Matched Random Ionomers: Carboxylate vs Sulfonate

Neena K. Tierney,[†] **Scott T. Trzaska,**[‡] **and Richard A. Register***

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

Received July 15, 2004
Revised Manuscript Received September 18, 2004

Introduction

Polymers are often selectively functionalized to alter their properties. In ionomers,[1] associations between the functional groups—typically metal salts—strongly influence the solid state and particularly the melt rheological behavior,[2] where a quantitative understanding of the influence of functional group type and content requires polymers which are otherwise "matched"—in chain architecture, molecular weight, and molecular weight distribution, all of which also impact the melt dynamics. Ionomers are commonly prepared by direct copolymerization with a functionalized comonomer as with the well-known ethylene–methacrylic acid ionomers;[3] however, precisely matching the polymer's molecular weight distribution and branching (if any) is extremely difficult in separate syntheses with chemically different comonomers. Postpolymerization routes ideally allow the functionalization of polymers to arbitrary levels with different functional groups, without any side reactions which induce chain scission or branching. However, the differing solubilities of the ionic and nonionic units complicates characterization (e.g., by size-exclusion chromatography), such that it is often difficult to assess whether any such backbone rearrangements occurred.

Aromatic nuclei are popular loci for functionalization, and in a pioneering study, Lundberg and Makowski[4] compared ring-sulfonated and ring-carboxylated polystyrene ionomers derived from the same parent polystyrene. For both types of ionomer, the melt viscosity (in a melt indexer) was much higher than for the unfunctionalized polystyrene and increased monotonically with ion content. Those authors also found the sulfonate ionomers to have melt viscosities some 3 orders of magnitude higher than the carboxylate ionomers at comparable functionalization levels. This difference was interpreted to reflect stronger associations, hence longer association lifetimes, between the sulfonate groups due to their greater polarity. Because of the difficulty in synthesizing "matched" ionomers, this work still represents the only direct comparison of the melt rheology for randomly functionalized ionomers with different anion type; the conclusion that sulfonation yields stronger associations and higher viscosities (vs carboxylation) has become essentially axiomatic.[2,5,6]

Recently, we[7] have applied Lundberg and Makowski's[4] sulfonation procedure to styrene–ethylene–butene (SEB) random terpolymers of narrow molecular weight distribution, synthesized by anionic polymerization and catalytic hydrogenation; that work demonstrated and quantified the influence of both chain length and degree of sulfonation on the melt dynamics.[7] Lundberg and Makowski's parallel carboxylation procedure employed the complex between *n*-butyllithium (*n*-BuLi) and tetramethylethylenediamine (TMEDA) to lithiate the aromatic ring,[8] followed by reaction with CO_2. Attempts in our laboratory to apply this procedure to high molecular weight polystyrene resulted in branching and gelation.[9] Alternative carboxylation routes which yield soluble product have been presented in the literature,[10–13] but these reports often do not include sufficient characterization to exclude the possibility of side reactions leading to backbone rearrangements, which clearly occur in some cases.[13]

The complex between *sec*-butyllithium and TMEDA was long ago reported[14] to be a far more effective metallating agent than *n*-BuLi:TMEDA. Subsequent work[15–17] confirmed that this agent metalates the aromatic ring exclusively, though again no characterization of the product's macromolecular architecture was reported. Here, we metalate a narrow-distribution SEB terpolymer with the *sec*-BuLi:TMEDA complex, followed by carboxylation; demonstrate that functionalization proceeds with a minimum of backbone rearrangements; and find, surprisingly, that the carboxylate ionomer has a melt viscosity quite comparable to that of an analogous sulfonated SEB ionomer.

Experimental Section

Synthesis. The polymerization, hydrogenation, and detailed molecular characterization of the parent SEB terpolymer, SEB28, have been presented previously;[7] in brief, it has a weight-average molecular weight of 28.5 kg/mol, a polydispersity index of 1.06, 39 wt % styrene units distributed effectively randomly along the chain, no detectable olefinic unsaturation, and a glass transition temperature of −15 °C. In a nitrogen-atmosphere glovebox, using flame- or oven-dried glassware, 2.97 g of SEB28 was dissolved in 250 mL of cyclohexane (distilled from butyllithium). TMEDA (2.2 mmol; Aldrich, 99%, distilled from dibutylmagnesium; added as a 0.928 M solution in cyclohexane) and *sec*-BuLi (2.2 mmol; Aldrich, 1.3 M in cyclohexane) were then added. The solution immediately turned yellow; the reaction was allowed to proceed for 2 h, throughout which the polymer remained fully soluble. On a Schlenk line under constant nitrogen purge, a minimum of 100 g of CO_2 (BOC Gases, 99.999%) was condensed into a round-bottomed flask immersed in liquid nitrogen. The lithiated polymer solution was then added slowly to this flask via cannula. After warming to room temperature, the lithium carboxylate ionomer was recovered by precipitation into methanol, redissolved in tetrahydrofuran and reprecipitated into methanol, and finally stirred repeatedly with distilled water. Elemental analysis (Galbraith Laboratories, Knoxville, TN) indicated 0.13 wt % Li, corresponding to 5.1% of the styrene units functionalized, and a functionalization efficiency of 26% based on the *sec*-BuLi added.

