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Initiation via Haloboration in Living Cationic Polymerization. 3. Synthesis and Characterization of Functional Star-Branched Polyisobutylenes

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ABSTRACT: Functional star-branched polyisobutylenes (PIBs) were prepared in high yield based on living cationic polymerization via haloboration initiation. First, living PIBs carrying Cl_2B- head groups were prepared via haloboration initiation. Subsequently, the living ends were reacted with a small amount of divinylbenzene (DVB). The products were completely soluble and consisted of a cross-linked core of poly(DVB) to which almost-monodisperse PIB chains were radially attached. The star-branched PIBs were characterized by solution and solid-state NMR spectroscopy and size-exclusion chromatography using triple detection, RI, UV, and light scattering detectors.

Introduction

Recently we reported that using polar solvents in the presence of a proton trap to prevent initiation from protic impurities, BCl_3, alone can initiate the polymerization of isobutylene (IB).[1] Kinetic and mechanistic studies supported the proposed new initiation mechanism via haloboration and explained the apparent livingness of the polymerization.[2] The products are low molecular weight asymmetric telechelic polymers that are difficult to obtain by conventional methods, carrying a Cl_2B- head group and a *tert*-chloro end group. By using BBr_3/BCl_3 mixtures or the combination of BCl_3 with $TiCl_4$ as coinitiators, the molecular weight range was extended to a range of 1000−150 000.[3] These polymers are valuable intermediates to obtain asymmetric telechelic polyisobutylenes (PIBs) carrying a variety of functionalities. The head groups can be quantitatively converted to $(MeO)_2B-$ by quenching with methanol.[4] Hydrolysis of $(CH_3O)_2BCH_2C(CH_3)_2-PIB-CH_2-C(CH_3)_2Cl$ or $Cl_2BCH_2C(CH_3)_2-PIB-CH_2-C(CH_3)_2Cl$ with water under alkaline or acidic conditions led to a transformation to the corresponding boronic acid head groups.[4] Oxidation of $(CH_3O)_2BCH_2C(CH_3)_2-PIB-CH_2-C(CH_3)_2Cl$ by alkaline hydrogen peroxide in tetrahydrofuran at room temperature afforded α-hydroxy-ω-chloropolyisobutylenes in quantitative yields.[4]

Since the ω-chloro end is the dormant form in the living carbocationic polymerization of IB, it occurred to us that novel functional multiarm star polymers could be prepared by the use of well-established procedures demonstrated for the synthesis of multiarm star polymers by living anionic polymerization using divinylbenzene (DVB) as a linking agent.[5−11] The corresponding living cationic technique was not available until recently. The result of subsequent research was reported in a patent application filed December 1993.[12] About the same time Marsalko, Majoros, and Kennedy independently published a paper on the synthesis and proof of structure of multiarm star PIBs.[13] The synthesis involved the living polymerization of IB by the 2,4,4-trimethyl-2-chloropentane (TMPCl)/$TiCl_4$/triethylamine/dichloromethane−hexane 50:50 (v/v)/−40 °C system and the addition of DVB linking agent at complete monomer conversion. Since their method of preparation, namely, the arm first method, and the linking reaction are virtually identical to those of our method, in this publication we focus on the characterization of our functional multiarm star PIBs.

Experimental Section

A. Materials. Divinylbenzene (DVB), a mixture of DVB (78%) and ethylvinylbenzene (20%), was provided by Polysciences, Inc. Purification involved washing it with a 10% aqueous sodium hydroxide solution, followed by distilled water until neutral. After drying over $MgSO_4$, it was distilled from CaH_2 at a reduced pressure. Traces of water remaining after treatment with $MgSO_4$ were removed by adding dibutylmagnesium (DBM; 14 wt % heptane solution; Lithco) to DVB, followed by vacuum distillation. Boron trichloride (99.9%; Aldrich), boron tribromide (99.9%; Aldrich), 2,6-di-*tert*-butylpyridine (DTBP; 99.4% by GC; Aldrich), and methanol (reagent grade) were used as received.

B. Procedures. The preparation of the polyisobutylene arm was carried out at −40 °C in a MBraun 150M stainless steel glovebox. A 250-mL three-neck flask or 75-mL test tubes were used as polymerization reactors. The addition sequence of the reagents was (a) solvent (CH_2Cl_2), (b) proton trap (DTBP), (c) monomer (IB), and (d) Lewis acids (BCl_3 or BBr_3).

