Synthesis and Properties of Block Copolymers of Isoprene and 1,3-Cyclohexadiene

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ABSTRACT: Anionic block copolymerization of isoprene and 1,3-cyclohexadiene (1,3-CHD) was carried out in the presence of a dilithium initiator derived from 1,3-diisopropenylbenzene. A special seeding technique, namely multistep seeding with isoprene, was developed to promote the efficiency of the dilithium initiator. Triblock, PCHD-PI-PCHD, pentablock, PCHD-PS-PI-PS-PCHD, and heptablock copolymers, PCHD-PI-PS-PI-PS-PI-PCHD, were synthesized using multistep seeded dilithium initiators. Phase separation and mechanical properties of the resulting block copolymers were investigated by DSC, TEM, and tensile strength test.

Introduction

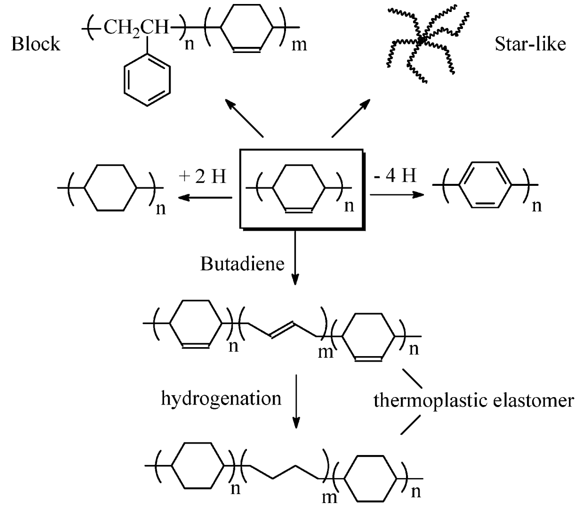
The polymerization of 1,3-cyclohexadiene (1,3-CHD) has received much attention with the aim to prepare high-performance polymers, with for example a high glass transition temperature (T_g around 150 °C[1]), good heat and chemical resistance, good weatherability and transparency, etc. As a precursor polymer, PCHD can be either hydrogenated to prepare polycyclohexylene,[1−3] a polymer with the highest T_g of hydrocarbon polymers, or dehydrogenated to make polyphenylene (Scheme 1).[4−6]

Anionic polymerization of 1,3-CHD in earlier literature achieved low to medium monomer conversion and resulted in low molecular weight products[2,4,5,7−10] due to the chain transfer to monomer. The polymerization was greatly improved by Natori[11] by using a chelating additive *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). The molecular weight of the resulting polymer increased linearly up to 1.8×10^4 g/mol with 1,3-CHD conversion, while the molecular weight distribution (MWD) remained narrow.[11] The reason is that ionic species disaggregate in the presence of TMEDA, leading to a larger polymerization rate and less extent chain transfer.[12] Similarly, Mays and co-workers[13] achieved controlled anionic polymerization of 1,3-CHD in benzene in the presence of *sec*-BuLi/1,4-diazabicyclo[2.2.2]octane (DABCO) or *n*-BuLi/dimethoxyethane.

A number of diblock, ternary, and quarter-block copolymers of 1,3-CHD with styrene, butadiene, and isoprene have been synthesized,[1,14−20] and some of them were hydrogenated to saturated hydrocarbon polymers.[1,16,17] Starlike polymers containing PCHD were also synthesized by different research groups.[6,19,21]

One of the interesting topics is to synthesize PCHD−polydienes−PCHD triblock copolymers, which is anticipated to show improved heat resistance than the commercially available thermoplastic elastomer, poly(styrene-*b*-butadiene-*b*-styrene), SBS, since the T_g of PCHD block is higher than that of PS. However, the synthesis of PCHD−polydienes−PCHD triblock copolymer is more complex than the styrenic analogue because of the chain transfer reactions, as already reported by Natori and co-workers on the synthesis of PCHD−polybutadine (PB)−PCHDs by sequential polymerization[1,14] and by dilithium initiator.[17]

Scheme 1. Macromolecular Engineering of PCHD and PCHD-Containing Polymers



In this work, we will present the results on the syntheses of a number of triblock, pentablock, and heptablock copolymers of 1,3-CHD and isoprene and/or styrene. The mechanical properties and the phase separation of the block copolymers are also discussed.

Experimental Section

Materials. 1,3-CHD (ACROS, 96%) and isoprene (Aldrich, 99%) were purified by passing through a neutral Al_2O_3 column, then refluxed on CaH_2, and distilled under a N_2 atmosphere at 80 and 34 °C, respectively. Before use, these monomers were freshly distilled over dibutylmagnesium (12 °C/35 mmHg for 1,3-CHD and 34 °C/760 mmHg for isoprene). Styrene (BASF, 10 ppm stabilizer) and *sec*-butyllithium (*sec*-BuLi) (Chemetall Co., 1.5 M in cyclohexane) were used as received. Cyclohexane (BASF) was dried by passing through an Al_2O_3 tower (large scale). 1,3-Diisopropenylbenzene (*m*-DIPB) (Aldrich, 97%) was stirred over CaH_2 for 4 h in nitrogen and distilled under reduced pressure (75 °C at 1 mbar). TMEDA (Aldrich, redistilled, >99.5%) and triethylamine (ACROS, 99.7%) were used as received.

