Novel Polyisobutylene Stars. XXVIII. A star block comprising three poly (isobutylene-*b*-acrylonitrile) arms radiating from an aromatic core: Synthesis and characterization*

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Summary

The synthesis and characterization of a novel three arm star-block comprising a cumyl core out of which radiate three poly(isobutylene-b-acrylonitrile) arms is presented. The synthesis strategy comprised three major steps (see Scheme 1): 1. The synthesis of $\varnothing(PIB\text{-}OH)_3$, 2. Quantitative transformation of the −OH termini to −OCOC(CH$_3$)$_2$Br termini, and 3. Controlled ATRP of acrylonitrile mediated by the latter termini. The definition of a suitable solvent system, methylene chloride/cyclohexanone (CH$_2$Cl$_2$/CHO) was critical for the synthesis. The $\varnothing(PIB\text{-}b\text{-}PAN)_3$, $M_{n,PIB\ block} = 6000$ g/mol and $M_{n,PAN\ block} = 1,800$ g/mol was characterized by solid state ^{13}C NMR spectroscopy, thermal gravimetric analysis, differential scanning calorimetry, and dynamic mechanical analysis.

Introduction

In the course of our continuing investigations on PIB-based star polymers (see ref. 1 and previous papers in this series) we have developed the synthesis of a new family of three arm stars consisting of an aromatic core out of which radiate three poly (isobutylene-*b*-acrylonitrile) (PIB-*b*-PAN) arms. We expected the rubbery PIB and the glassy PAN segments to be incompatible and to form phase segregated domains, and thus anticipated the formation of novel TPE's. The synthetic strategy leading to these novel stars was envisioned to involve three major steps (See scheme 1): 1. The synthesis of three-arm star Cl^t-telechelic PIB by living carbocationic polymerization (LC$^\oplus$Pzn)of IB followed by a series of well-known functionalization reactions to -OH termini, [2-7] 2. Quantitative transformation of the −OH arm termini to −OCOC(CH$_3$)$_2$Br termini, and 3. Living/controlled atom transfer radical polymerization (ATRP) of acrylonitrile [8-11] mediated by the latter macroinitaitor. This

paper concerns details of this synthesis, its limitations, and the characterization of the target novel three-arm star polymer.

Experimental

Materials and thier purification

All materials and their purification have been described. [1,3,8,11,12,17]. The synthesis of the macroinitiator was published;[19] M_n=18000 g/mol, M_w/M_n= 1.11.

ATRP of acrylonitrile

A typical procedure for the synthesis of PAN by ATRP was as follows: 40 mg Cu^IBr (0.280 mmol), 140 mg 2,2'-dipyridyl (dpy) (0.9 mmol), 2mL predistilled acrylonitrile monomer (AN), and 2 mL cyclohexanone (CHO) were placed in a 50 mL Shlenk flask and the flask was tightly sealed with a rubber septum. The charge was degassed three times under vacuum, and flushed with nitrogen. $\varnothing[PIB\sim(CH_2)_2CH_2OCOC(CH_3)_2Br]_3$ (0.5 g, 27.7 x 10^{-3} mmol) was dissolved in a mixture of cyclohexanone 2 mL, and methylene chloride 4 mL. The solution was degassed by three freeze-thaw cycles and injected by a syringe into the charge in the Shlenk reactor. The mixture was heated to 60 ºC in an oil bath for 24hrs. The product precipitated from solution during the of polymerization. The final product was filtered, washed several times with methanol, and extracted by hexanes for 24 hrs. The final product was dried in a vacuum oven at room temperature for 48hrs.

Characterization

The molecular weights of PIB were determined by ^1H NMR spectroscopy using a varian Gemini-300 MHz instrument at ambient temperature.

Solid-state ^{13}C NMR spectra were obtained by a Varian Unityplus-200 (4.7T) spectrometer with a Doty Scientific Extended VTMAS probe. The sample was packed to a 7 mm silicon nitride rotor with Kel-F end caps and spectra were acquired with 2.2 KHz magic angle spinning speed at 160°C. ^{13}C chemical shifts were corrected by using hexamethylbenzene (δ_{Me}=17.3ppm) as external reference. For purposes of quantitation, a ^{13}C spin lattice relaxation measurement was performed to determine the longest ^{13}C T_1 (1.7 sec). The ^{13}C Bloch decay spectrum was acquired by using 10 sec relaxation delay, 4.6 μs 90° pulse, and 60 KHz decoupling field, with a total experiment time of 7.5 hrs.