1. For the synthesis of star polyisobutylenes with longer arms, BCl_3 was used. IB (0.94 M) was polymerized in the presence of DTBP (4.7 mM) using BCl_3 (0.5 M) at −40 °C in dichloromethane for about 3 h, which led to PIB ($M_n = 3000-4000$) with narrow molecular weight distribution ($M_w/M_n < 1.3$). After polymerization, the reaction mixtures were warmed to room temperature and the excess boron trichloride and CH_2Cl_2 were evaporated. CH_3Cl/hexane (40/60, v/v) was added to dissolve the polymer (13.9 mM), followed by the addition of $TiCl_4$ (27.4 mM). The temperature was lowered to −60 °C, and DVB was introduced. After the required reaction time, the linking reaction was terminated by adding prechilled methanol. The polymer was purified by repeated dissolution−precipitation using dichloromethane/hexane−methanol and dried in vacuo. In contrast to products obtained using CH_2Cl_2/hexane (40/60, v/v) for the linking reaction that resulted in a moderate amount of insolubles, the star polymer obtained in CH_3Cl/hexane (40/60, v/v) was completely soluble and therefore this solvent mixture was utilized.

2. For the synthesis of star PIBs with shorter arms ($M_n \sim 400$), BBr_3 was used in CH_2Cl_2 at −40 °C. Since the polymerization was rather slow (~35% conversion in 4 h; $M_n \sim 400$, $M_w/M_n = 1.2$), the unreacted monomer was evaporated after 4 h of polymerization by warming the solution to room temperature. The mixture was cooled to −60 °C, and BCl_3 was added. Then DVB was introduced. The reactions were terminated by adding prechilled methanol. The polymer was purified as above.

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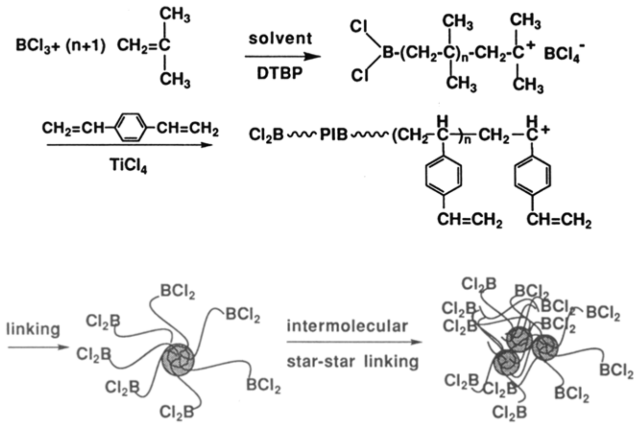
Scheme 1



Molecular weights were measured using a Waters HPLC system equipped with Model 510 HPLC pump, Model 410 differential refractometer, Model 486 UV/vis detector, Model 712 sample processor, and five ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. The flow rate of THF was 1.0 mL/min. For characterization of PIB arms data acquisition and computing using a calibration curve obtained by well-characterized narrow MWD (<1.1) PIB (made by living polymerization), a Waters Baseline chromatography workstation was used. The molecular weights of the star polymers were measured with the same GPC system, using a miniDAWN multiangle laser light scattering detector (Wyatt Technology Inc.). As the refractive index increments (dn/dc) were unknown, 100% recovery of the injected mass was assumed in the calculations. The absolute molecular weights, molecular weight distributions (MWDs), and the average dn/dc values were calculated with the ASTRette software. On the basis of the composition, M_n(arm), and M_n(star), the number of arms per molecule (f) and the number-average core molecular weight (M_n(core)), defined by eqs 1 and 2, were calculated.

$$f = (\text{weight fraction of isobutylene}) \times M_n(\text{star})/M_n(\text{arm}) \tag{1}$$

$$M_n(\text{core}) = (\text{weight fraction of DVB}) \times M_n(\text{star}) \tag{2}$$

It should be noted that f is the “average” number of arms per molecule, because the star polymer is not “monodisperse” in arm number and in molecular weight. The star polymer yields were obtained based on the calculated eluted mass of the unlinked PIB arm. For instance, a 94% yield indicates that 6% of the PIB arms remained unattached.

