Photosensitive poly(ether sulfone)s for thiol/ene UV curable coatings: synthesis, characterization and crosslinking

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Abstract: Novel photocrosslinkable poly(ether sulfone)s copolymers with allyl pendants (AS-PES) have been synthesized from 3,3'-diallyl-4,4'-dihydroxydiphenyl sulfone (DA-DHDPS), 4,4'-dihydroxydiphenyl sulfone (DHDPS) and 4,4'-dichlorophenylsulfone (DCDPS). The resulting polymers could be photocrosslinked in the presence of thiol at room temperature. The crosslinking process was monitored by “Real Time Fourier Transform Infrared Spectroscopy” (RTIR). It proves that a small amount (1.0 wt%) of the thiol crosslinker addition is sufficient to form a chemical network under UV irradiation. After UV curing, AS-PES-20 coating showed high Tg, good thermal stability and excellent resistance to the acid, salt, and alkali. Accordingly, this method could successfully provide a new approach to make rapidly photocrosslinking poly(ether sulfone) coatings without losing their good thermal properties.

Introduction

Known for their excellent mechanical, thermal and chemical properties, poly(ether sulfone)s are widely used in aviation, aerospace, biological engineering and other high-tech fields [1]. Compared with other high-performance polymers, such as poly(ether ketone)s and polyimides, poly(ether sulfone)s possess lower cost and better solubility. Therefore, they can be applied as coatings through a typical solution spraying method. However, they are solvent sensitive, in some cases, poly(ether sulfone)s have to be sintered at a high temperature of 380 °C to obtain crosslinked high performance coatings [2]. In another way, the introduction of reactive groups to poly(ether sulfone)s can greatly improve its solvent resistance ability and stress cracking performance. Generally these crosslinking poly(ether sulfone)s are fabricated by thermo-cured method and undergo a high-temperature treatment above their TgS, which limit their applications and cause high energy wastage [3].

UV irradiation induced crosslinking is thought to be one of the most effective methods to generate three-dimensional polymer networks owing to its easiness, relative safety and low cost as well as high initiation rate under intense illumination [4]. The polymers having unsaturated functional groups either on the backbone or on the pendant groups can crosslink upon UV irradiation with photoinitiator. High photosensitivity, thermal stability and good solubility are essential requirements for the practical use of a polymer as UV crosslinkable coatings.

The increasing demands of UV radiation cured high-performance polymers have urged many unremitting studies on them. Heo et al [5] synthesized a crosslinkable sulfonated poly(ether sulfone) s copolymer with 4,4'-dihydroxystilbene. After UV
curing, the resulting films had better chemical resistance and higher proton conductivity than uncured ones. In our previous work, we have obtained porous crosslinking poly(ether sulfone)s by radiation method [6]. The radiated sample can remain in the microcellular structure well, even when treated at 265 °C.

Great performance improvement of poly(ether sulfone)s have been achieved by UV crosslinking method. However, few studies focus on how to enhance the efficiency of photopolymerization. In this work, we synthesized a series of allyl-contained poly(ether sulfone)s (AS-PES) copolymers and use RTIR technology to investigate photocrosslinking behaviors of crosslinkable poly(ether sulfone)s. At the same time, an aromatic thiol was introduced to AS-PES for target at high performance photocrosslinkable poly(ether sulfone)s. The thermal properties of crosslinking polymers were also investigated by DSC and TGA.

**Results and discussion**

In order to prepare a series of poly(ether sulfone)s with crosslinkable pendants, a bisphenol monomer, 3,3'-diallyl-4,4'-dihydroxydiphenyl sulfone (DA-DHDPS), was synthesized in a two-step synthetic process including a nucleophilic substitution reaction of 4,4'-dihydroxydiphenyl sulfone (DHDPS) and allyl bromine in the presence of potassium carbonate and a Claisen rearrangement procedure (Scheme 1). The bisphenol was obtained as white crystal after the recrystallization in toluene and its structure was identified by IR and NMR spectroscopy.