T_g's were determined by a Dupont Instrument, Model DSC2910) differential scanning calorimeter. Samples were heated to 150 ºC at 10 ºC/minute to remove thermal history effects and then cooled to -100ºC. The heating and cooling cycles were repeated three times and the thermograms were recorded during the third cycle. The thermal stability was studied by a thermogravimetric analyzer (TA instruments Model HI-Res TGA 2950) under N_2 by heating samples from ambient to 150 ºC at 10 ºC/min.

DMA spectra were obtained using a dynamic mechanical spectrometer (Advanced Rheometric Expansion System). Copolymer samples were prepared by molding 200

mg of Ø(PIB 6K-*b*-PAN 1.8K)₃ between 8 mm diameter parallel plates at 125 °C for 30 minutes. The gap between the plates was 0.5 mm. The spectrometer was equipped with a 200-2000 g.cm dual range force rebalance transducer. The method allows to command a sinusoidal strain at a constant frequency of 1.0 rad/s and 1% strain while taking successive measurements to obtain the temperature dependence of G' and G" in the 30°C to 300 °C range. The ramp rate was 2.0 °C/minute.
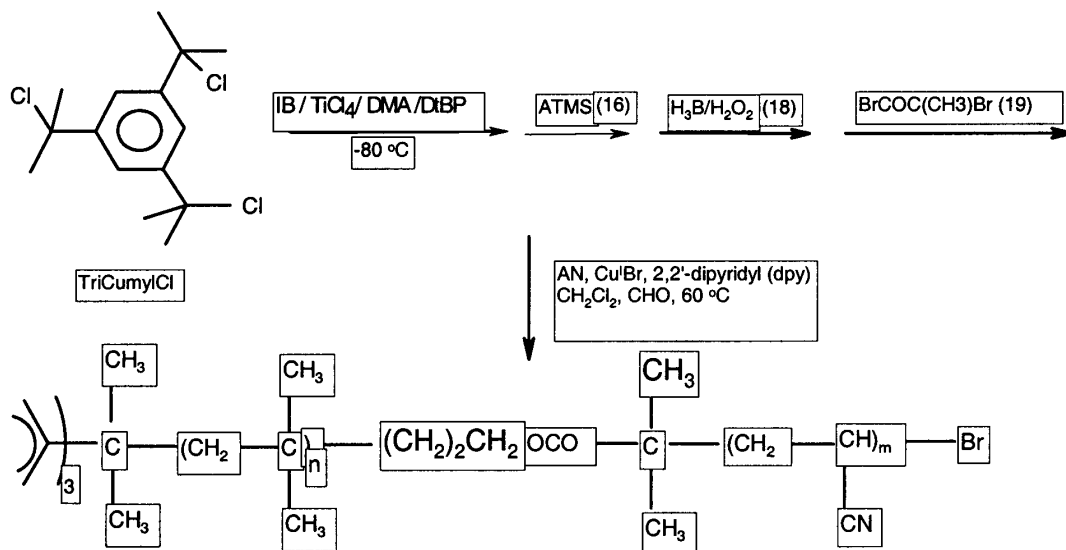
Scheme 1. Strategy for the synthesis of Ø(PIB-*b*-PAN)₃.

Results and Discussion

Synthesis of the Ø[PIB~(CH₂)₂CH₂OCOC(CH₃)₂Br]₃ macroinitiator

The quantitative conversion of the −Cl^t termini of PIB[1] to −OCOC(CH₃)₂Br groups occurred in three steps: 1. First by the in situ quantitative conversion of −Cl^t termini to −CH₂CH=CH₂ groups.[16] 2. Quantitative conversion of the allyl groups to −OH termini,[18] and, 3. Quantitative conversion by bromoisobutyrylbromide[19] to the sought macroinitiator Ø[PIB~(CH₂)₂CH₂OCOC(CH₃)₂Br]₃. The ¹H NMR spectrum of the latter and its quantitative analysis has been described.[19]

ATRP of AN

The finding of a suitable solvent medium was a key development for the synthesis of Ø(PIB-*b*-PAN)₃. The challenge was to identify a solvent or solvent system that dissolves the non-polar PIB-based macroinitiator, and at the same time, is conducive for the ATRP of AN to PAN. PAN is a highly polar solid insoluble in its own monomer, and soluble only in a few special solvents. In addition to these solubility demands due to the different polymer moieties, the maintenance of the stability of the active Cu^{I}Br-dpy complex during ATRP was a further critical requirement.