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Polymerization. All of the reactions were performed in a 500 mL round-bottom flask equipped with a gas inlet, a thermometer, a silicon rubber septum, and a condenser connected to a overpressure valve which can keep about 0.1 bar back-pressure inside the flask. Before polymerization, the glass apparatus was dried by three cycles of N_2 flush−pump/heating−N_2 flush.

Homopolymerization. The procedure that follows was developed by Natori.[11] As an example, 0.5 mL of *sec*-BuLi solution (0.8 mmol) and 0.18 mL (1.5 mmol) of TMEDA were added in 320 mL of cyclohexane at 40 °C for 10 min. The solution became deep red in color after mixing. Then 10 mL (8.4 g, 0.1 mol) of 1,3-CHD was added with a syringe. The solution slowly became yellowish. Samples were taken at predetermined periods. The polymerization was terminated with 2-propanol at 130 min. The final reaction mixture was stored in the presence of Irganox 1010 (0.5 wt % based on polymer). Monomer conversion: 93%. $M_n = 14\,000$ g/mol, PDI = 1.3.

Synthesis of Dilithium Initiator, DiLi. *sec*-BuLi (20 mL, 1.5 M cyclohexane solution, 0.030 mol) and triethylamine (6 mL) were mixed in cyclohexane (250 mL) for 15 min. *m*-DIPB (2.34 g, 0.015 mol) was added slowly while the temperature was kept below 15 °C with the aid of an ice/water bath. The mixture was then warmed at 50 °C for 80 min to obtain a dark solution (DiLi).

Seeding of Dilithium Initiator, PI-DiLi. A freshly prepared DiLi solution was cooled in an ice/water bath. Isoprene (8 mL) was added, and an exothermic effect was observed within 20 min. After cooling, the reaction mixture was put into an oil bath at 40 °C for 1 h. A deep brown solution was obtained (PI-DiLi).

Multistep Seeding of Dilithium Initiator, PI-PI-DiLi. For the multistep activation, isoprene was fed three times (3 × 8 mL = 24 mL) at intervals of 20 min into the freshly prepared DiLi, which was cooled to 10 °C beforehand. Finally, the mixture was heated at 40 °C for 30 min and then at 50 °C for 30 min. A slightly orange solution was obtained (PI-PI-DiLi). The concentration of the bifunctional initiator was approximately 0.05 mol/L.

Triblock Copolymer by Bifunctional Initiator. Let us take the polymerization initiated by PI-PI-DiLi as an example. A solution of isoprene (20.4 g, 0.3 mol) in cyclohexane (320 mL) was warmed to 40 °C before the addition of PI-PI-DiLi (6.5 mL, 0.32 mmol) with a syringe. The polymerization stood for 2 h. TMEDA (0.18 mL, 1.5 mmol) was injected, and the solution was stirred for 10 min. Then 1,3-CHD (11.8 g, 0.15 mol) was added, and the reaction was kept at 40 °C for 5 h. The polymerization was terminated by 2-propanol, and the final solution was stabilized by Irganox 1010 (0.5 wt % based on polymer). Composition: 78/22 (molar ratio of isoprene/1,3-CHD units); $M_n = 93\,000$ g/mol, PDI = 1.6.

Pentablock Copolymer Using Bifunctional Initiator. The polymerization of the central block was the same as above, with isoprene (13.6 g, 0.2 mol) and PI-PI-DiLi 6.5 mL (0.32 mmol). After the polymerization of isoprene, TMEDA (0.18 mL, 1.5 mmol) was added, and the mixture was stirred at 40 °C for 10 min. Styrene (8.2 g, 0.08 mol) was fed into the flask, and the reaction stirred for 1 h at an elevated temperature, 50−60 °C. Then the mixture was cooled to 40 °C followed by the addition of 1,3-CHD (7.6 g, 0.09 mol). The reaction continued for 6 h and was terminated by 2-propanol. The final solution was stabilized by Irganox 1010 (0.5 wt % based on polymer). Composition: isoprene/styrene/1,3-CHD units = 58/27/15 (molar ratio); $M_n = 65\,000$ g/mol, PDI = 2.0.

Heptablock Copolymer Using a Bifunctional Initiator. The polymerizations of isoprene and styrene together with the addition of TMEDA are the same as above, with isoprene (10 mL, 6.8 g, 0.1 mol), PI-PI-DiLi 6.5 mL (0.32 mmol), styrene (10 mL, 9.1 g, 0.09 mol), and TMEDA (0.18 mL, 1.5 mmol). After the mixture was cooled to 40 °C, a second batch of isoprene (10 mL, 6.8 g, 0.1 mol) was transferred into the flask. The polymerization stood for 2 h. Then 1,3-CHD (9 mL, 7.6 g, 0.09 mol) was added with a syringe, and the reaction stood for 5 h at 40 °C. The polymerization was terminated by 2-propanol, and the final solution was stabilized by Irganox 1010 (0.5 wt % based on polymer). Composition: isoprene/styrene/1,3-CHD units = 66/23/11 (molar ratio); $M_n = 64\,000$ g/mol, PDI = 2.0.

