

A Simple Postsulfonation of Poly(arylene ether sulfone) Radel[®] R

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ABSTRACT: Commercially available Radel[®] R, a poorly acid resistant biphenol-based poly(arylene ether sulfone), was successfully sulfonated by a simple and rapid postsulfonation reaction using oleum as the sulfonating agent. Polymer degradation due to contact with acid could easily be minimized by adjusting reaction conditions. The suitable reaction conditions, when the 1 : 3 molar ratio of the polymer to the sulfonating agent was used, were: 10% of oleum in chloroform, 10% concentration of Radel[®] R in

chloroform, and temperature between 0 and 50°C. Under these conditions, the reaction was complete within 45 min. Thermal properties, degradation characteristics and the viscosity of the postsulfonated polymer are reported. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 973–976, 2011

Key words: functionalization of polymers; ionomers; ion exchangers; sulfonation; Radel[®] R

INTRODUCTION

Sulfonated poly(arylene ethers), or sPAE, has excellent thermal and mechanical properties. It is therefore commonly used as a thermostable supportive matrix for conductive polymers and as ion-exchange membranes for separation applications.^{1,2} sPAE can be produced by sulfonating poly(arylene ethers). This is the postsulfonation method as sulfonation occurs postpolymerization. Sulfonation of the monomer before polymerization is known as presulfonation, or direct-polymerization. Compared to presulfonation, postsulfonation produces sPAE with a lower degree of sulfonation (DS) because only one sulfonate group can be attached to each monomer unit of the polymer;³ however, postsulfonation is much simpler, faster, and easier than the sulfonation of the monomer followed by a polymerization step.^{3,4} Furthermore, a high DS is not always desired because it leads to water-swelling of the polymer membranes in applications such as fuel cells and filtration of aqueous media.

Radel[®] R is a commercial biphenol-based poly(arylene ethers) that has good mechanical properties, but is less resistant to acids than poly(arylene ethers) such as polyethersulfone (PES) and poly(ether ether ketone) (PEEK). Because of their acid resistance, PES and PEEK can be readily postsulfonated using concentrated sulfuric acid and oleum.^{5–7} All chemical agents suitable for sulfonating poly(arylene ethers) are acidic and, therefore, only mild sulfonation conditions can be used so that the polymer chains are not degraded. Several successful postsulfonation methods have been reported for Radel[®] R,^{3,8} but they all involve complex reaction systems and long reaction times (>10 h). Furthermore, all these methods cause a significant reduction in chain length which may affect mechanical properties.

This work reports on a simple, mild, and rapid postsulfonation method for sulfonating Radel[®] R using oleum, a readily available sulfonating agent. Chain degradation and thermal properties of the sulfonated polymer obtained from the postsulfonation were examined at two reaction temperatures and compared with those reported in literature for sulfonated Radel[®] R, produced by the utilization of the postsulfonation technique with a different sulfonating agent and of the direct-polymerization of presulfonated monomers. Note that the same test conditions were applied to this present study.

EXPERIMENTAL

Materials

Radel[®] R ($M_n = 24,000$), or poly(arylene ether sulfone), was a gift from Solvay advanced polymers.

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Oleum (65% w/v SO_3) purchased from Merck was used as a sulfonating agent. Chloroform and the other chemicals mentioned were analytical reagent grade or higher and used directly.

Postsulfonation of Radel® R

A molar ratio of the polymer to the sulfonating agent was 1 : 3 in all experiments. A three necked round bottomed flask equipped with a mechanical stirrer in the center neck and glass stoppers in the other necks, was used to dissolve 2 g of oven-dried Radel® R in 20 mL of chloroform at room temperature overnight while stirring. A dropping funnel was used for drop-wise addition of a dispersion of 1 mL of 65% oleum and 10 mL of chloroform into the agitated flask over a period of 30 min, during which temperature of the polymer solution was set at 0°C (or 50°C). The reaction was then allowed at that temperature for a further 15 min and stopped by adding a sufficient quantity of methanol to cover the precipitate formed in the reaction flask. The precipitate was recovered by filtration and neutralized by rinsing with deionized water. The precipitate was dried in an oven at 60°C for 24 h and then at 80°C in a vacuum oven for a further 24 h. Sulfonated Radel® R, or sRAD, was thus obtained.

Characterizations

Thin sheets of the polymer samples prepared by solution casting technique were used to measure the FTIR spectra in a Perkin-Elmer Spectrum GX FTIR Spectrometer (Perkin-Elmer). The DS of synthesized products was calculated from the $^1\text{H-NMR}$ spectra, obtained from a Bruker Avance-300 NMR spectrometer, as the ratio of the peak areas for the protons adjacent to the pendant ionic groups to that of the other aromatic protons.