To generate the acid derivative for FTIR, an excess of concentrated hydrochloric acid was added to a small portion of the ionomer solution immediately after carboxylation. To obtain the ethyl ester derivative for size exclusion chromatography (SEC), 0.30 g of the ionomer was dissolved in 15 mL of 2/1 (v/v) tetrahydrofuran/ethanol with 1.0 g of *p*-toluenesulfonic acid, and the solution refluxed for 2 weeks. The esterified polymer was precipitated into methanol, redissolved in tetrahydrofuran, and reprecipitated into methanol.

Characterization. FTIR spectra of thin films on NaCl plates were collected on a Nicolet 730 spectrometer. SEC data

---

[†] Present address: Johnson & Johnson Consumer & Personal Products Worldwide, Skillman, NJ 08558.

[‡] Present address: Schering-Plough Research Institute.

* To whom correspondence should be addressed: e-mail register@princeton.edu.

10.1021/ma0485540 CCC: $27.50

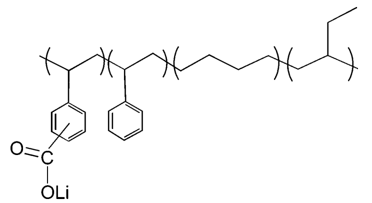

Figure 1. Structure of the repeat units, randomly distributed along the backbone, which make up the carboxylated SEB ionomer. For LiCSEB28-5, the molar ratio of the four units is 1:19:26:31 (carboxystyrene:styrene:diethylene:butene).

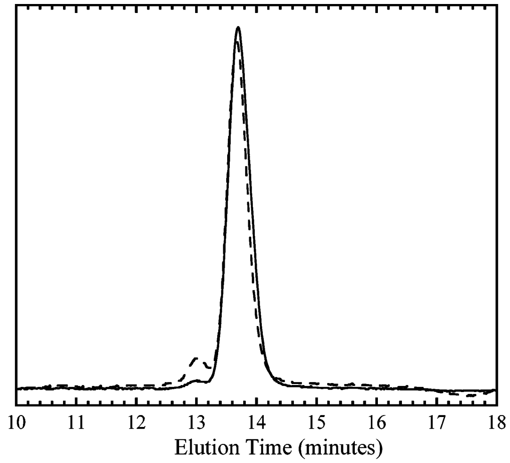

Figure 2. SEC chromatograms (differential refractive index signal) of SEB terpolymer (solid) and ethyl ester derivative of the carboxylated SEB ionomer (dashed line). No horizontal shifting has been applied.

were obtained in toluene at 35 °C, using refractive index detection (Waters 410) and two 30 cm PLgel Mixed-C columns (Polymer Laboratories). Disk specimens for rheometry were prepared under vacuum in a closed mold at 50−100 °C. Dynamic shear measurements were conducted using a Rheometrics mechanical spectrometer (RMS-800), over 10^{-2}−10^{2} rad/s and 30−120 °C, with a strain amplitude of 0.5−5%, within the linear viscoelastic regime.

Results and Discussion

The structures of the repeat units in the carboxylated SEB ionomer are shown in Figure 1. Styrene units constitute 39 wt % of the SEB precursor; 5.1% of these were carboxylated in the material discussed here, yielding an average of 5.4 −COOLi groups per chain ($\bar{n}$) in the ionomer. Functionalization is evident in the FTIR spectrum of the ester derivative through the −COOEt stretch at 1722 cm^{-1}, while the acid form shows the −COOH stretch at 1691 cm^{-1}, indicating ring (vs backbone) carboxylation;[18] the position of substitution on the ring has been previously reported as 2:1 meta:para[15,19] from ^{13}C NMR spectroscopy. Comparison of the SEC chromatograms for the SEB precursor and the ethyl ester derivative (Figure 2) reveals that no substantial branching or chain scission occurs during the lithiation. The principal peak in the chromatogram remains narrow and shifts very slightly to shorter elution times, reflecting a small increase in hydrodynamic volume upon addition of the ethyl ester groups. The small peak near 13 min, reflecting coupled chains in the SEB precursor, increases in the functionalized product. We speculate that this additional coupling may reflect reaction of a ring-lithiated styrene unit with a CO$_2$-functionalized unit, by analogy with known side reactions during end-functionalization of polystyryllithium with CO$_2$.[20]