Measurement. Gel permeation chromatography (GPC) was carried out using three styrene−divinylbenzene gel columns "PLgel Mixed-B" (particle size 10 μm, linear range of $M_w = 500-10^7$, Polymer Laboratories Co.) calibrated by narrow polystyrene standard (500−5 000 000 g/mol). THF was used as eluent at a flow rate of 1.5 mL/min at 23 °C. The system was equipped with a Waters 410 RI and a Spectra series UV 100 detector. Molecular weight and polydispersity were obtained relative to polystyrene standard using WinGPC 6.20 data processing software (Polymer Standards Service GmbH, Mainz).

^{1}H NMR spectra were measured on a Bruker Aviance 500 type NMR spectrometer operating at 500 Hz, using deuterated tetrahydrofuran as solvent.

Transmission electron microscopy (TEM) was performed on specimen microtomed from cast film at −120 °C. Slices with thickness of about 80 nm were collected with 700 mesh grids and stained in OsO_4 vapor. The measurement was conducted on a LEO912 instrument at an accelerating voltage 120 kV.

Differential scanning calorimetry (DSC) was performed on a 2920 MDSC V2.5F instrument which was calibrated with the onset temperature of the melting peaks of the standards adamantane, water, indium, tin, and lead. The enthalpy calibration was performed with the melting enthalpy of indium. The glass transition temperature (T_g) was determined as that temperature, where the cp curve has reached the half step-height, constructed by extrapolation of the linear range below and above the glass transition. All samples were heated to 180 °C at a rate of 2 °C/min and then cooled to −125 °C with liquid nitrogen.

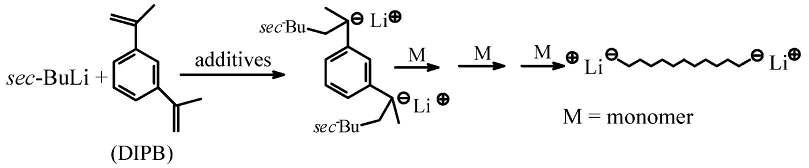
Tensile tests were carried out according to ISO 527 on a Zwick Z010 testing instrument, using specimen of 4.10 mm width and 1.10 mm thickness at a tensile velocity of 50 mm/min.

Results and Discussion

Before discussing the block copolymerization, we would briefly describe the general behavior of homopolymerization of 1,3-CHD. We followed the approach developed by Natori,[11] using TMEDA as chelating agent. The red solution of *sec*-BuLi/TMEDA gradually changed to yellowish upon the addition of 1,3-CHD. The clear solution became opaque during the polymerization, consistent with the observation of a slightly heterogeneous reaction mixture by Long and co-workers.[21] It is necessary to mention here that Quirk et al.[22] isolated an insoluble crystalline fraction which contains a high (>98%) percent of 1,4-enchainment from the anionic polymerization of 1,3-CHD in cyclohexane in the absence of TMEDA. The opacity in the present work may, however, be a consequence of low solubility of the resulting polymers whose regioregularity is low due to the presence of TMEDA, as indicated by NMR analysis (next paragraph). The M_n of the resulting polymer increases linearly with monomer conversion during the polymerization, indicating that the chain grew in a living manner. However, the controllability is lower than that in traditional styrene anionic polymerization. It is difficult to obtain high molecular weights with low dispersities. For example, a product with $M_n = 3.7 \times 10^4$ g/mol (by adjusting the ratio of monomer/BuLi) shows a polydispersity of 1.6. In fact, PCHD with M_n higher than 3.0×10^4 g/mol and narrow distribution was never reported previously.

The resulting PCHD contains, as estimated by NMR,[12,23] approximately 80% 1,2- and 20% 1,4-enchainment. DSC curve shows a clear glass transition around 150 °C.

Scheme 2. Preparation and Seeding of the Dilithium Initiator



Synthesis of CHD-I-CHD Triblock Copolymers.

Traditionally, ABA type triblock copolymers were synthesized through three strategies:[24] (1) sequential polymerizations of monomers A, B, and A, (2) polymerizations of A and B followed by a coupling reaction, and (3) sequential polymerizations of B and A using a bifunctional initiator. All of these three approaches work well for SBS preparation. For the synthesis of PCHD-PI-PCHD, approach 3 is obviously advantageous over others because the polymerization of isoprene is free of residual 1,3-CHD and, therefore, avoid forming, by chain-transfer reaction, diblock copolymers and homopolymers that are detrimental to the mechanical properties of the products.

Approach 3 requires a hydrocarbon-soluble dilithium initiator in order to obtain higher content 1,4-enchainment in the central block. The preparation of hydrocarbon-soluble bifunctional initiators has been disclosed previously, by using 1,3-bis(1-phenylethenyl)benzene derivatives[25] or *m*-diisopropenylbenzene (*m*-DIPB),[26−28] the latter being commercially available and being used in our work (Scheme 2).