Initial experiments indicated that various solvents (benzene, toluene, xylene, anisole) and solvent mixtures (toluene/ethylene carbonate, toluene/dimethyl sulphoxide, carbon tetrachloride/ethylene carbonate, tetrahydrofuran/dimethyl formamide), some of which have been found suitable for the ATRP of monomers other than AN (e.g., MMA, see ref., 20), could not be used because PAN is insufficiently soluble in them and because the catalytic Cu^I site is unstable during the ATRP of AN (the brown Cu^I changes to green Cu^{II} indicating oxidation of Cu^I to Cu^{II} in less than one hour).

While we were unable to identify an ideal medium for the envisioned ATRP blocking of AN from PIB, we have found that CH_2Cl_2/CHO mixtures maintain the catalytic activity of Cu^I centers and keep the star-block in solution for a sufficient length of time before precipitation occurs. Precipitation prevents the formation of PAN segments higher than ~ 1800 g/mol. Thus CH_2Cl_2 is a good solvent for the macroinitiator and we have shown that it stabilizes the Cu^Idpy

complex for at least 24 hours; however, CH_2Cl_2 cannot be used for the ATRP of AN, because it is a nonsolvent for PAN and its boiling point is too low (40 ºC). CHO stabilizes the Cu^Idpy complex, has a sufficiently high bp (155 ºC) for ATRP but it is a nonsolvent for the macroinitiator. Gratifyingly, 1:1 vol. CH_2Cl_2/CHO mixtures exhibit most of the necessary requirements except they have limited solubility for the growing PAN block above ~ 1800 g/mol. We have used this solvent system for the synthesis of well defined target three arm stars blocks, Ø(PIB-*b*-PAN)$_3$, of limited block molecular weights, $M_{n,PIB\ block}$ <18,000 g/mol and $M_{n,\ PAN\ block}$ <1,800 g/mol.

Characterization

Figure 1 shows the FT-IR spectrum of ∅(PIB 6K-*b*-PAN 0.106K)$_3$. The spectrum shows the characteristic stretches of (**CH$_3$, CH$_2$**) of PIB at 1375 and 1425 cm^{-1} respectively, and the characteristic (**C≡N**) peak of PAN at 2240cm^{-1}. The prominent peak at 1700 cm^{-1} is attributed to the carbonyl group of the macroinitiator ∅[PIB~(CH$_2$)$_2$CH$_2$**OCOC**(CH$_3$)$_2$Br]$_3$.

^{1}H NMR Spectroscopy

When the molecular weight of the PAN segment is <1000 g/mol, the PIB segment can pull the PAN segment into THF, CH_2Cl_2, CHCl$_3$ and hexanes solutions. Figure 2 shows the ^{1}H NMR spectrum of Ø(PIB 6K-*b*-PAN 0.106K)$_3$. Integration of the methine proton -CH$_2$–**CH**(CN)- of the PAN segment at δ =3.15 ppm relative to the three aromatic protons (internal control) at δ = 7.19 ppm indicates the presence of two AN units blocked to each PIB arm. When $M_{n,PAN\ block}$ >1000 g/mol, Ø(PIB-*b*-PAN) becomes insoluble in common solvents and ^{1}H NMR spectroscopy becomes difficult.