Solution ^{1}H NMR spectra were obtained at 270 MHz with a Bruker WP-270 spectrometer in $CDCl_3$. Solid-state ^{13}C NMR spectra were obtained with a Chemagnetics CMX-200 instrument (^{13}C frequency 50 MHz) with ^{1}H dipolar decoupling and magic angle sample spinning at a rate of about 6000 Hz.

Results and Discussion

1. Star-Branched Polyisobutylene Synthesis.

Scheme 1 describes the synthesis of star PIB.

The results for DP_n(arm) = 6 are shown in Table 1 and Figure 1. On addition of DVB to the polymer solution, linking proceeds immediately. After 10 min according to Figure 1 and Table 1, most of the linear PIB arms have been linked to form the star-branched polymer with a much higher molecular weight. A small peak with an elution volume close to that of the linear arm, exhibits an intense UV response. Therefore, it is most likely a linear polymer containing a few units of DVB. With increasing reaction time, the concentration of this product decreased, while the concentration and the molecular weight of the star polymer increased. After 4 h, the linear PIB arm is completely consumed as shown in Table 1, and star polymer with a relatively narrow molecular weight distribution (M_w/M_n = 1.4) was obtained.

Table 1. Star-Shaped PIBs Obtained at Varying Reaction Times (DP_n(arm) = 6)[a]

reaction time	M_n(star) × 10^{-3} LS	M_n(star) × 10^{-3} GPC	M_n(core) × 10^{-3}	f	yield (%)
0		0.4			
10 min	7.7	1.1	5.9	6	95
30 min	7.7	1.5	5.9	6	97
1 h	8.0	1.6	6.1	6	98
4 h	11.0	1.9	8.4	9	100
14 h	11.8	1.9	9.0	9	100

[a] Reaction conditions: polymerization, $BBr_3/CH_2Cl_2/-40$ °C; linking reaction, $BCl_3/CH_2Cl_2/-60$ °C. [DVB]/[PIB] = 7. [PIB] = 46.9 mM. f = average arm number.

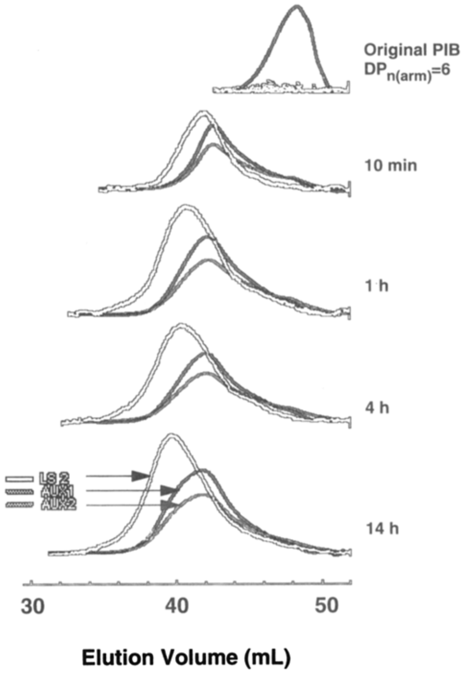


Figure 1. GPC traces (LS, laser light scattering detector signal; AUX1, RI detector signa; AUX2, UV detector signal) of the original PIB (DP_n(arm) = 6) and star-branched PIB obtained after different linking times.

Table 2. Star-Shaped Polyisobutylene Obtained at Varying Reaction Times (DP_n(arm) = 69)[a]

reaction time	M_n(star) × 10^{-3} LS	M_n(star) × 10^{-3} GPC	M_w/M_n	M_n(core) × 10^{-3}	f	yield (%)
0	3.9	3.6	1.2			
10 min	26.0	5.4	1.6	8.1	5	47
30 min	37.9	7.7	1.8	11.8	7	66
1 h	40.5	9.1	2.0	12.6	7	73
4 h	53.5	14.3	2.9	16.6	9	86
14 h	265.0	104.8	3.8	77.3	44	94

[a] Reaction conditions: polymerization, $BCl_3/CH_2Cl_2/-40$ °C; linking reaction, $TiCl_4/CH_3Cl$/hexane (40/60, v/v)/−60 °C. [DVB]/[PIB] = 10. [PIB] = 13.9 mM. f = average arm number.