The earlier publications[26−32] on the synthesis of DIPB-based initiators gave controversial results, none of which was checked by the synthesis of triblock copolymers. Later, Jérôme et al.[33−35] revised the approach systematically in an attempt to synthsize PMMA−PB−PMMA block copolymers and found the mechanical properties of the so-produced polymer were poor. The reason is that the initiating efficiency was not very high due to the strong aggregation of dilithium species. Therefore, they improved the procedure by seeding the dilithium initiators with butadiene and obtained narrow disperse SBS model block copolymers.[34] Nevertheless, they observed a bimodal distribution in the synthesis of PMMA−PB−PMMA copolymers,[35] which required a polar solvent in the second step.

It should be noted that Natori et al.[17] reported the synthesis of PCHD−PB−PCHD by a dilithium initiator derived from *m*-DIPB. They used an unseeded initiator and obtained unimodal distributions when TMEDA was added at the start of the polymerization. However, with this procedure the percentage of 1,4-enchainment in the central block was low (cf. Figure 1 in ref 17). Therefore, it is of great interest to develop an efficient dilithium initiator that can afford high percentage of 1,4-enchainment, which is closely related to the mechanical property of the product.

In the synthesis of the bifunctional initiator, *m*-DIPB was dropped slowly into a solution of *sec*-BuLi in cyclohexane in the presence of triethylamine to form the diadduct as a dark solution, which is coded DiLi. The dark solution was not very stable, resulting in some precipitation in a short period. The freshly prepared diadduct was used to initiate the polymerization of a small amount of isoprene to obtain the seeded initiator, PI-DiLi, which was orange in color and stable in storage.

As a demonstration, Figure 1 shows the GPC curves of polyisoprene initiated by DiLi and PI-DiLi. The former is asymmetric with a tailing part, whereas the latter shows a much narrower distribution. The tailing in the former can be ascribed to slow initiation due to strong aggregation of the adducts.

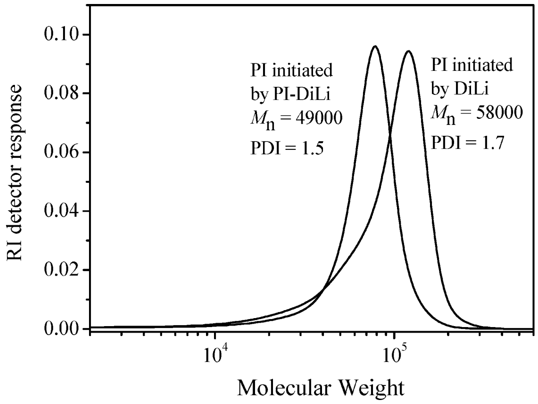


Figure 1. Polyisoprenes prepared by the initiation of DiLi (a) and PI-DiLi (b).

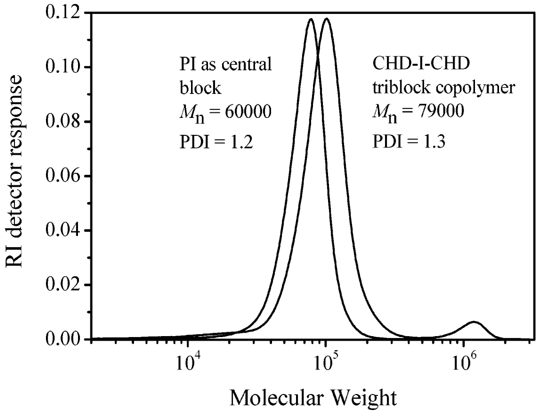


Figure 2. Preparation of triblock copolymer, PCHD-PI-PCHD, by PI-DiLi in which TMEDA was fed from the start of the polymerization.

The seeded initiator was then used in the preparation of triblock copolymers. When TMEDA was added from the start of the polymerization, narrow distributions of the central block and the final triblock copolymer, PCHD−PI−PCHD, were obtained (Figure 2). The composition of 1,4-enchainment is, however, very low (see next). If TMEDA was added after the polymerization of isoprene and before the polymerization of 1,3-CHD, a bimodal distribution was obtained. This is not due to the chain transfer reaction upon the addition 1,3-CHD because the bimodal distribution was also observed even when *styrene* was used as the second monomer, as shown in Figure 3. Thus, it is possible that part of the adducts of DIPB and *sec*-BuLi remained dormant due to strong ionic aggregation in cyclohexane during seeding and polymerization process. When the solvent was switched to a polar solvent on adding TMEDA, these species became active and initiated new polymerization, leading to a bimodal distribution of the product. The present results resemble the bimodal MWD observed

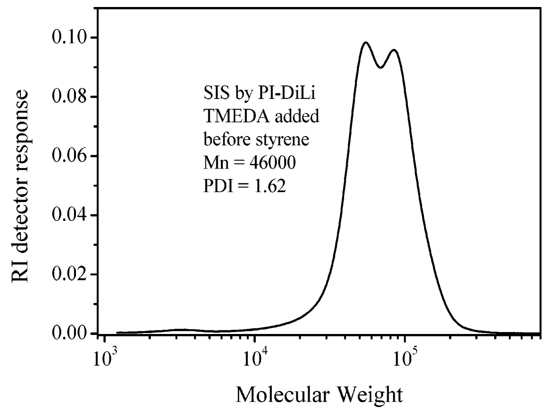


Figure 3. SIS initiated by PI-DiLi in which TMEDA was fed after the polymerization of isoprene.

