Synthesis and Properties of Poly(aryl sulfone) Containing Cross-linkable Dicyanovinyl Group

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Abstract: Poly(sulfone- enamionitrile)s, (PSENs), as new soluble, aromatic high performance thermosetting polymers, were synthesized and their thermal and solubility properties were examined. These polymers had moderate to low molecular weights with inherent viscosities in the range of 0.10−0.19 dL/g. These polymers underwent a "curing" reaction above 280°C without generation of volatile byproducts to give insoluble materials, which was evidenced by thermal analysis (DSC, TGA) and IR spectroscopy. The uncured polymers showed good solubility in various organic solvents. After thermal curing, however, the materials were totally insoluble in most solvents, except in concentrated sulfuric acid.

Introduction

Thermally stable, high-performance polymers have been a subject of extensive research efforts over the past 30 years. Interest has been heightened because of the growing application of thermally stable polymers in the fields of aerospace and electronics. Of the variety of thermally stable, high-performance polymers developed, most are aromatic, rigid polymers because of performance requirements, and therefore they present great difficulties in processing due to their low solubility, high glass transition and/or melting temperature, and also high melt viscosity. Therefore, compromises have been necessary between performance and processability. One approach to solve this problem is to synthesize more soluble linear polymer with reactive functional moieties on the molecule for further reaction. The reactive groups eventually react or polymerize and give cross-link to further improve materials performance. These high performance thermosetting resins can be telechelic oligomers or high molecular weight polymers having reactive functional groups for cross-linking reactions. High performance thermosetting resins are very useful in highly demanding

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environment to provide special properties. They usually possess high dimensional stability at elevated temperature, excellent thermal and thermooxidative resistance, low water absorption, good chemical resistance, high mechanical strength, etc. All these properties are useful for advanced composites and for fabricating electronic components.

Poly(aryl sulfone)s are important industrial engineering thermoplastics. They possess excellent tensile properties as well as fracture toughness. However they are solvent sensitive and undergo stress cracking in their application.

Poly(enameleminonitrile)s (PEANs) are soluble, high molecular weight polymers with analogous backbone structures of aramids in which the carbonyl groups are replaced by dicyanovinylidene groups, \((C=\text{C} (\text{CN})_2)^4\). During the last decade, PEANs with various structures have been synthesized and their unique thermal and solution properties were investigated. These polymers show good solubility in various organic solvents, which is compared to the very limited solubility of aramids and other rigid aromatic polymers. Introduction of this rather bulky and polarizable group makes the polymer more soluble in common solvents, also provide sites for the thermal curing (without evolution of volatile byproducts) at elevated temperatures to give excellent thermal and dimensional stability to these materials. In our previous report, we have prepared and characterized poly(Thermodenamoleminonitrile)s to identify thermally cross-linkable, soluble polyimide copolymer. In this work aromatic poly(ether sulfone) containing thermally crosslinkable dicyanovinyl groups have been synthesized as reactive oligomers. Their curing reaction provided high performance characteristics for the polymers.

Experimental

Chemicals. NMP and malononitrile were purified by vacuum distillation after stirring over CaH\(_2\). 1,4-Diazabicyclo[2.2.2]octane (Dabco) was sublimed twice. Dichlorodi phenylsilane (DCDPS) and bisphenol-A (BPA) were recrystallized twice from hot toluene. 4-Aminophenol was purified by sublimation. 3-Aminophenol was purified by recrystallization from toluene. Other chemicals and solvents were purchased in high purity and used without further purification.

Measurements. IR spectra were obtained on a Unicam 1000 FT-IR Spectrometer. NMR spectra were taken on a Varian Unity Inova 500 MHz Spectrometer. Thermal analysis (TGA, DSC) was carried out on a Perkin-Elmer 7 Series thermal analysis system with a heating rate of 10 K/min\(^1\).

Solution viscosity of polymer was measured using an Ubbelohde viscometer with THF at 30°C.

1,4-Bis(1-chloro-2,2-dicyanovinyl) benzene [DCVB]; DCVB monomer was prepared by the methods previously reported; Terephthaloyl chloride and two equivalent malononitrile were condensed using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base in THF to provide bisenolate-DBU salt, followed by recrystallization from methanol to give yellow crystals in ca. 60% yield. [M\(_p\) (DSC) 187°C. IR(KBr): 2933, 2195(CN), 1649, 1517, 1380 cm\(^{-1}\). \(^1\)H NMR (DMSO-d\(_6\)): 9.65(NH, 2H), 7.52(arom. protons, 4H), 1.5-3.5 (protons in DBU, 32H)]. Above prepared salt was chlorinated using POCl\(_3\) in CH\(_2\)Cl\(_2\) and the product was flash column chromatographed to separate yellow crystalline solid after removing eluent, which was recrystallized twice from chloroform/hexane to give off-white crystals as the desired monomer (75% yield). M\(_p\) (DSC) 178°C (Lit. 177-9°C).

