Stage II; MeCH = 15 mL, IB = 4.5 mL, $TiCl_4$ = 2.04 x 10^{-3} mol, 40 min; blocking of *p*ClSt = 6.25 mL, CH_3Cl = 8 mL, MeCH = 12 mL, $TiCl_4$ = 2.45 x 10^{-3} mol, 150 min.

21-2: Stage I; **1** = 3.19 x10^{-5} mol, CH_3Cl = 10 mL, IB = 1 mL, DMA = 5.0 x 10^{-4} mol, D*t*BP = 3.0 x 10^{-4} mol, BCl_3 = 7.65 x 10^{-4} mol, 60 min; Stage II; MeCH = 15 mL, IB = 3.2 mL, $TiCl_4$ = 2.04 x 10^{-3} mol, 20 min; two incremental additions of (IB = 4.2 mL + CH_3Cl = 6 mL + MeCH = 9 mL followed by $TiCl_4$ = 1.22 x 10^{-3} mol, 30 min each; blocking of *p*ClSt = 6.25 mL, CH_3Cl = 8 mL, MeCH = 16 mL, $TiCl_4$ = 3.06 x 10^{-3} mol, 150 min.

21-3: Stage I; **1** = 3.19 x10^{-5} mol, CH_3Cl = 10 mL, IB = 1 mL, DMA = 5.0 x 10^{-4} mol, D*t*BP = 3.0 x 10^{-4} mol, BCl_3 = 7.65 x 10^{-4} mol, time = 60 min; Stage II; MeCH = 15 mL, IB = 3.2 mL, $TiCl_4$ = 2.04 x 10^{-3} mol, 20 min; two incremental additions of (IB = 4.2 mL + CH_3Cl = 6 mL + MeCH = 9 mL followed by $TiCl_4$ = 1.22 x 10^{-3} mol, 30 min each; blocking of *p*ClSt = 7.9 mL, CH_3Cl = 17 mL, MeCH = 26 mL, $TiCl_4$ = 2.45 x 10^{-3}, 180 min.

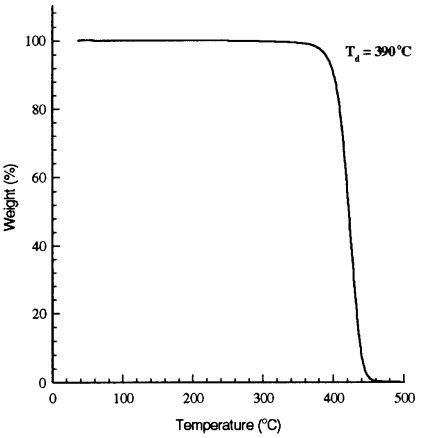

Figure 5. TGA thermogram of a representative star-block (sample 21-2, Table 1) in N_2 atmosphere.

Figure 5 shows the TGA thermogram of a representative star-block. The 5% decomposition temperature, T_d, was 390°C in N_2 atmosphere. Mechanical properties were analyzed on compression molded samples without removing the contaminants (~15 % consisting of P*p*ClSt and/or diblock, see Figure 2). Figure 6 shows stress-strain traces of select octa-arm star-blocks. Stress-strain measurements showed high tensile strengths (22-27 MPa) and elongations (400-650%) in spite of the presence of contaminants. The tensile strength increased with an increase in P*p*ClSt content. Star-blocks with 29% P*p*ClSt, (P*p*ClSt/16-b-PIB/38)$_8$-C8, showed the highest strength, ~ 27 MPa whereas the star with relatively high P*p*ClSt content (51%), (P*p*ClSt/19-b-PIB/18)$_8$-C8, showed plastic like behavior, i.e., high modulus, yield point, and short elastic

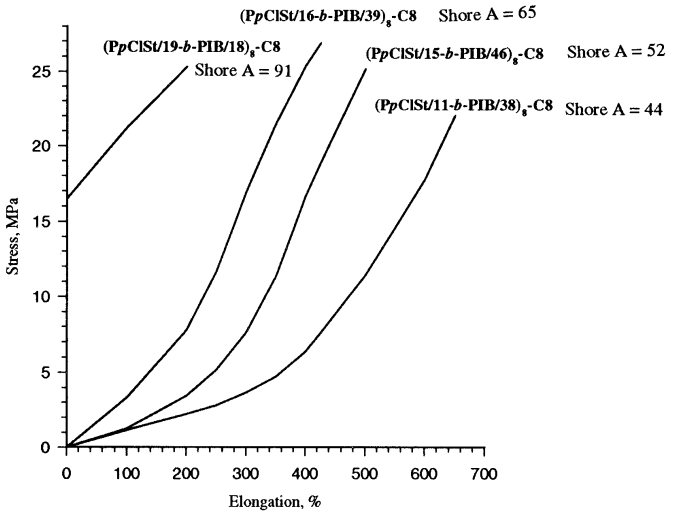

Figure 6. Stress-strain traces of select star-blocks. Shore A numbers indicate hardness values.

extension. P*p*ClSt containing TPEs show higher tensile strengths and moduli, and lower elongations than similar stars with PSt-*b*-PIB arms (5, 6), which is most likely due to the higher T_g of the P*p*ClSt blocks. The tensile strengths of these star-blocks are superior to those of similar three-arm star-blocks and triblock TPEs (1).

Figure 7 shows the TEM micrograph of a representative star-block containing 22% P*p*ClSt. The P*p*ClSt phase appears as spherical domains with a diffuse interphase irregularly dispersed in the PIB matrix. The formation of irregular domains and diffuse interphase is most likely due to compatibilization by the ~15% diblock contaminants.

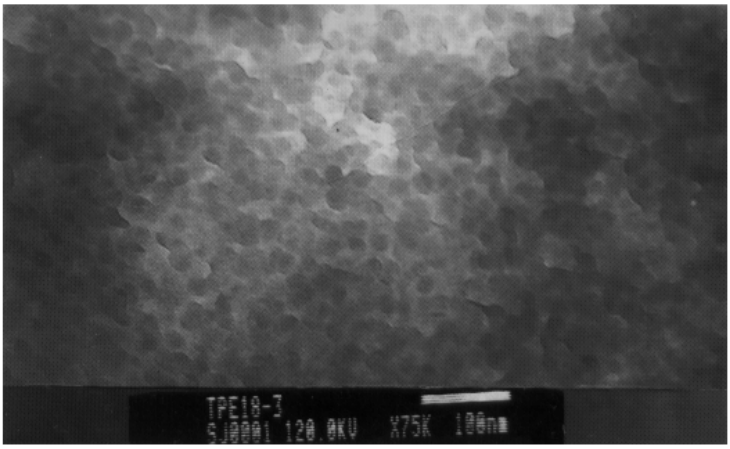

Figure 7. TEM micrograph of star-block 18-3 (P*p*ClSt content, 22%).

Conclusions

The synthesis of novel stars comprising eight P*p*ClSt-*b*-PIB arms radiating from a calix[8]arene core has been accomplished. Overall compositions and relative molecular weights of the glassy segments can be controlled by suitable choice of blocking conditions, such as solvent polarity, reagent concentrations and blocking time. In spite of the presence of 10-15% contaminants (P*p*ClSt and/or P*p*ClSt-*b*-PIB diblocks), the star-blocks exhibit an excellent combination of thermoplastic elastomer properties with up to 27 MPa tensile stress and ~500% elongation.

Acknowledgment

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