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Multi-arm star-branched polyisobutylene ionomers

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Summary

A series of multi-arm star-branched polyisobutylenes was synthesized *via* living carbocationic polymerization. Arms with molecular weights ranging from 10,000 to 30,000 g/mol were prepared using the cumyl chloride/$TiCl_4$/pyridine initiation system in 60/40 (v/v) hexane/methyl chloride at -80°C and linked by sequential addition of divinylbenzene. The weight average number of arms per star polymer, $\overline{N}_w$, scaled inversely with arm molecular weight and ranged from 32 to 5. Star-telechelic ionomers were produced by sulfonation of the aromatic initiator residue at the end of each arm, followed by neutralization. Sulfonation was quantitative as indicated by acid-base titration. Potassium ionomers were elastic solids which were marginally soluble in THF; the precursors were tacky and freely soluble in THF. Ionic modification did not alter the glass transition temperature (-66°C), but the thermal decomposition temperature in N_2 was increased from 375 to 400°C.

Introduction

The synthesis of multi-arm star-branched polyisobutylenes (PIB)s with arms end-capped by a single aromatic ring have recently been reported. (1) Their synthesis involved initiation of living isobutylene (IB) polymerization using the 2-chloro-2-propylbenzene (cumyl chloride) (CumCl)/$TiCl_4$/pyridine initiation system in 60/40 (v/v) hexane/methyl chloride at -80°C. The monofunctional PIB chains were linked *in situ* by addition of divinylbenzene (DVB) in 10-fold excess relative to PIB chain ends.

The use of CumCl as the initiator for the PIB arms enables the synthesis of highly functional star-telechelic polymers by post-polymerization reactions involving the terminal aromatic moieties. This paper describes sulfonation of the aromatic rings, followed by neutralization with a base, to form star-telechelic ionomers, as shown in Figure 1. Such modification is expected to profoundly affect the bulk physical properties of the star polymers by creating a thermally reversible network through intermolecular aggregation of the ionic chain ends.

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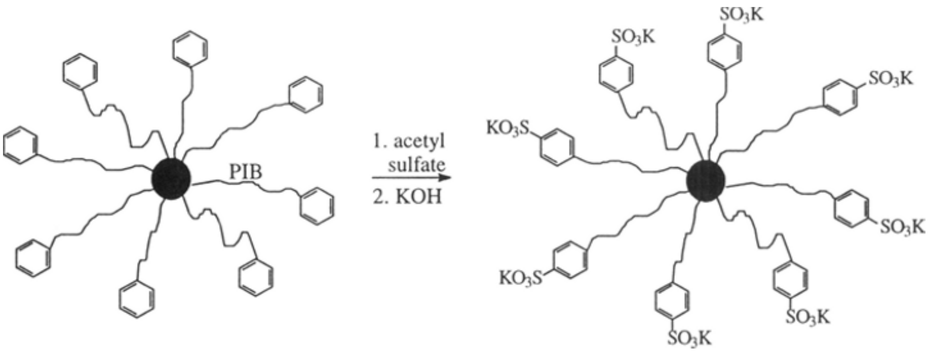

Figure 1: Star-telechelic ionomer with polyisobutylene arms and divinylbenzene core.

Experimental

Sulfonation of Polyisobutylene Multi-Arm Star-Branched Polymers. Preparation and molecular weight characterization of the precursor star polymers have been described. (1,2,3) Sulfonated star-telechelic ionomers were prepared by sulfonation of the aromatic cumyl end groups, using acetyl sulfate, followed by titration of the sulfonated polymer with the appropriate amount of potassium hydroxide solution. A representative sulfonation procedure was as follows: Into a 250 mL round bottomed flask equipped with a magnetic stirrer and condenser were charged 2.22 g of the star polymer ($\overline{M}_{w,star}$ = 440,000 g/mol) and 41 mL $MeCl_2$. Acetic anhydride, 0.04 g (3.9×10^{-4} mol), was added to the stirred solution, and stirring was continued for 10 min, after which time 0.02 g sulfuric acid (2.0×10^{-4} mol) was added. The reaction mixture was allowed to reflux at 42°C with stirring for 6 h. The polymer solution was then steam stripped by slowly pouring the solution into vigorously stirred, boiling deionized (DI) water. The white crumb was collected by filtration, washed with DI water several times, kneaded in acetone to remove water and residual acetic acid, and vacuum dried at 60°C for 24 h.