![Scheme 1. Synthesis of DA-DHDPS.](image)

As shown in Scheme 2, the crosslinkable poly(ether sulfone)s were synthesized from DA-DHDPS, DHDPS and 4,4'-dichlorophenylsulfone (DCDPS) via nucleophilic substitution reaction. The reaction temperature was controlled below 165 °C to avoid gel generation from the crosslink of unsaturated pendant groups. Four copolymers were prepared and named as AS-PES-X, where X refers to the feed ratio of DA-DHDPS monomer. The obtained copolymers exhibited the inherent viscosities in the
range of 0.28-0.30 dl/g and number average molecular weights above 30,000 measured by GPC (Table 1).

**Tab. 1.** Molecular weights and properties of the polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>m/k</th>
<th>(\eta_{\text{inh}}) (dl/g)\textsuperscript{a}</th>
<th>(M_n)\textsuperscript{b}</th>
<th>(M_w/M_n)\textsuperscript{c}</th>
<th>(T_g(\degree C))\textsuperscript{d}</th>
<th>(T_d(\degree C))\textsuperscript{e}</th>
</tr>
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<tbody>
<tr>
<td>AS-PES-10%</td>
<td>1:9</td>
<td>0.28</td>
<td>30100</td>
<td>2.52</td>
<td>221</td>
<td>442</td>
</tr>
<tr>
<td>AS-PES-20%</td>
<td>2:8</td>
<td>0.29</td>
<td>39800</td>
<td>2.02</td>
<td>220</td>
<td>448</td>
</tr>
<tr>
<td>AS-PES-30%</td>
<td>3:7</td>
<td>0.30</td>
<td>40800</td>
<td>2.61</td>
<td>219</td>
<td>431</td>
</tr>
<tr>
<td>AS-PES-40%</td>
<td>4:6</td>
<td>0.28</td>
<td>34700</td>
<td>2.39</td>
<td>208</td>
<td>440</td>
</tr>
<tr>
<td>AS-PES-20 UV cured</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>242</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Inherent viscosity measured with 0.5 g/dl at 25 °C in DMF.
\textsuperscript{b} Number-average molecular weight determined by GPC.
\textsuperscript{c} Polydispersity.
\textsuperscript{d} Glass transition temperature from the second heating cycle of DSC.
\textsuperscript{e} Temperature at 5% weight loss in Nitrogen.

FTIR and \(^1\)H-NMR spectra were used to confirm the chemical structure of AS-PESs. FT-IR spectra of the polymers with different content of allyl are shown in Fig.1. The absorption bands at 965 cm\(^{-1}\) could be found due to the symmetric and asymmetric double bond stretching vibrations of propenyl groups. This characteristic peak increased with the feed ratio of DA-DHDPS. The above results indicated that allyl groups in DA-DHDPS have rearranged to propenyl groups under the alkalescent polymerization condition, which is in accordance with the previous reports [7].

![FT-IR spectra of AS-PESs](image)

**Fig. 1.** FT-IR spectra of AS-PESs.

Fig. 2 shows a typical \(^1\)H-NMR spectrum of AS-PES-40. The peaks corresponding to aromatic hydrogens are in the range of 7-8.5 ppm. The peaks of aliphatic hydrogens are well separated from each other. The peak at 1.73 ppm corresponds to methyl hydrogens of propenyl groups. The peaks of the methylene hydrogens of allyl groups can also be found at 3.60 ppm, indicating that the isomerized reaction went on incompletely in polymerization process. Calculated from the integral area ratio of these two peaks, 65% allyl groups have isomerized to propenyl groups during polymerization. Because the photo-reactivity of propylene group is higher than that of
allyl group for the conjugation of double bond to benzene ring, such isomerization will favor the photocrosslinking reaction of corresponding polymer. However, in order to avoid gel generation, a low polymerizing temperature of 165 °C must be controlled and thus we cannot obtain completely isomerized products. Comparing the areas of above two peaks to that of aromatic hydrogens of ortho-position of sulfone group, including 1, 4, 5 in the Fig. 2, 37.5% aliphatic-containing units must have been introduced into polymer, similar with the feed ratio of DA-DHDPS (40%).

Fig. 2. $^1$H NMR spectrum of AS-PES-40.