For measuring the intrinsic viscosity, the polymer samples were dissolved in dimethylacetamide (DMAc) and measured at 25°C using a Ubbelohde U-tube viscometer. To test tensile strength using a Hounsfield H50KS universal testing machine (UK), a 10-by-1 cm thin polymer membrane was subject to a speed of 0.2 mm/min at room temperature (25°C). The thermal properties were determined in an STD 2960 simultaneous DTA/TGA (TA Instruments). Measurements of thermal properties were carried out under a nitrogen atmosphere at up to 800°C with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Sulfonated Radel® R, sRAD, was successfully produced by postsulfonation with oleum under mild conditions that minimized damage to the acid sensitive parent polymer. The reactor setup is simplified,

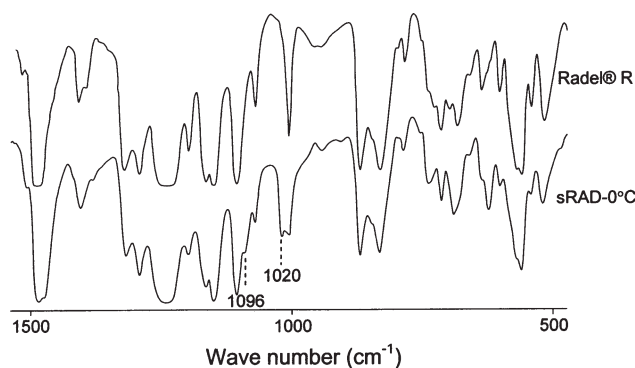


Figure 1 FTIR spectra of Radel® R and sRAD synthesized at 0°C.

compared to the other published postsulfonation methods.^{3,8} There is no need for a condenser nor a nitrogen atmosphere during the reaction. The polymer produced was in the protonated-form which is suitable for making proton-conducting membranes of a fuel cell or of other applications.^{3,4,9}

The suitable reaction conditions that did not damage the acid-sensitive Radel® R were found after many failed experiments: a dilute solution of oleum in chloroform ($\sim 10\%$ v/v), the polymer solution in chloroform ($\sim 10\%$ w/v), and a low temperature (approximately 0–50°C). It is necessary to remind that temperature less than 0°C might not be desirable as it significantly lengthened the reaction time. Use of temperature greater than 50°C or relatively concentrated acidic solutions caused chain degradation, yielding brittle polymer samples that readily dissolved in water. In addition, as reported previously,³ the acidic solution had to be added to the reactor very slow to prevent polymer precipitation.

Properties of the polymer samples produced under the preferred processing conditions were characterized. Figure 1 shows the FTIR spectra of Radel® R and the product polymer synthesized at 0°C. The absorption peaks at 1020 and 1096 cm^{-1} correspond to the presence of sulfonate groups, confirming that postsulfonation was achieved. The same peaks were also discerned from the sRad synthesized at 50°C. The DS in Table I was increased with raising reaction temperature due to the enhanced rate of the sulfonation reaction.

The intrinsic viscosity of a polymer solution is indicative of the hydrodynamic volume of the polymer molecules. Postsulfonation was observed to increase the intrinsic viscosity relative to the precursor polymer (Table I). This was because the electrostatic repulsion associated with the ionized sulfonated groups increased the effective hydrodynamic diameter of the polymer molecules. The intrinsic viscosity of the product obtained at 50°C was lower than the product produced at 0°C (Table I). This was because of a greater degradation of the poly(arylene ether sulfone) chains

TABLE I
Properties of Radel[®] R and sRAD

Reaction temperature (°C)	DS ^a (%)	$[\eta]_{25}^{\text{DMac}}$ (cm ³ /g)	Ultimate tensile strength (MPa)	$T_{5\%}^b$ (°C)	Char yield at 700°C ^c (%)	T_g (°C)
n/a ^d	0	67	44.96	544	45.7	224
0	48	248	30.16	374	50.5	233, 320
50	56	175	27.46	345	51.3	261, 315

^a Degree of sulfonation (DS) values were obtained from ¹H-NMR spectra (not shown here).

^b The 5% weight loss temperature ($T_{5\%}$).

^c Char yield at 700°C was obtained from TGA curves.

^d The sample was commercial Radel[®] R.

Note that all experiments were repeated at least twice with similar results.

at 50°C compared to at 0°C,^{7,10} which was confirmed by the decrease in the ultimate tensile strength shown in Table I. This degradation notwithstanding, the sRAD samples produced at 50°C could be satisfactorily cast into transparent nonbrittle thin films using the solution casting method.