Analytical Titration of Sulfonated Multi-Arm Star-Branched Polyisobutylene. The concentration of sulfonic acid groups in the sulfonated star polymer was determined as follows: Into a tared 250 mL Erylmeyer flask equipped with a magnetic stirrer were charged ~0.5 g of sulfonated star polymer in 100 mL THF and a few drops of phenolphthalein solution in ethanol. The solution was titrated with 0.0046 N potassium hydroxide (KOH) solution in ethanol. Normality of the KOH solution was determined by titration of a standardized HCl solution. Sulfonic acid equivalent weight of the sample was calculated using the dry mass of the sample, which was determined by evaporation of the THF and ethanol in an oven at 50°C and vacuum drying at 60°C until a constant weight was obtained.

Differential Scanning Calorimetry (DSC). DSC analyses were conducted using a Mettler TAS811 thermal analyzer equipped with a DSC305 differential scanning calorimetry cell. Polymers were dried to constant weight in a vacuum oven; 5-10 mg samples were weighed into aluminum pans and sealed. A heating rate of 10°C/min and a nitrogen purge were employed.

Thermogravimetric Analysis (TGA). TGA was performed using a DuPont 9900 thermal analyzer equipped with a 951 thermogravimetric analyzer module. Temperature scans from 25°C to 600°C were performed on dried samples, 5-20 mg, at a heating rate of 10°C/min under a nitrogen atmosphere.

Results and discussion

The PIB star polymers that served as precursors to the ionomers are described in Table 1. Molecular weights of the arm and star polymers were determined by gel permeation chromatography with on-line multi-angle laser light scattering. Arm molecular weights were found to be close to the targeted values calculated from the [IB]/[CumCl] ratios, and molecular weight distributions were narrow. The weight-average number of arms per star molecule ($\overline{N}_w$) was calculated using equation **1**, which is strictly valid only in the limit of monodisperse arms and assumes complete conversion of IB. The conversion of DVB, ρ_L, was taken to be unity.

$$\overline{N}_w = \frac{\overline{M}_{w,star}}{\overline{M}_{w,arm} + \rho_L R M_L} \tag{1}$$

$\overline{M}_{w,star}$ = weight average molecular weight of star polymer by light scattering
$\overline{M}_{w,arm}$ = weight average molecular weight of arms by light scattering
ρ_L = conversion of linking comonomer
R = molar ratio of core-forming comonomer to living chains
M_L = molecular weight of the linking (core-forming) comonomer

It was anticipated that sulfonation of the terminal aromatic rings could be carried out to high conversion, using excess acetyl sulfate as sulfonating reagent, without sulfonation of the aromatic rings within the DVB core. Acetyl sulfate exhibits poor solubility in hydrocarbon, and thus it was not expected to penetrate into the vicinity of the core where the concentration of PIB chain segments is highest. Furthermore, the DVB rings are sterically hindered against further substitution, being already di-substituted with two polymer chain segments (assuming complete conversion of DVB double bonds).

Ionomers were synthesized from the star-branched PIBs by sulfonation of the terminal phenyl rings using acetyl sulfate, according to the method of Makowski *et al.*, (4) followed by titration to determine the extent of sulfonation. From the titration results, an appropriate quantity of base (KOH) was used in a large scale preparative neutralization. As shown in Table 2, titrations revealed that the sulfonations were essentially quantitative, assuming that sulfonation was restricted to the terminal aromatic rings. Theoretical equivalent weights of the samples were calculated by assuming one phenyl ring per arm and an effective molecular weight per arm of $\overline{M}_{n,arm} + \rho_L R M_L$ = $\overline{M}_{n,arm}$ + 1,300 g/mol.