Similar results were obtained for DP_n(arm) = 69 (Table 2 and Figure 2). The linking reaction, however, was slower, and the final yield of star polymer did not reach 100%. M_n(star) increases linearly with star polymer yields up to 4 h (86% yield). However, there is a large increase in the molecular weight from 4 to 14 h, while the conversion of the linear polymer to star-branched polymer increased from 86 to 94% only. It indicates that at longer reaction times the intermolecular star−star linking reaction is predominant. When the CH_2Cl_2/hexane (40/60, v/v) solvent system was used

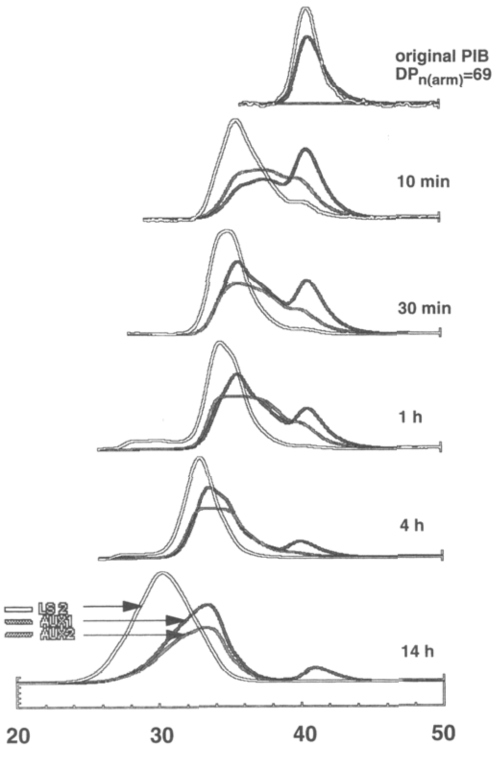


Figure 2. GPC traces (LS, laser light scattering detector signal; AUX1, RI detector signal; AUX2, UV detector signal) of the original PIB (DP_n(arm) = 69) and star-branched PIB obtained after different linking times.

for the linking reaction, the star–star linking was much faster and occurred simultaneously with linking of the PIB arms. This reaction was not observed when BCl_3 was used; therefore, we suggest that intermolecular alkylation is responsible for the star–star linking. Intermolecular alkylation has been observed in the polymerization of styrene[14] and *p*-methylstyrene[15] under similar conditions.

The M_n(star) values for DP_n(arm) = 6 as well as for DP_n(arm) = 69 (Tables 1 and 2) obtained by light scattering are clearly higher than the corresponding values based on a calibration curve obtained with linear PIB standards. It is well established that the hydrodynamic volume of a star-branched structure is smaller (i.e., the polymer is more compact) than the linear counterpart of the same molecular weight. M_n(star)s were calculated by assuming constant composition over the GPC trace, which, as was pointed out by one of the reviewers, may not hold. Therefore, the refractive index increment may not be constant, giving rise to uncertainty in M_n(star) and consequently in the number of arms, *f*. Since PIB is UV transparent, change in the star polymer composition over the GPC trace can be evidenced by a corresponding change in the RI/UV (or UV/RI) ratio. The RI/UV ratio plotted vs elution volume across the GPC trace is shown in Figure 3 for the star-branched polymer obtained after 14 h (last entry in Table 2). The ratio remains fairly constant across the GPC trace; therefore, our assumption is validated.

2. Effects of Reaction Conditions. The effects of DP_n(arm), and the DVB/PIB mole ratio, on the yield, M_n(star), and the number of arms (*f*) were investigated. The results are summarized in Table 3.

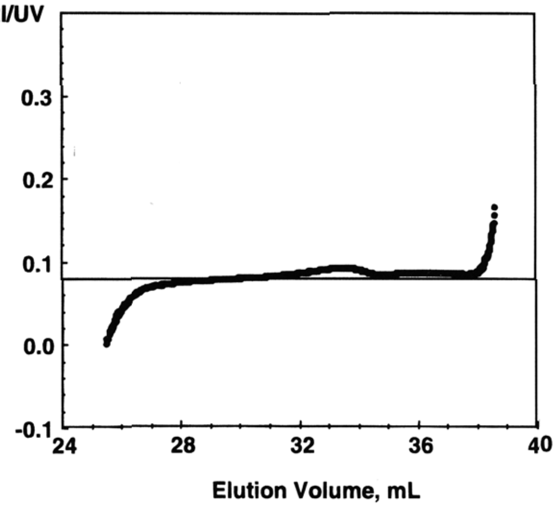


Figure 3. RI/UV ratio vs elution volume across the GPC trace for the star-branched polymer obtained after 14 h (last entry in Table 2).