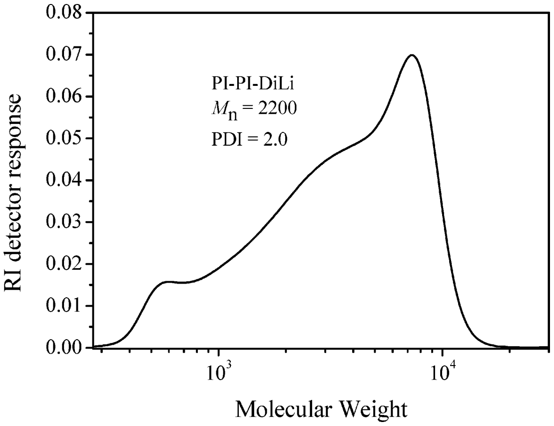


Figure 4. GPC curve of a multistep seeded initiator, PI-PI-DiLi.

by Jérôme et al.[35] when they changed the solvent from cyclohexane to tetrahydrofuran in the synthesis of PMMA−PB−PMMA.

To activate as many organolithium species in DiLi as possible, a multistep activation procedure was developed in which isoprene was added into the reaction vessel three times. Figure 4 shows the GPC curve of a three-step seeded initiator, PI-PI-DiLi. The multimodal distribution indicates that more diadducts are activated on each batch of isoprene feeding. During the seeding procedure, the reaction solution became pale orange. This solution can be stored for a long time, for instance, 1 month, in a refrigerator without any precipitation.

PI-PI-DiLi-initiated copolymerization of isoprene and 1,3-CHD resulted in triblock product exhibiting much narrower GPC curve (Figure 5) than that in Figure 3, even when TMEDA was added after the polymerization of the first block. During the polymerization, the viscosity of the reaction mixture increases steadily. An exothermic effect was observed for all cases after the polymerization had been running for about 35 min, with the temperature rising rapidly to 46 °C while the bath was kept at 40 °C. After 2 h, the temperature decreased to 40 °C, indicating the completion of isoprene polymerization. At this time the reaction mixture had practically gelled due to the aggregation of the ionic species. On the addition of TMEDA, the gel became fluid immediately to form a red solution. On adding 1,3-CHD, the red color became yellowish, indicating the initiation of the second block.

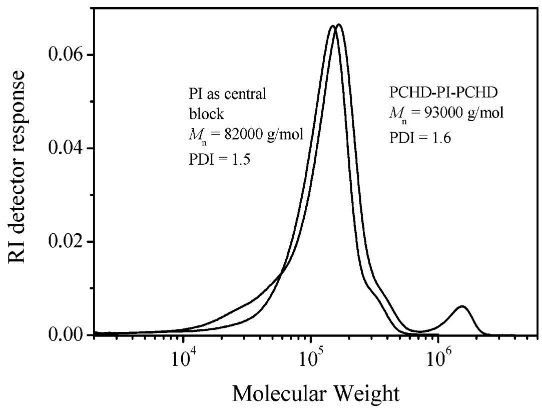


Figure 5. GPC curves of the first block and the final copolymer in the synthesis of PCHD-PI-PCHD initiated by PI-PI-DiLi. TMEDA was fed after the polymerization of isoprene.

It should be pointed out that the GPC traces (Figure 5) and the polydispersities (Table 1) of the resulting block copolymers are not as narrow as that of traditional anionically polymerized polystyrene or polydienes. The broad molecular weight distribution is a consequence of a number of reasons: (a) Not all of the diadducts of *sec*-BuLi and *m*-DIPB were activated even in the multistep seeding procedure developed in this work. Therefore, in the polymerization of the first and second block, those unactivated adducts initiated slowly new chains in addition to those initiated by the seeded species. When TMEDA was added from the start, almost all living centers were activated and initiate the polymerization simultaneously, leading to a relatively narrow distribution (sample no. 6 in Table 1). (b) Chain transfer in the polymerization of 1,3-CHD caused some termination (see Introduction), even in Natori's TMEDA-improved process. (c) There was an additional high molecular weight peak in the polymerization of 1,3-CHD (cf. Figures 2, 5, and 7). The reason for the presence of the peak is unclear. An extremely high molecular weight fraction was also reported previously in the preparation of 1,3-CHD-containing block copolymers[18,20] and was ascribed to micelle formation. However, we also observed this peak in the homopolymerization of 1,3-CHD.