Table 1: Linear Polyisobutylene Arms and Multi-Arm Star-Branched Polymers Therefrom

Linear Polyisobutylene Arms[a]

Sample	Target $M_{n,arm}$ (g/mol)	[CCl] (mol/L) x 10^3	[Py] (mol/L) x 10^3	Rxn Time (min)	$M_{w,arm}$ (LS) (g/mol)	MWD (LS)
Linear-10	10,000	5.5	3	29	12,200	1.14
Linear-12	12,000	4.7	2	30	13,100	1.07
Linear-20	20,000	2.8	2.8	76	21,000	1.01
Linear-30	30,000	1.86	2	210	31,000	1.08

Multi-Arm Star-Branched Polyisobutylenes[b]

Sample	Rxn Time (min)	$M_{w,star}$ (LS) g/mol	MWD (LS)	N_w	Residual Arm %
Star-10	26	435,000	1.64	32	1.3
Star-12	24	444,000	1.11	31	1.4
Star-20	48	554,000	1.07	25	2.0
Star-30	384	174,000	1.53	5	8.0

[a] $[IB]_o = 1.0$ M; $[CumCl]_o = [TiCl_4]/15$; 60/40 (v/v) hexane/methyl chloride; -80°C
[b] $[DVB]_o = 10[CumCl]_o$; 60/40 (v/v) hexane/methyl chloride; -80°C

Table 2: Titration of Sulfonated Star Polymers

Sample	$M_{n,arm}$ (g/mol) (LS)	Theoretical Eq.wt. (g/mol)	Sample Aliquot (g)	mL 0.46 N 0.47 KOH	% Sulfonation
Star-10	10,700	12,000	0.5255	8.81	93
Star-12	12,200	13,500	0.5101	8.26	101
Star-20	20,800	22,100	0.4790	4.59	97
Star-30	28,800	30,100	0.3489	2.32	92

Thermal properties of the star-branched ionomers compared to the hydrocarbon precursors were evaluated with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the data are shown in Table 3. DSC revealed that regardless of $\overline{M}_{w,star}$, only one glass transition temperature (T_g) was observed, and it remained at about -66°C for both the ionomers and hydrocarbon precursors. However, TGA showed that the incorporated metal sulfonate groups enhanced thermal stability of the star polymers. For example, for the sample produced with 12,000 g/mol arms, the T_d increased from 375 to 400°C; this trend was reflected in all the sulfonated star polymers independent of arm or star molecular weight.

The appearance and feel of the star polymer ionomers were very different from the hydrocarbon precursors. The unsulfonated star polymers were colorless but translucent, tacky, and dissolved easily in THF; in comparison, the sulfonated star polymers were light brown, elastic, and slow to dissolve into THF.

Table 3: Thermal Properties of Star-Telechelic Ionomers and Precursors

	Ionomer		*Precursor*	
Sample	**T_g (°C) (DSC)**	**T_d (°C) (TGA)**	**T_g (°C) (DSC)**	**T_d (°C) (TGA)**
Star-10	-66	398	-67	376
Star-12	-66	400	-68	375
Star-20	-65	405	-67	372
Star-30	-64	397	-66	376

Conclusions

Monofunctional PIB initiated from CumCl was linked using DVB to create star polymers which possess a single aromatic ring at the end of each arm. Sulfonation and purification of the star polymers yielded sulfonic acid equivalent weights by titration that are in excellent agreement with theoretical values, which were calculated by assuming sulfonation exclusively at the terminal aromatic groups. It was concluded that the DVB core is too non-polar and immobilized, and the individual aromatic rings too sterically restricted to undergo sulfonation. The resulting ionomers were elastic solids with enhanced thermal stability and reduced solubility compared to the hydrocarbon precursors.

Acknowledgement

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