As shown in Table I, the introduction of sulfonate groups affected the thermal properties of Radel[®] R. On sulfonation, the 5% weight loss temperature ($T_{5\%}$) was reduced by 30% or more, depending on the DS (Table I). As shown in Figure 2, thermal degradation of sRAD at 300°C and 480°C followed a two-step process compared with the one-step degradation of the pristine Radel[®] R. In two-step degradation, the first step was attributed to a loss of sulfonate groups. Hence, in the first step, the weight loss of sRAD with the higher DS was greater and began slightly earlier than the weight loss of the polymer with the lower DS (Fig. 2). The second weight loss step of sRAD occurred at the same temperature as for the pristine Radel[®] R and was, therefore, attributed to the decomposition of the polymer backbone.

The char yield for polymer decomposition at 700°C and the glass-transition temperature (T_g) increased

with increasing DS (Table I). The higher char yield of the more sulfonated polymer indicates that sulfonation improved the flame resistance of the polymer. An increasing glass transition temperature as a consequence of increasing sulfonation occurred because the presence of the ionized sulfonate groups reduced the flexibility and the mobility of the polymer chain. The two T_g values (Table I) for the sRAD were associated with the hydrophobic and the ionic clusters. Dual T_g values are typical of random amorphous ionomers in which the ionic clusters are large enough to hinder the movement of the nearby chain segments.^{11,12}

Similar effects of the DS on the intrinsic viscosity and the thermal properties of the polymer have previously been reported.³ In this study,³ a biphenol-based poly(arylene ether sulfone), that was chemically identical to Radel[®] R, was postsulfonated using trimethylsilyl chlorosulfonate. Thermal properties of sRad produced in the current work were also found to be comparable to those previously reported.³ In contrast to the earlier study,³ for a comparable DS achieved by postsulfonation, the intrinsic viscosity at the same temperature of our sulfonated polymer was about one order of magnitude greater. Our intrinsic viscosity was close to a product produced previously by direct polymerization.^{3,4} Normally, a high intrinsic viscosity is expected for sulfonated poly(arylene ether sulfone) produced by direct polymerization because this method does not subject the polymer to acid degradation. Our work confirms that postsulfonation of Radel[®] R under suitable conditions can be used to produce sulfonated poly(arylene ether sulfone) that is quite comparable to the same product obtained by direct polymerization. In addition, our values of $T_{5\%}$, the char yield at 700°C and T_g for the polymer produced by postsulfonation were comparable to the values reported for the polymer produced by direct polymerization.⁴

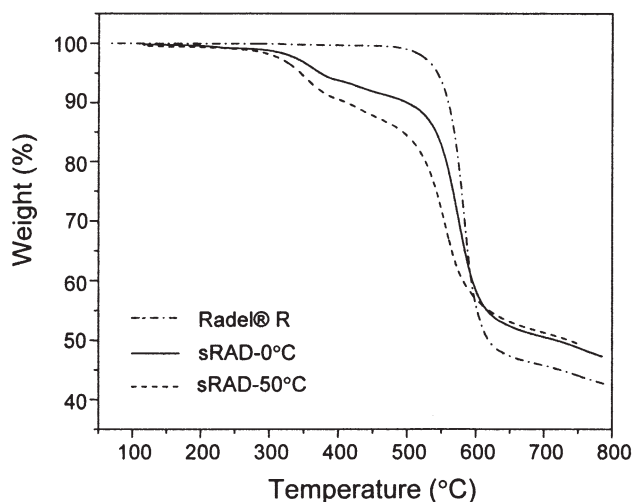


Figure 2 TGA curves of Radel[®] R and sRAD's synthesized at 0 and 50°C.

CONCLUSIONS

A simple, mild and rapid method for postsulfonation of the acid sensitive commercial poly(arylene

ether sulfone) Radel[®] R was established. Postsulfonation always requires acid conditions and the methods reported in the literature are unsatisfactory for use with Radel[®] R because they produce severely degraded brittle sulfonated Radel[®] R. For the molar ratio of the polymer to sulfonating agent being 1 : 3, suitable sulfonation reaction conditions involved the use of readily available oleum at a concentration of 10%, a Radel[®] R concentration in the range of 10%, and temperature between 0 and 50°C. The reaction was completed within 45 min. Previously, sulfonated poly-(arylene ether sulfones) with properties comparable to those obtained in this study, had been produced only by direct polymerization from a presulfonated monomer. This suggests a strong potential of the proposed simple postsulfonation method.

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