The percent of 1,4-enchainment in the diene block is high when PI-PI-DiLi was used as the initiator. As shown in Figure 6, the percentage of 1,4-addition, $P_{1,4-}$, for product with TMEDA added after the polymerization of isoprene (sample in Figure 5) can be estimated by areas of different protons:

$$P_{1,4-} = A_{\mathrm{Ha}}/(A_{\mathrm{Ha}} + A_{\mathrm{Hb}}/2)$$

For product with TMEDA being added from the start (sample in Figure 2), 1,2-enchainment is present and $P_{1,4-}$ becomes

$$P_{1,4-} = A_{\mathrm{Ha}}/(A_{\mathrm{Ha}} + A_{\mathrm{Hb}}/2 + A_{\mathrm{Hb}}'/2)$$

Therefore, products in Figure 5 contain a high percentage of 1,4-enchainment (92%) and low 3,4-enchainment (8%), while that in Figure 2 contains low 1,4- (27%), high 3,4- (51%), and some 1,2-enchainments (25%).

A number of triblock copolymers were synthesized using PI-PI-DiLi. The results are summarized in Table 1. It is noted that the measured percentage of 1,3-CHD units in the copolymer is always lower than the feed, while in a reference system (no. 1) the obtained compositions of isoprene and styrene are nearly equal to the feed ratio. There is also a rough tendency that the higher the relative feed amount of 1,3-CHD, the larger

Table 1. Triblock, Pentablock, and Heptablock Copolymers Synthesized with Multistep Seeded Initiator, PI-PI-DiL

	composition[a] (molar ratio)		mol wt / g/mol				mechanical strength		T_g/°C by DSC	
run no.	practical by NMR	feed	$M_\mathrm{n}/10^3$	$M_\mathrm{w}/10^3$	$M_\mathrm{p}/10^3$	PDI	TS[b]/MPa	TE[c]/%	T_g1	T_g2
1[d]	61:39	60:40	66	133	136	2.0	9.5	1060	−62	83
2	65:35	32:68	49	101	106	2.1	15.4	4.8	−62	143
3	72:28	55:45	111	161	168	1.5	8.2	422		
4[e]	74:26	69:31	57	92	87	1.6	16.8	406	3	163[h]
5	78:22	67:33	93	152	168	1.6	4.1	1099	−60	140[h]
6[e]	83:17	67:33	79	102	103	1.3	16.9	519	4	143[h]
7	86:14	75:25	92	193	182	2.1	2.8	1500	−61	158[h]
8[f]	56:26:18	53:21:26	73	141	160	1.9	14.5	781	−61	155[h]
9[f]	58:27:15	54:22:24	65	127	128	2.0	10.8	762		
10[f]	62:17:21	54:17:29	67	121	122	1.8	7.4	609		
11[g]	54:32:14	43:32:25	63	109	106	1.7	16.8	510		
12[g]	66:23:11	57:20:23	64	129	120	2.0	11.6	780	−68[h]	162[h]
13[g]	71:24:5	62:20:18	150	223	220	1.5	12.2	1039		

[a] Compositions are given in I:CHD repeating units in molar ratio. [b] Tensile strength. [c] Tensile elongation at break. [d] Reference system SIS with the composition I:St. [e] TMEDA was added from the start of the polymerization. [f] Pentablock copolymers with the composition I:St:CHD (molar ratio). [g] Heptablock copolymers with the composition I:St:CHD (molar ratio). [h] End temperature of broadened transition.

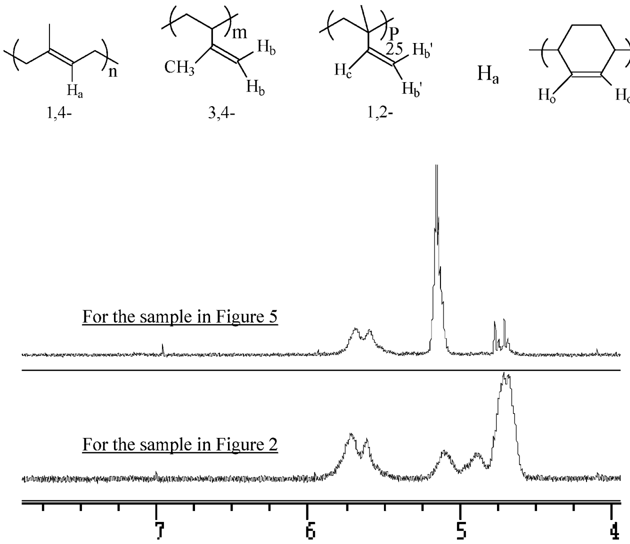


Figure 6. NMR of the block copolymers synthesized by anionic polymerizations in which TMEDA was fed from the start (sample in Figure 2) and between the polymerizations of isoprene and 1,3-CHD (sample in Figure 5).

the difference between feed and obtained compositions. The difference is a consequence of chain transfer reactions that leads to an incomplete 1,3-CHD polymerization. The higher the feed amount of 1,3-CHD, the higher the degree of chain transfer.

We also synthesized a number of pentablock and heptablock copolymers using dilithium initiator. These copolymers are included in Table 1 (no. 8−10 for pentablock and no. 11−13 for heptablock) as well, and their GPC curves are shown in Figure 7. The synthetic procedure is quite similar to that of triblock copolymers, with additional polymerization of styrene and isoprene (in heptablock). The structures of the resulting block copolymers are schematically shown in Scheme 3, in which PCHD is always the outer block.