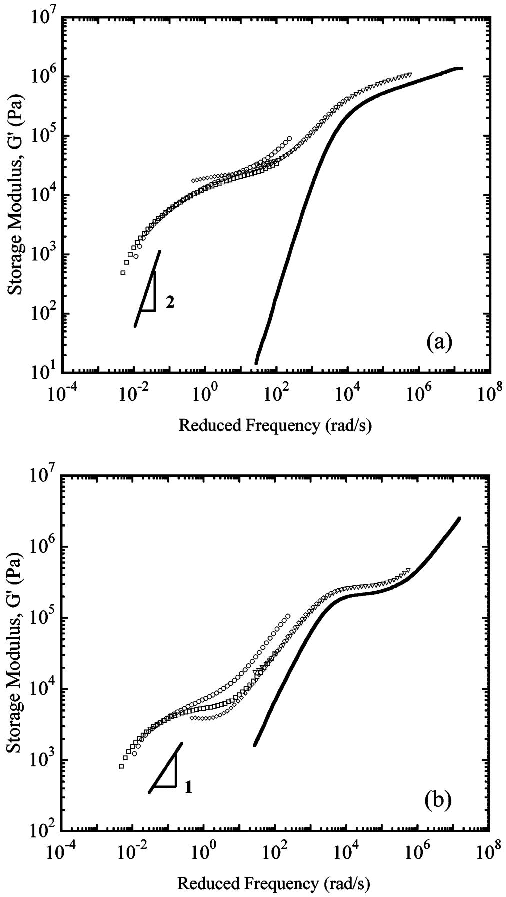

Figure 3. Pseudomaster curves for (a) storage modulus G' and (b) loss modulus G'' for LiCSEB28-5 (symbols), referenced to 120 °C. Master curves for the unfunctionalized SEB terpolymer,[7] which obeys time−temperature superposition, are presented as solid curves for comparison. For LiCSEB28-5, where time−temperature superposition fails, data sets corresponding to different temperatures are coded by symbol: 30 (▽), 60 (◇), 90 (○), 120 °C (□).

This small extent of coupling does not obscure the large rheological changes imparted by functionalization.

While the unfunctionalized SEB precursor obeys time−temperature superposition closely, the sulfonated SEB ionomers do not, as they exhibit multiple relaxation mechanisms with different temperature dependences.[7] End segments of the chain (between the chain end and the outermost ionic group) relax faster and with a smaller activation energy than the ionic associations or the polymer's center-of-mass motion. Given the architectural similarity of the carboxylated and sulfonated SEB ionomers, similar relaxation mechanisms and failure of time−temperature superposition are expected. Figure 3 shows G' and G'' pseudomaster curves at a reference temperature of 120 °C for the lithium-neutralized carboxylated SEB ionomer described above (average number of ionic groups per chain $\bar{n} = 5.4$, denoted LiCSEB28-5 henceforth). These pseudomaster curves approach the master curves for the unfunctionalized SEB terpolymer at the highest reduced frequencies, where neither entanglements nor ionic associations relax, but carboxylation extends the terminal relaxation time by several orders of magnitude, out of our measurement window. At intermediate frequencies, a plateau is observed, with a modulus of 20 kPa (G' at G'' minimum, 1.4 rad/s); this is far below the entanglement plateau modulus measured on a high-molecular-weight unfunctionalized SEB terpolymer (780 kPa)[7] due to

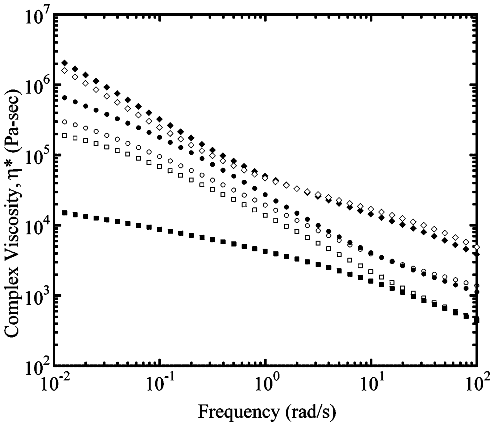

Figure 4. Comparison of the complex viscosity η^* for LiCSEB28-5 (open symbols) and NaSSEB28-6 (solid symbols) at 60 (◆, ◇), 90 (●, ○), and 120 °C (■, □). Frequency axis is unshifted.

dilution of the entanglement network through relaxation of the end segments. This modulus value compares quite well with the 29 kPa measured[7] for an analogous sodium-neutralized sulfonated SEB ionomer (NaSSEB28-6, $\bar{n} = 5.6$), again confirming the architectural similarity between the carboxylated and sulfonated ionomers.