Preparation of Amine-terminated Poly (ether sulfone) Oligomer and In-situ Polymerization with DCVB Monomer: A typical procedure for the preparation of 1.00 g mol\(^{-1}\) amine terminated polysulfone (PSF) oligomer and following polymerization with DCVB monomer was described as follows; i) A 100 mL three-necked flask was equipped with a gas inlet/outlet, a Dean Stark trap with reflux condenser, and a magnetic stirrer. The glassware was flame-dried under argon to remove moisture. The flask was charged with 1.4413 g (5.0194 mmol) of DCDPS, 0.9176 g (4.0196 mmol) of BPA and 15 mL of NMP. To the solution, 0.7778 g (5.6274 mmol) of K\(_2\)CO\(_3\), 0.2183 g (2 mmol) of 3-aminophenol and 10 mL of toluene were added. The reaction mixture was stirred and heated to 145°C, and maintained at this temperature for 4-5 h to ensure
dehydration of the system. Then the temperature was increased to 170 °C and the mixture was allowed to react for 8 h. ii) After formation of amineterminated poly(aryl sulfone) oligomer as described above, one-pot polycondensation with DCVB monomer was carried out. The reaction mixture was cooled to 60 °C and Dean Stark trap was replaced with a dry condenser before addition of 0.2991 g (1 mmol) of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene and 0.2243 g (2 mmol) of Dabco in 5 mL of NMP, subsequently. The reaction mixture was stirred for 10 h at 60 °C, and additional 2 h at 80 °C. The resulting mixture was then poured into 300 mL of water/methanol (1:1) solvent with stirring vigorously. The brown precipitate was filtered and washed with methanol, and then dried in vacuo at 120 °C for 24 h.

Analytical Data: Yield: 90—95% (65—80% yield was obtained from the reactive poly(aryl sulfone) oligomer prepared by using 4-aminophenol as end-capping reagent, instead of 3-aminophenol), IR(KBr): 3250 (NH), 2219 (CN), 1151 (SO2), 1259 (O-) cm⁻¹. ¹H NMR(DMSO-d6): δ 10.9 (NH), 6.5-8.3 (arom. protons), 1.6 (CH3).

Results and Discussion

Synthesis and Characterization. Amine terminated PSF oligomers with predetermined molecular weights were prepared as the procedure reported by McGrath et al.⁷ In the step-growth polymerization, molecular weight control can be obtained by using stoichiometric imbalance of A:A, and B:B type monomer or via addition of monofunctional reagent, which is based on well-known Carother's equation. As an example, the synthesis of the arylamine terminated PSF oligomer with a PSF block molecular weight of 3,000 g/mol (molecular weight of repeat unit=442.53 g/mol) could be achieved based on the following calculation.

$$DP = \frac{3,000 \text{ g/mol}}{442.53 \text{ g/mol}} = 6.780$$

$$<X_o> = 2(DP) = 13.56$$

When conversion, p, is assumed to approach unity,

$$<X_o> = \frac{1+r}{1-\frac{1}{r}}$$

where r is the stoichiometric ratio of functional groups.

By substituting the value in equation (1) into equation (2), a value of r=0.8626 is obtained. This implies that by maintaining a stoichiometric imbalance of monomers with the DCDPS present in excess (1,000 mol DCDPS and 0.8626 mol of BPA), a chlororenoplyphenyl terminated PSF oligomer with <Mn>=3,000 g/mol will be produced. At the same time, the amount of PSF oligomer will be 0.1374 mol (1,000 mol DCDPS - 0.8626 mol BPA). If 0.2748 mol (2×0.1374 mol) of 4-aminophenol (or 3-aminophenol) as end-functionalizing reagent were present in the original reaction mixture, amine terminated PSF oligomer will be produced. Then above prepared PSF oligomers, with both end capped with aryl amine, are reacted with the same molar amount of DCVB monomer to polymerize to form higher molecular weight PSENs (Scheme I).

Two different amine terminated PSF oligomers with Mw of 1,000 and 2,000, respectively, were prepared and polymerized in situ with DCVB monomer in NMP. The results are shown in Table I. The reaction proceeded homogeneously in solu-

![Scheme I](image)

Table I. Characteristics of PSENs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>ηsp² (dL/g)</th>
<th>Tg (°C)</th>
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<tbody>
<tr>
<td>PSEN 1000</td>
<td>0.12</td>
<td>178</td>
</tr>
<tr>
<td>PSEN 2000</td>
<td>0.19</td>
<td>203</td>
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*Measured in THF 0.5 g/dL, 30 °C.
tion and the polymer yields were 90~95\%. The molecular weight of the polymer, however, seemed to be relatively low when estimated from the inherent viscosities ranging from 0.10 to 0.19 dL/g. Probably a quantitative formation of oligomeric PSF, which was estimated through assumption of complete conversion, was hardly obtained in the reaction conditions, resulting in deviation from stoichiometric balance in the following polymerization step. Also the small scale of the polymerization reaction might be responsible for the low molecular weight of these polymers. Figure 1 and Figure 2 show the IR and $^1$H NMR spectra of the polymers. The characteristic ether and sulfone absorption bands at 1240 and 1151 cm$^{-1}$, respectively, and also nitrile band at about 2219 cm$^{-1}$ are shown in the IR spectra. $^1$H NMR spectrum showed aromatic protons at 6.5~8.3 ppm, NH proton of enaminonitrile group at 10.9 ppm and methyl protons at 1.6 ppm, respectively. Both IR