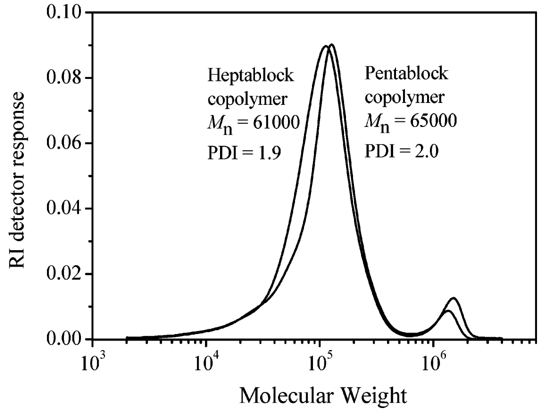
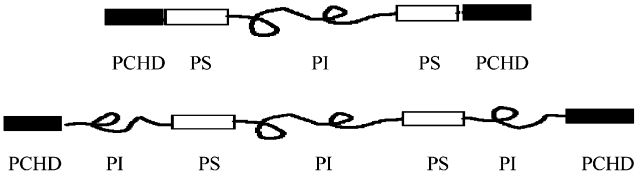


Figure 7. GPC curves of a pentablock copolymer, PCHD-PS-PI-PS-PCHD (no. 9), and a heptablock copolymer, PCHD-PI-PS-PI-PS-PI-PCHD (no. 13).

Scheme 3. Schematic Structures of Pentablock and Heptablock Copolymers



Tensile Properties of the Block Copolymers. The samples in Table 1 vary in composition, exhibiting properties from hard to soft. The tensile elongation at break increases with an increasing content of isoprene units. The tensile strength is lower than that of the commercial SBS, possibly due to the contamination of diblock and/or homopolymer caused by new initiation of the dormant adduct and by the chain transfer reaction even in the presence of TMEDA. When TMEDA was fed from the start, the obtained tensile strength is larger (no. 6 in Table 1), which correlates to a narrower molecular weight distribution. All of the tensile measurements were performed on the samples dried directly from the reaction mixture without any purification procedure.

The stress−strain curves for tri-, penta-, and heptablock copolymers are shown in Figure 8. Typical behavior for thermoplastic elastomers was observed for triblock copolymers (no. 5 and 6). However, the test piece of no. 5 prepared with TMEDA being added after first block crept at break due to contamination of homopolymer and/or diblock copolymers. Indeed, the GPC curve of no. 5 is obviously broader than that of no. 6. Pentablock copolymer (no. 8) shows shear yielding behavior because the sample contains a high percent of plastic component, which may form a continuous phase in the test piece. Interestingly, heptablock copolymer, no. 12, behaves like hard elastomer after a slight yielding. The rubber/plastic composition is 66/35, within

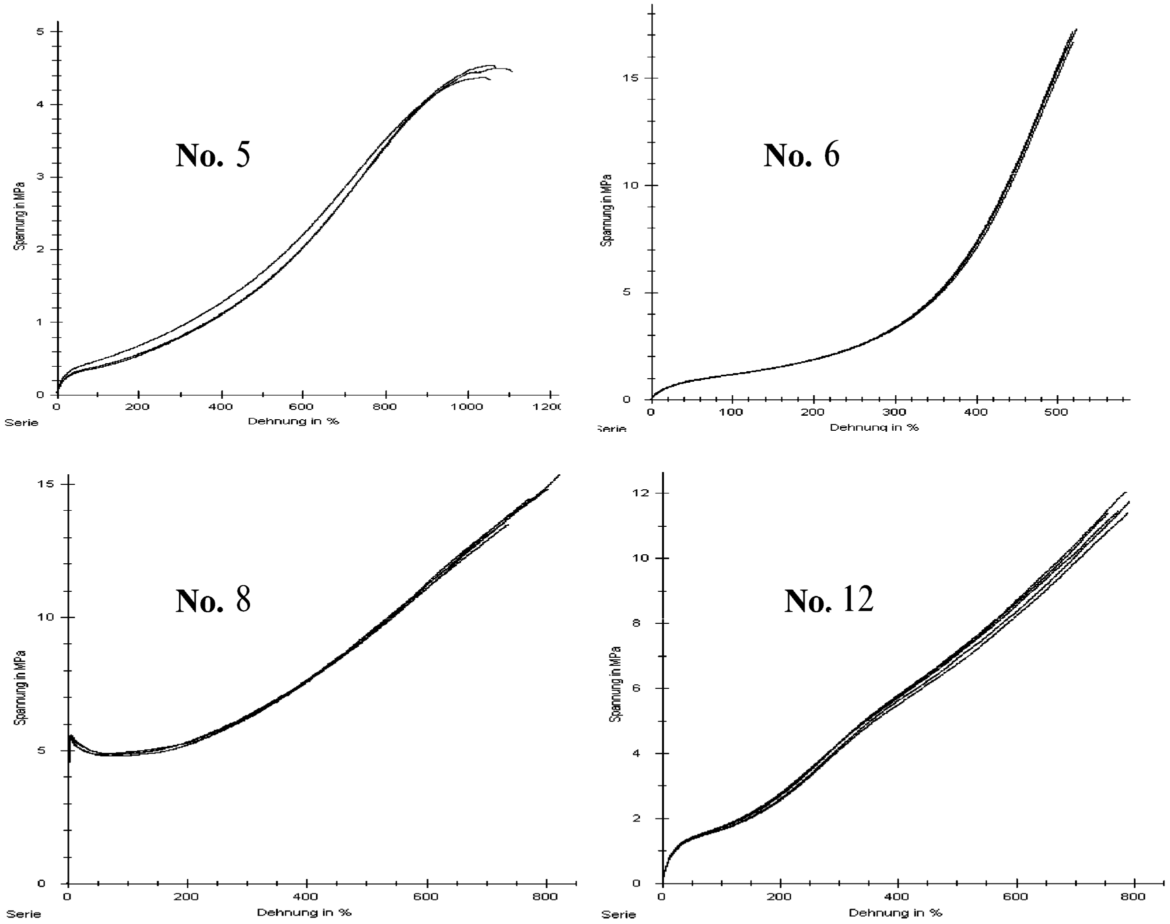
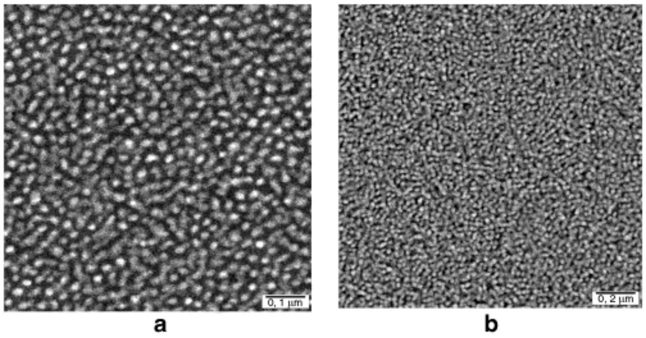