Table 3. Effect of Reaction Conditions[a]

DP_n(arm)	[DVB]/[PIB]	M_n(star) × 10^{-3} LS	GPC	M_n(core) × 10^{-3}	*f*	yield (%)
88	5	24.6	17.5	4.5	4	47
88	7	36.0	21.9	8.6	6	61
88	10	41.1	26.6	12.8	6	74
109	]5	24.5	19.7	2.5	4	10
109	7	25.2	20.6	3.4	4	28
109	10	35.1	26.9	6.5	5	46

[a] Linking reaction time: 4 h. Reaction conditions: polymerization, $BCl_3/CH_2Cl_2/-40$ °C; linking reaction, $TiCl_4/CH_3Cl$/hexane (40/60, v/v)/−60 °C. *f* = average arm number.

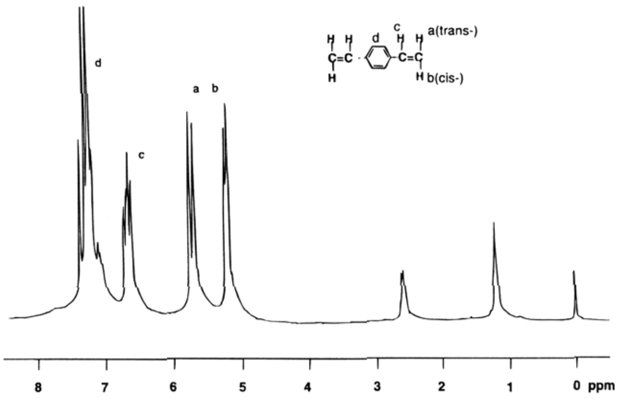


Figure 4. ^{1}H NMR spectrum of DVB (78%).

As shown in Table 3, the yield and M_n(star) depend on the reaction parameters. As expected, with constant DP_n(arm), the yield, M_n(star), and *f* increased with an increase of the DVB/PIB mole ratio. The increase in the DVB/PIB mole ratio leads to a parallel increase in M_n(core); however, *f* increases only modestly. This may suggest that styryl cations add to the double bonds faster than PIB cations. With constant *r*, higher yields were obtained in 4 h with lower DP_n(arm), most probably due to the higher concentration of the living centers. *f* also increased as DP_n(arm) decreased. A similar effect was found in the synthesis of star-shaped polymers of alkyl vinyl ethers,[11] and it was concluded that the intermolecular linking reaction is sterically less hindered for a shorter chain.

3. NMR Characterization of Star-Shaped Polymers. Solution ^{1}H NMR Spectroscopy. Figures 4–6 show the solution ^{1}H NMR spectra of DVB (80%) and the products of linking reactions with PIBs of DP_n(arm) = 69 and 6, respectively. For DP_n(arm) = 69, after 10 min the resonances corresponding to the vinyl protons (5.15, 5.62, 6.60 ppm) and aromatic ring (7.2

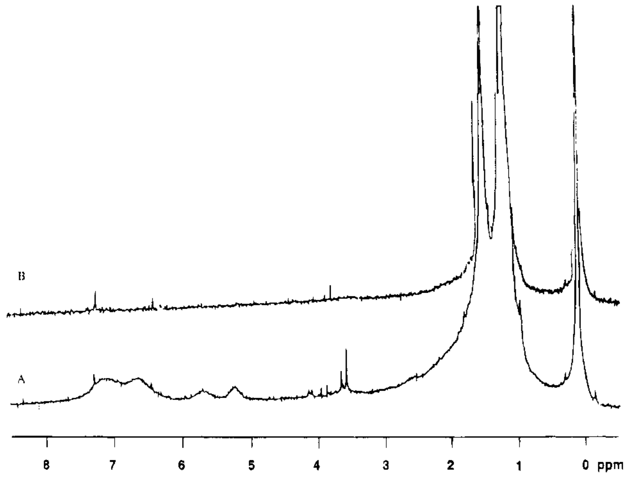


Figure 5. ^1H NMR spectra of star-branched PIB (DP_n(arm) = 69): (A) 10 min and (B) 14 h after addition of DVB. The peak at 3.5 ppm is assigned to the $(CH_3O)_2B-$ head group.