Because time–temperature superposition fails for both the carboxylated and sulfonated ionomers, Figure 4 directly compares the complex viscosity η^* for LiCSEB28-5 and NaSSEB28-6 at three temperatures. Previous rheological studies of ethylene–methacrylic acid[3] and ethylene–acrylic acid[21] random ionomers have shown little melt viscosity difference ($<2\times$) between the Li^+ vs Na^+ forms; for low-molecular-weight carboxy-telechelic polybutadiene ionomers, up to an order of magnitude difference has been reported, but with Otocka et al.[22] reporting a higher viscosity for the Li^+ form and Horrion et al.[23] a higher viscosity for the Na^+ form. In any case, these differences are small relative to the 3 orders of magnitude viscosity enhancement of sulfonate over carboxylate ionomers reported by Lundberg and Makowski,[4] from which we anticipated a much lower viscosity (shorter terminal relaxation time) for the carboxylated ionomer. However, Figure 4 shows quite a different result: the shapes of the η^* curves for the two ionomers are quite similar, as are the magnitudes of the η^* values. In fact, at the highest temperature (120 °C) and lowest frequencies, where terminal behavior is most closely approached (though not reached), the carboxylated ionomer has a complex viscosity which *exceeds* that of its sulfonated analogue. Thus, the axiom that sulfonated ionomers always possess much stronger associations (and much higher melt viscosities) than their carboxylated analogues seems hardly universal; the lifetime of the ionic associations in ionomers clearly depends on much more than the acid strength of the functional group.

Acknowledgment. Financial support for this project was provided by DuPont Packaging & Industrial Polymers and by the donors of the Petroleum Research Fund, administered by the American Chemical Society (30658-AC7). The authors thank Dr. Douglas H. Adamson for assistance with the lithiation procedure.

References and Notes

(1) Eisenberg, A.; Kim, J.-S. *Introduction to Ionomers*; John Wiley & Sons: New York, 1998.
(2) Register, R. A.; Prud'homme, R. K. In *Ionomers: Synthesis, Structure, Properties and Applications*; Tant, M. R., Mauritz, K. A., Wilkes, G. L., Eds.; Chapman & Hall: New York, 1997; p 208.
(3) Tierney, N. K.; Register, R. A. *Macromolecules* **2002**, *35*, 2358.
(4) Lundberg, R. D.; Makowski, H. S. In *Ions in Polymers*; ACS Adv. Chem. Ser. 187; Eisenberg, A., Ed.; American Chemical Society: Washington, DC, 1980; p 21.
(5) Venkateshwaran, L. N.; Tant, M. R.; Wilkes, G. L.; Charlier, P.; Jérôme, R. *Macromolecules* **1992**, *25*, 3996.
(6) Hird, B.; Eisenberg, A. *Macromolecules* **1992**, *25*, 6466.
(7) Tierney, N. K.; Register, R. A. *Macromolecules* **2003**, *36*, 1170.
(8) Chalk, A. J. *Polym. Lett.* **1968**, *6*, 649.
(9) Taylor-Smith, R. E.; Register, R. A. Unpublished results.
(10) Nemes, S.; Borbély, J.; Borda, J.; Kelen, T. *Polym. Bull. (Berlin)* **1991**, *27*, 123.
(11) Hird, B.; Eisenberg, A. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1377.
(12) Liu, L.; Jiang, M. *Macromolecules* **1995**, *28*, 8702.
(13) Lochmann, L.; Fréchet, J. M. J. *Macromolecules* **1996**, *29*, 1767.
(14) Borg-Warner Corp. British Patent 1,172,477, issued Dec 3, 1969.
(15) Clouet, G.; Brossas, J. *Makromol. Chem.* **1979**, *180*, 867.
(16) Xue, T. J.; Jones, M. S.; Edbon, J. R.; Wilkie, C. A. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 509.
(17) Janata, M.; Lochmann, L.; Brus, J.; Vlèek, P. *Macromolecules* **2001**, *34*, 1593.
(18) Evans, D. C.; George, M. H.; Barrie, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 247.
(19) Evans, D. C.; Phillips, L.; Barrie, J. A.; George, M. H. *Polym. Lett.* **1974**, *12*, 199.
(20) Quirk, R. P.; Yin, J.; Fetters, L. J.; Kastrup, R. V. *Macromolecules* **1992**, *25*, 2262.
(21) Bonotto, S.; Bonner, E. F. *Macromolecules* **1968**, *1*, 510.
(22) Otocka, E. P.; Hellman, M. Y.; Blyler, L. L. *J. Appl. Phys.* **1969**, *40*, 4221.
(23) Horrion, J.; Jérôme, R.; Teyssié, P.; Marco, C.; Williams, C. E. *Polymer* **1988**, *29*, 1203.

MA0485540