Figure 8. Stress–strain curves of triblock (no. 5 and 7), pentablock (no. 9), and heptablock (no. 13) copolymers synthesized with dilithium initiators.



a

b

Figure 9. TEM morphology of triblock copolymers (a; no. 7 in Table 1) and pentablock copolymer (b; no. 8 in Table 1).

the typical range of thermoplastic elastomer. The special stress–strain behavior can be a consequence of smaller domain size because the polyisoprene block is interconnected by the polystyrene block.

Interestingly, the mechanical strength of the penta- and heptablock copolymers is generally higher than those of triblock copolymers with similar molecular weights. The reason could be that the contamination of homopolymer and/or diblock copolymers is lower because more and more initiating species were activated during the additional polymerization of styrene and isoprene in the intermediate block.

Phase Separation of Block Copolymers. Phase separation of the block copolymers was investigated by the measurement of glass transition temperature and the morphology observation of the samples. The results of DSC were included in Table 1. The reference sample, poly(styrene–isoprene–styrene), SIS, shows two clear T_gs at −62 and 83 °C. Sample no. 2 containing a higher percentage of PCHD also showed two clear T_gs at −62 and 143 °C that correspond to the PI and PCHD segments, respectively. However, for the samples containing lower percentages of PCHD (no. 4–7 in Table 1) or the pentablock (no. 8) and heptablock (no. 12) block copolymers, the glass transition of the hard block was smeared, indicating fine domains of the hard block or high content of interface in the samples. In addition, the T_g of the PI block is affected by the presence of TMEDA during the polymerization. For instance, product no. 5 with TMEDA being added after the polymerization of isoprene shows T_g at −60 °C, whereas no. 6 with TMEDA added from the start shows a T_g at 4 °C. This agrees with the relative content of 1,4- and 3,4- (and/or 1,2-) in the central block between these two samples estimated by NMR.

The morphology of triblock copolymers was investigated using films cast from cyclohexane. Parts a and b of Figure 9 are TEM micrographs of a triblock, PCHD-PI-PCHD (no. 7 in Table 1), and a pentablock copolymer, PCHD-PS-PI-PS-PCHD (no. 8), respectively. PCHD domains are dispersed in the PI matrix, which is quite common in ABA type thermoplastic elastomers. The pentablock copolymer shows finer morphology than the triblock copolymer.

Conclusions

Although the controllability of anionic homo- and copolymerization of 1,3-CHD is lower than that of styrene even in the presence of TMEDA, a series of tri-, penta-, and heptablock symmetrical copolymers containing PCHD segments were successfully synthesized using a dilithium initiator. The efficiency of the dilithium initiator is greatly enhanced by means of a multistep seeding procedure, which not only affords the high content of 1,4-enchainment in the central block but also ensures a relatively narrow distribution of the product when the polymerization media was switched from aploar to polar ones.

The morphology and clearly separated T_gs in some cases demonstrate phase separation between PCHD and PI segments. The block copolymers show typical stress–strain behavior of thermoplastic elastomers. Of special interest is the high T_g of the hard block, which means that the copolymers can be regarded as a new class of thermoplastic elastomers for use at high temperatures when the polyisoprene block has been hydrogenated.

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