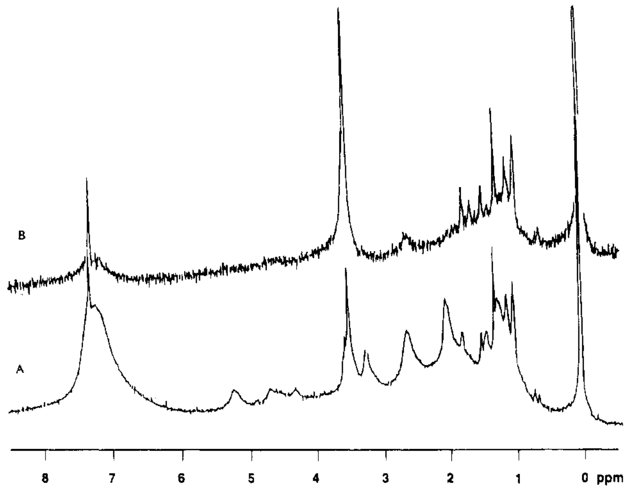


Figure 6. ^1H NMR spectrum of star-branched PIB (DP_n(arm) = 6): (A) 10 min and (B) 14 h after addition of DVB.

ppm) are seen, as are the protons of PIB (CH_2 at 1.40 ppm and CH_3 at 1.10 ppm). After 14 h, however, all of the DVB-related signals are absent, while the PIB resonances are still visible. For DP_n(arm) = 6, initiation of the star-forming reaction is so fast that the vinyl groups disappeared in 10 min; the aromatic ring protons are still visible at 10 min but are nearly gone after 14 h. These results are consistent with the formation of a star-shaped polymer with mobile PIB arms and a DVB microgel core. The core initially has some degree of intramolecular mobility but hardens as cross-linking progresses. The loss of intramolecular mobility eventually causes the ^1H NMR signals of the core to be broadened beyond detectability.

Solid-State ^{13}C NMR Spectroscopy. Two different types of solid-state ^{13}C NMR experiments were used to prove the structure and degree of molecular mobility of the star PIB components. Bloch decay (direct acquisition) with a long relaxation delay time between scans provides quantitative ^{13}C spectra for the determination of composition. The same technique using short relaxation delay times suppresses the signals from rigid (and therefore slowly relaxing) components of the polymer, providing a spectrum of mainly the mobile components. The cross-polarization (CP) technique transfers magnetization from hydrogen to ^{13}C during a period called the contact time. Rigid species cross-polarize quickly, giving a maximum signal in short contact times (on the order of 1 ms or less), while mobile species cross-polarize inefficiently if at all, requiring longer contact times to reach a maximum signal. Thus, the Bloch decay and CP experiments are complementary in discriminating mobile and rigid species.

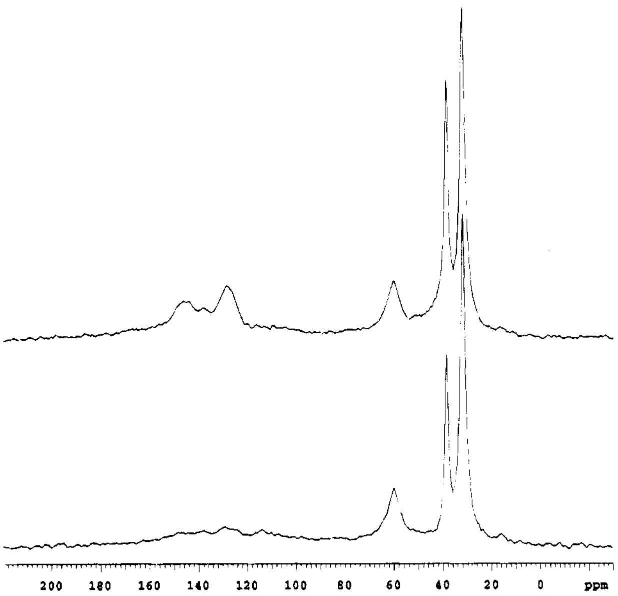


Figure 7. Solid-state Bloch decay ^{13}C NMR spectra of star-branched PIB (DP_n(arm) = 69) with relaxation delays (top to bottom) 60 and 2 s.