^{13}C NMR Spectroscopy

Due to the insufficient solubility of ∅(PIB-*b*-PAN)$_3$ in common solvents and consequent difficulty with ^{1}H NMR spectroscopy, representative samples with $M_{n,PIB\ block}$ >1000 g/mol, were characterized by solid-state ^{13}C NMR spectroscopy. Figure 3 shows the spectrum obtained with ∅(PIB 6K-*b*-PAN 1.8K)$_3$. Integration of the
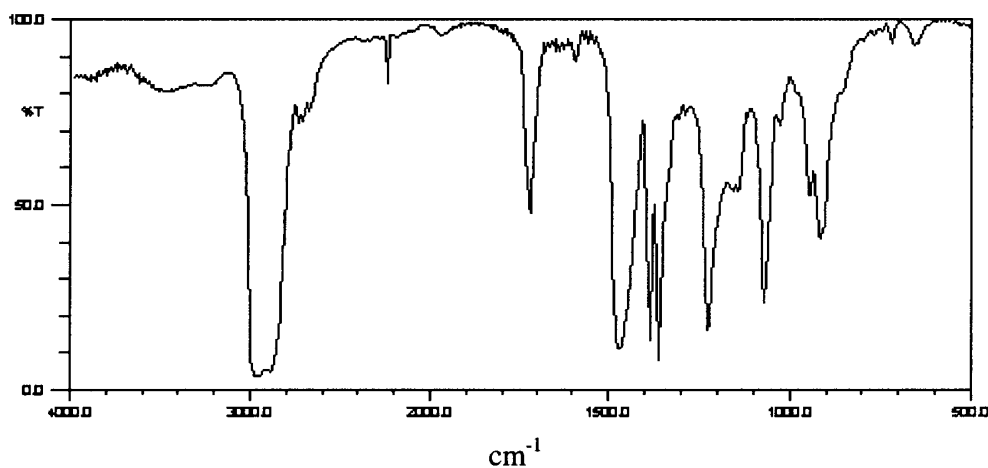
Figure 1. FT-IR spectrum of ∅(PIB 6K-*b*-PAN 0.106K)₃

Figure 2. ¹ H NMR spectrum of ∅(PIB 6K-*b*-PAN 0.106K)₃ .

(C≡N), resonance at δ =120 ppm, relative to the quaternary carbon of PIB at δ = 60 ppm indicates block formation and the presence of a star-block of ∅(PIB 6K-*b*-PAN 1.8K)₃. Due to the high temperature used, the methine carbons of PAN overlap with the methyl carbons of PIB at δ = 31 ppm, and the methylene carbons of PIB and PAN
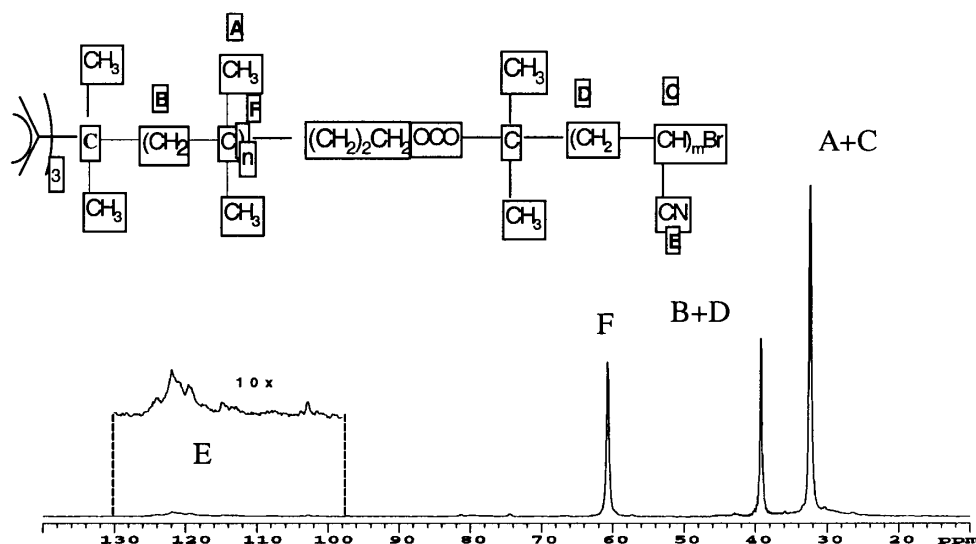
groups appear at 39 ppm.