DSC measurements show the glass transition temperature ($T_g$) of AS-PES copolymers decrease with the contents of aliphatic pendants and range from 225 °C to 215 °C due to the flexibility of aliphatic pendants. No other thermal transition behavior except glass transition can be found in DSC curve, indicating the amorphous nature of obtained copolymers. As a result, all the copolymers showed good solubility in common organic solvents, such as CHCl$_3$, DMF, DMSO and NMP. AS-PES copolymers have good thermal stability as summarized in Table 1. The temperature at 5% weight loss of these copolymers are about 430-450 °C in nitrogen.

The synthesis of the crosslinker, bis(4-mercaptophenyl)sulfone (BMPS), is based on a sulfone activated chloro-displacement by hydrosulfide via an aromatic nucleophilic substitution reaction as shown in Scheme 3. The structure of BMPS was confirmed by IR and $^1$H NMR. Current thiols using in thiol/ene systems mainly include mercapto carboxylic acid esters, alkyl thiols and thiophenols. According to the Kharasch MS reported in article [8], activities of different types of thiols compounds in a reaction listed in the following order: Aryl-SH> HOOCCH$_2$-SH>> RCH$_2$-SH> R$_1$R$_2$CH-SH> R$_1$R$_2$R$_3$C-SH. Considering the mercaptan reactivity in the photopolymerization process and the structural similarity to the polymer matrix, BMPS is preferable to be used in the thiol/ene system.

Scheme 3. Synthesis of BMPS.
Although the polymers with allyl groups may be crosslinked under some special conditions, the low photoreaction speed is unfavorable for the coatings applications. Thus, the introduction of a high efficient crosslinker is necessary. The effects of BMPS concentration on photocrosslinking of AS-PES-20 with 1.0 wt% TPO were also monitored by RTIR and the results are shown in Fig. 3. It can be seen that the polymerization rate and final double bond conversion significantly increased with the addition of BMPS. With 1.0 wt% addition of BMPS concentration in this thiol/ene system, the final conversion of double bonds ranges from 45% (without any BMPS) to 79% after UV-cured for 900 s and the photopolymerization rate is also greatly increased. Above 1.0 wt% BMPS addition, these thiol/ene systems show similar photo-polymerization rates and final conversions. Aided to obtain a good heat resistance coating with high sensitive, 1.0 wt% BMPS concentration was enough to achieve an adequate photocrosslinking thiol/ene coating.

![Graph](image_url)

**Fig. 3.** The double bond conversion as a function of irradiation time for polymerization of AS-PES-20% composite in the presence of different molar ratio of thiol and ene at room temperature (TPO = 1.0 wt%, I =50 mW/cm²).

In thiol/ene system, the initiator TPO absorbs the light and generates the primary free radicals, which could react with thiol to form thiol free radical and induce the photopolymerization. Fig. 4 shows the effects of the TPO concentration on the photocrosslinking process of AS-PES-20 containing 1.0 wt% BMPS (molar ratio of thiol:ene is 10:100) monitored by RTIR. It demonstrates that the polymerization rate increases with TPO concentration. When TPO concentration reaches 1.0 wt%, the final conversion of double bonds was close to 80% after UV-cured for 900 s, which is a high value for photopolymerization. Above 1.0 wt% TPO concentration, these thiol/ene system show similar photopolymerization rates and final conversions. It is interesting that even without any photoinitiator, photocrosslinking reaction could still proceed in this thiol/ene system. However, it shows much slower polymerization than that with 1.0 wt% TPO and the final conversion was only 40% after UV irradiation of 900 s. Therefore, in the following investigations, 1.0 wt% TPO concentration was used in thiol-ene system for sufficient photocrosslinking.
Fig. 4. The allyl double bond conversion as a function of irradiation time for polymerization of AS-PES-20 composite with different concentration of TPO at room temperature (thiol:ene=10:100, I = 50 mW/cm²).