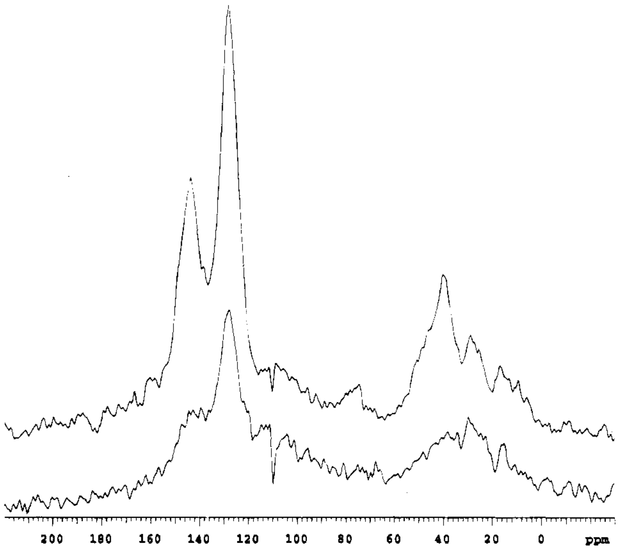


Figure 8. Solid-state Bloch decay ^{13}C NMR spectra of star-branched PIB (DP_n(arm) = 6) with relaxation delays (top to bottom) 60 and 5 s.

Figures 7 and 8 are Bloch decay ^{13}C spectra of star PIBs with different arm lengths. For DP_n(arm) = 69 (Figure 7), the spectrum with a 60-s relaxation delay has signals for the core aromatic carbons (120–160 ppm) and the PIB CH_2, C, and CH_3 (60, 38, and 32 ppm); the absorption of the core aliphatic carbons occurs in a broad resonance (40–50 ppm) which is mostly obscured by the PIB carbons. When the relaxation delay is reduced to 2 s, the peaks from the mobile, fast-relaxing PIB carbons remain about the same size, while the resonances for the rigid, slowly relaxing core nearly disappear. A sample with DP_n(arm) = 6 (Figure 8) behaves similarly, with the PIB peak (only the CH_3 at 32 ppm is large enough to be visible here) remaining constant while the core peaks grow with increasing relaxation delay.

Figure 9 shows the CP ^{13}C NMR spectrum of the sample with DP_n(arm) = 69. The aromatic CH carbons

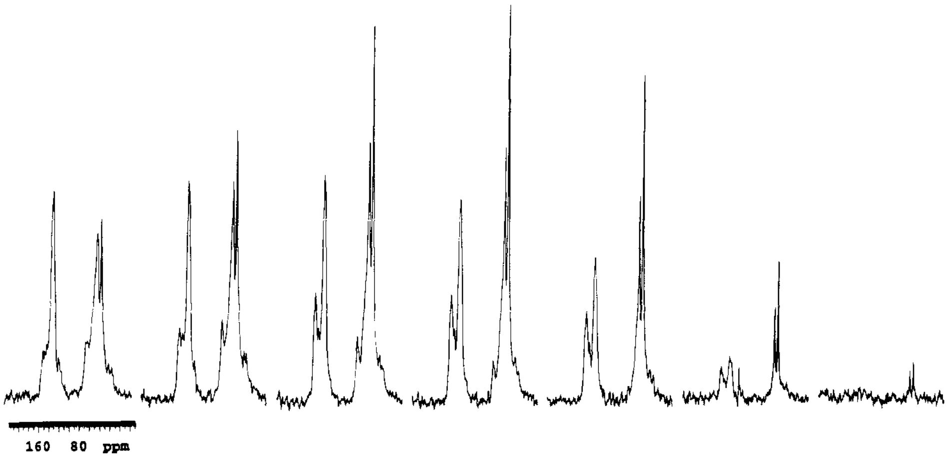


Figure 9. Solid-state CP ^{13}C NMR spectrum of star-branched PIBs (DP$_n$(arm) = 69) with contact times (left to right) 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 ms. The region shown is −30 to +220 ppm.