Figure 3. Solid state ^{13}C NMR spectrum of Ø(PIB 6K-*b*-PAN 1.8K)$_3$

Thermal properties

The thermal stability of Ø(PIB 6K-*b*-PAN 1.8K)$_3$ has been studied by TGA in N$_2$. As shown by the thermogram in Figure 4, this block loses 5% of its weight at 150 °C . Interestingly, the TGA trace indicates smooth thermal degradation and levels off at ~ 7% weight loss at ~230 °C. This fact together with the observation that the color of the initially white product turns brown during heating suggest extensive thermal cyclization of the PAN blocks[21] which enhances the thermal stability of the partially degraded star-block. The DSC trace (not shown) indicates two T_g's (PIB at - 61.2°C and PAN at 81.3 °C), which suggests microphase separation between the PIB and the PAN domains. The glass transition of the PAN segment is difficult to observe because of its relatively low molecular weight.
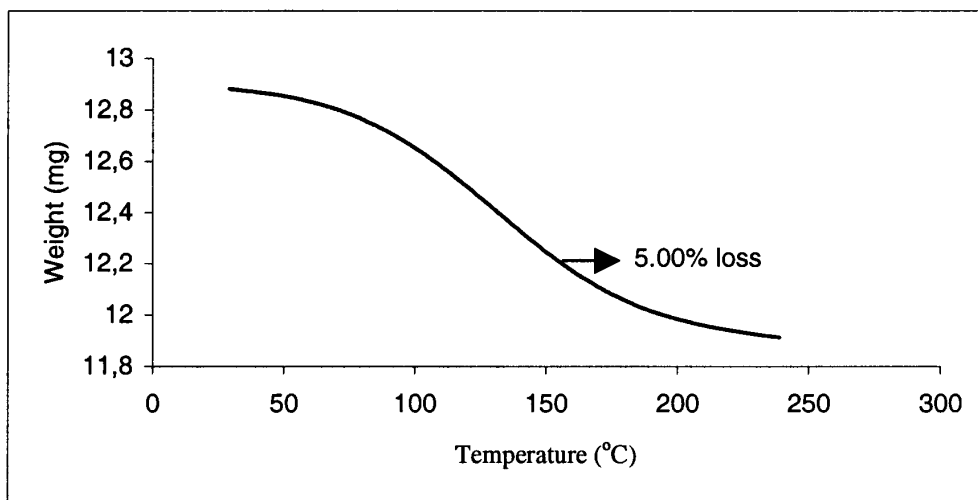

Figure 4. TGA trace of Ø(PIB 6K-*b*-PAN 1.8K)$_3$

Dynamic mechanical analysis

Figure 5 shows the storage modulus (G') and loss modulus (G"), as a function of temperature of Ø(PIB 6K-*b*-PAN 1.8K)$_3$. Both moduli, G' and G", are flat up to ~100 °C, however, after this range the mechanical properties (particularly visible by the G' trace) show an unexpected increase. This phenomenon may be due to intermolecular crosslinking mediated by -CN groups. The material starts to lose mechanical properties beyond ~ 250 °C as indicated by the drop in G' and G".

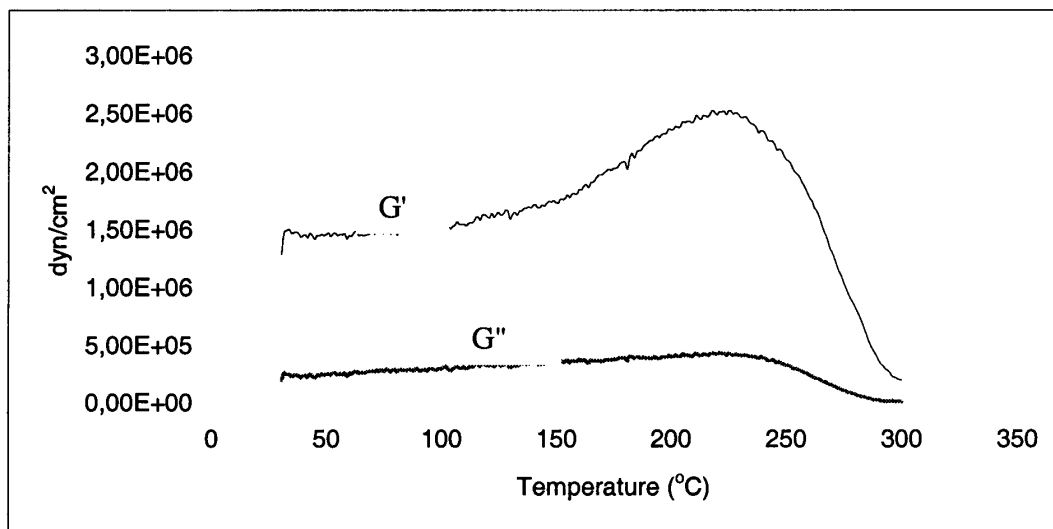**Figure 5**. Storage modulus (G') and loss modulus (G") vs. temperature for Ø(PIB 6K-*b*-PAN 1.8K)$_3$

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