We have known that one of the greatest advantages for poly(ether sulfone) coatings is their high thermal resistance. In this study, both DSC and TGA were used to evaluate the thermal properties of the coatings. The glass transition temperatures ($T_g$) of the AS-PES-20 and AS-PES-20 UV cured (blends TPO 1.0 wt% and BMPS 1.0 wt%) films were determined by DSC. The $T_g$ value of AS-PES-20 is found to be 220 °C. After sufficiently UV cured, its $T_g$ increased to 242 °C due to the formation of chemical networks. In order to investigate the thermal stability of this new photosensitive copolymer for specific resist applications, the thermo-gravimetric analyses were carried out in air and nitrogen atmosphere in the range of 50–800 °C. The 5% decomposition temperature of AS-PES-20 and AS-PES-20 UV cured films in nitrogen are 448 and 425 °C, respectively. After UV curing, the thermal stability of AS-PES-20 slightly decreased probability for the remains of reactive radicals in polymer. These results indicate that the thiol/ene systems of AS-PESs have good thermal stability required for the high heat-resistant grade anti-corrosion coatings applications.

It is noticed that after curing yellowish, transparent, hard and flexible coatings are formed. Compared with uncured fragile and soluble samples, cured ones showed good mechanical strength and they could not be dissolved in common solvents. All coating samples was AS-PES-20 blends 1wt% BMPS and 1% TPO within 10 minutes of irradiation. The cured coatings showed excellent results. The hardness characteristics of the prepared AS-PES coating reached 3H measured by the Pencil hardness test and 0.72 measured by the Persoz hardness within 10 minutes of irradiation. The prepared AS-PES coating has excellent adhesion and good impact resistance ability. All coated plates showed good resistance in the acid, salt, and alkali corrosion tests, and no obvious change was observed after soaking them in the 5 wt% aqueous solution of HCl, NaOH or NaCl for 72 hours.

Conclusions

In summary, we have successfully prepared a new type of photosensitive poly(ether sulfone)s. The photocrosslinking reactions based on the current system showed both high reaction speed and high conversion ratio. Especially, the cured AS-PES-20
coating had good thermal stability, improved mechanical properties and other properties for coatings applications.

**Experimental part**

**Materials**

4,4'-Dichlorodiphenyl sulfone (DCDPS) and 4,4'-dihydroxydiphenyl sulfone (DHDPS) were purchased from Shanghai Chemical Factory. 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TPO) was obtained from BASF (China). All the other chemical reagents were purchased from Beijing Chemical Reagent and purified by conventional methods.

**Measurements**

$^1$H (500 MHz) NMR spectra were recorded on a Bruker 510 NMR spectrometer with tetramethyl silane as a reference. Gel permeation chromatograms (GPC) were obtained on a Waters 410 instrument with N,N-dimethylformamide (DMF) as an eluent and monodisperse polystyrene as standard. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821e instrument at a heating rate of 10 °C/min under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere using a heating rate of 10 °C/min and polymers were contained within open aluminum pans on a PERKIN ELMER TGA-7. The UV-visible absorption spectra were recorded on a UV2501-PC spectrophotometer. IR spectra (KBr pellets or films) were measured on a Nicolet Impact 410 Fourier transform infrared (FTIR) spectrometer. Inherent viscosities of the polymers were measured at 25 °C on a 0.5 g/dL solution in DMF.

Pencil hardness was evaluated on photocured films according to the standard test method ASTMD3363-74. Pendulum hardness was evaluated on photocured films according to the standard test method ISO 1552-1982. Impact Resistance was evaluated on photocured films according to the standard test method ASTM G14-77. Adhesion was evaluated on photocured films according to the standard test method ASTM D 3359-93.

**Irradiation**

In a typical UV curing experiment, the films (~20 μm) were cast from a CHCl$_3$ solution containing the AS-PES polymer, the thiol compound and the photoinitiator onto an aluminum plates for thermo and coating properties measurements. Samples were exposed at ambient temperature to the radiation of a 500W medium-pressure mercury lamp (Beijing Huiyixin electric-light-source Technology Development Co. Ltd.) in air at a given time. The maximum light intensity at the sample position was measured by radiometry (UV-A, Beijing Normal University, China) was 50 mW/cm$^2$ in the UV range.