**Figure 1.** IR spectra of PSENs.

and NMR spectra evidenced the formation of poly(aryl sulfone) containing enaminonitrile groups. The prepared polymers exhibited good solubility in chloroform, THF and m-cresol as well as in typical polar aprotic solvents such as DMF, NMP, DMSO.

**Thermal Properties.** PSENs exhibit excellent thermal stability, without losing any mass below 450°C in both air and nitrogen as determined by dynamic TGA. The polymers retained 50~55\% of their mass at 800°C in nitrogen. Figure 3 shows the TGA thermograms of the polymers in nitrogen. DSC thermogram shows a broad, exothermic transition, as a typical one is shown in Figure 4 (PSEN 1000), between 280°C and 350°C. This peak was completely absent when the sample was cooled and rescaned. The glass transitions of PSEN 1000 and PSEN 2000 appeared at 178°C and 203°C, respectively, as determined by the mid-point of the heat capacity change in DSC. As previously reported,\(^4\) polymers containing enaminonitrile groups on the backbone undergo irre-

**Figure 3.** TGA thermograms of PSENs in nitrogen.

**Figure 4.** DSC thermograms of PSEN 1000.
versible curing reaction by the mechanism of intramolecular cyclization and subsequent intermolecular crosslinking processes. The broad and strong exothermic transition observed from DSC is responsible for this curing reaction. The DSC thermogram of PSEN 2000 sample showed similar results, except relative weakness in its transition, which is ascribed to the lower concentration of enaminonitrile group within the same molar volume. As are shown in TGA thermograms of PSENs, no mass change is observed during this curing process. This indicates the occurrence of a thermally induced curing without generating any volatile by-products.

Curing and Solubility Property. The change in chemical structure and solubility upon curing was studied in detail using PSEN samples. The PSEN 1000 sample was heated at 350°C for 30 min under nitrogen atmosphere. IR spectra were taken to monitor chemical changes during the curing process. The cured sample changed from yellow to brown, and became insoluble in all organic solvents tested, except concentrated sulfuric acid in which the sample was partially soluble. IR spectra showed that the enamine N-H and the nitrile CN stretching bands at about 3250 and 2200 cm⁻¹, respectively, decreased to a great extent as shown in Figure 5. PSEN 2000 sample was cured at 375°C for 20 min, instead. The results of solubility test from both uncured and cured PSEN samples are shown in Table II. The changes both in the IR spectra and in solubility suggest the thermal curing reaction involving enaminonitrile group and formation of crosslinked rigid-thermoset in this polymer system.

Further studies on the preparation of higher molecular weight, film-forming PSEN polymers using different aminophenol derivatives, and their thermomechanical properties are in progress.

Conclusion

Poly(sulfone-2-amino-5-nitro)PSEns, as new soluble, cross-linkable high temperature polymers were synthesized by condensation polymerization of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene with two different diamine-terminated oligomeric poly(aryl sulfone)s. These polymers had moderate to low molecular weights with inherent viscosities in the range of 0.10−0.19 dL/g. The glass transition temperatures were 178°C and 203°C, respectively. PSEns exhibited good thermal stability retaining their mass to 400−450°C and about 50−55% of their mass at 800°C in nitrogen (TGA). These polymers underwent a “curing” reaction above 280°C without emission of volatile byproducts to give insoluble materials. DSC thermograms showed a broad exothermic transition at around 280−350°C corresponding to this irreversible curing process. The uncured polymers

<table>
<thead>
<tr>
<th>Table II. Solubility Change after Curing</th>
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<tbody>
<tr>
<td>PSEN</td>
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<tr>
<td>------</td>
</tr>
<tr>
<td>PSEN 1000</td>
</tr>
<tr>
<td>PSEN 2000</td>
</tr>
<tr>
<td>Cured PSEN 1000</td>
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<tr>
<td>Cured PSEN 2000</td>
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</tbody>
</table>

○: soluble, ▽: soluble by heating, X: insoluble.

were soluble in many organic solvents including acetone, THF, chloroform, m cresol, NMP, DMSO and DMF. After thermal curing, the materials were totally insoluble in organic solvents.

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References

(7) M. J. Jurek and J. E. McGrath, Polymer, 30, 1552 (1989).