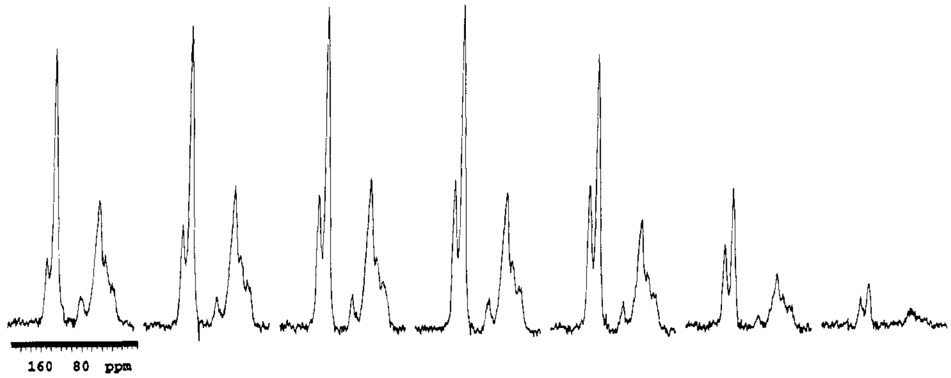


Figure 10. Solid-state CP ^{13}C NMR spectrum of star-branched PIBs (DP$_n$(arm) = 6) with contact times (left to right) 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 ms. The region shown is −30 to +220 ppm.

cross-polarize very quickly, reaching nearly their full intensity in the first spectrum, after 0.1 ms contact time. (The quaternary aromatic carbons, lacking attached hydrogens, require a longer time, as is typical.) The PIB carbon peaks show some intensity at 0.1 ms contact time but then continue their growth more slowly, not approaching their ultimate intensity until 0.5−1.0 ms contact time. Even then, comparison with the quantitative Bloch decay spectrum (Figure 7) shows that the PIB carbons are severely underrepresented in the CP spectrum. This indicates that most of the PIB arm carbons are too mobile to cross-polarize efficiently, and they never polarize to the same degree as the more rigid core carbons. However, a small fraction of the PIB carbons did show intensity at short contact times, suggesting that a few PIB carbons may be in a more restricted environment; presumably these are the PIB carbons closest to the point of attachment to the core.

The DP$_n$(arm) = 6 sample (Figure 10) shows similar rigid behavior for the aromatic core. However, in this case, the PIB arm resonances cross-polarize as efficiently as the core resonances do. This suggests that the arms in this sample are too short to display mobility in the solid state; instead they remain entangled close to the core. In other words, all of the arm carbons in the DP$_n$(arm) = 6 sample suffer the same restriction of motion as the innermost arm carbons of the DP$_n$(arm) = 69 sample.

Conclusion

Functional star-branched PIBs were synthesized via haloboration initiation followed by linking usinv DVB. The structural properties of star PIB such as molecular weight, arm number, and yield are affected by DP$_n$(arm) and [DVB]/[PIB]. The star-branched PIBs were characterized by solution ^{1}H NMR, solid-state ^{13}C NMR, GPC, and light scattering. The results are in line with the structure of star-branched PIB consisting of a cross-linked core of poly(DVB) to which almost-monodisperse PIB chains are radially attached.

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References and Notes

(1) Balogh, L.; Wang, L.; Faust, R. *Macromolecules* **1994**, *27*, 3453.
(2) Balogh, L.; Fodor, Zs.; Kelen, T.; Faust, R. *Macromolecules* **1994**, *27*, 4648.
(3) Wang, L.; Svirkin, J.; Faust, R. *Polym. Mater. Sci. Eng.* **1995**, *72*, 173.
(4) Wang, L.; Svirkin, J.; Faust, R. *Polym. Mater. Sci. Eng.*, to be submitted to *Macromolecules*.
(5) Eschwey, H.; Burchard, W. *Polymer* **1975**, *16*, March, 180.
(6) Lutz, P.; Rempp, P. *Makromol. Chem.* **1988**, *189*, 1051.
(7) Zelinski, R. P.; Wolford, C. F. *J. Polym. Sci., Part A* **1965**, *3*, 93.
(8) Bi, L. K.; Fetters, L. J. *Macromolecules* **1976**, *9* (5), 732.
(9) Gnanou, Y.; Lutz, P.; Rempp, P. *Makromol. Chem.* **1988**, *189*, 2885.
(10) Hadjichristidis, N.; Guyot, A.; Fetters, L. J. *Macromolecules* **1978**, *11* (4), 668.
(11) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24* (9), 2309.
(12) Wang, L.; McKenna, S. T.; Faust, R. MacroAkron, Abstract, **1994**, 95.
(13) Marsalko, T. M.; Majoros, I.; Kennedy, J. P. *Polym. Bull.* **1993**, *31*, 665; MacroAkron, Abstract, **1994**, 79.
(14) Fodor, Zs.; Györ, M.; Wang, H. C.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *30* (5), 349.
(15) Fodor, Zs.; Faust, R. *J. Macromol. Sci.* **1994**, *31* (12), 1983.

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