**RTIR spectroscopy**

Representative samples of photo-curable formulations consisting of BMPS (1.0 wt%) and AS-PES (98.0 wt%) in presence and absence of TPO (1.0 wt%) were applied between two NaCl crystals. The samples were placed in the compartment of a Fourier transform infrared spectrometer (Nicolet 5700 FT-IR) and were simultaneously exposed to a UV light source (Rolence-100 UV) and an IR analyzing
light beam. The light intensity on the sample was 50 mW/cm² (UV-A, Beijing Normal University, China). The decrease of the C–H absorption peak area from 923 to 987 cm⁻¹ accurately reflects the extent of the polymerization since the change of the absorption peak area was directly proportional to the number of the propenyl that had polymerized. After baseline correction, conversion of the functional groups could be calculated by measuring the peak area at each time of the reaction and determined as follows:

\[
DC(\%) = \frac{(A_0 - A_t)}{A_0} \times 100
\]

where DC is the degree of propenyl double bond conversion at t time, A₀ is the initial peak area before irradiation and Aᵣ is the peak area of the double bonds at t time [9]. Every data point was repeated for three times.

### Synthesis of DA-DHDPS

In a 500mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser were placed DHDPS (40.04 g, 0.16 mol), allyl bromide (46.46 g, 0.384 mol), anhydrous potassium carbonate (26.496 g, 0.192 mol), DMF (200 mL) and the mixture system was heated at 110 °C. After 8 h, water was added in and the crystalline material was collected. After washing for several minutes with boiling 95% ethanol, the solid was then filtered and dried in oven. The solid was then kept at 240 °C under nitrogen for 30 min to carry out Claisen rearrangement reaction. After cooled at room temperature, DA-DHDPS were obtained as pale crystals. Finally, DA-DHDPS was purified by recrystallization in toluene [10]. m.p.: 138.5 °C (DSC); yield: 70%. IR (KBr, cm⁻¹): 1639, 1587, 1498, 1358, 914. \(^1\)H-NMR (500 MHz, DMSO, δ ppm): 7.69 (d, 1H, H-1), 7.56 (m, 1H, H-2), 6.93 (m, 1H, H-3), 5.91 (m, 1H, H-5), 5.07 (m, 2H, H-6), 5.03 (s, 1H, -OH), 3.33(m, 2H, H-4).

### Synthesis of AS-PES

In a 100mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean–Stark trap, and a condenser were placed DA-DHDPS (0.66 g, 2 mmol), DHDPS (2.00 g, 8 mmol), DCDPS (2.88 g, 10 mmol), anhydrous potassium carbonate (0.725 g, 5.3 mmol), \(N,N\)-dimethylacetamide (DMAc) (30 mL), and toluene (10 mL) and the mixture was allowed to reflux for 2 h. After toluene was removed by distillation, the system was heated at 165 °C for 20 h. The viscous mixture was poured into 1000mL acidic water. The threadlike polymer was pulverized, washed with hot ethanol and water several times, and dried at 80 °C under vacuum to give essentially quantitative yield of white polymer, AS-PES-20. Yield: 95%. IR (KBr, cm⁻¹): 1650, 1321, 1240, 1103, 965. \(^1\)H-NMR (500 MHz, CDCl₃, δ ppm): 8.18 (m, 2H), 7.95 (m, 6H), 7.25 (m, 4H), 7.14 (m, 2H), 6.90(m, 2H), 6.51(m, 2H), 1.73(m, 6H).

### Synthesis of BMPS

In a 500mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser were placed DCDPS (43.1 g, 0.150 mol), sodium hydrosulfide (35.7 g, 0.450 mol), anhydrous potassium carbonate (31.1 g, 0.225 mol), dimethyl sulfoxide (DMSO) (100 mL) and the mixture system was heated at 120 °C. After 20 h, the dark brown reaction mixture was cooled, added to ice water, filtered, and slowly acidified with concentrated hydrochloric acid to a pH<1. An off-white precipitate was formed immediately upon acidification. The crude product was dissolved in 5% \(K_2CO_3\) aqueous solution and precipitated by adding concentrated HCl. The white
granular product was collected, washed well with deionized water, and vacuum dried at 80 °C for 24 h [11]. m.p.: 145-146 °C (DSC); yield: 60%. IR (KBr): 2532, 1307, 1109 cm⁻¹. ¹H-NMR (500 MHz, DMSO-d₆, δ, ppm): 7.77-7.74 (d, 4H, 1), 7.51-7.49 (d, 4H, 2), 3.60 (s, 2H, -SH).

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References