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Polymer 48 (2007) 6241–6245
polymer
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Synthesis and characterization of poly(aryl ether sulfone) copolymers containing terphenyl groups in the backbone

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Received 5 July 2007; received in revised form 8 August 2007; accepted 10 August 2007
Available online 19 August 2007

Abstract

A linear rigid bisphenol monomer, 4,4′-dihydroxyterphenyl (DHTP), has been incorporated into poly(aryl ether sulfone)s (PAESs) in a study to impart crystallization to these amorphous polymers. The PAES made from DHTP and dichlorodiphenylsulfone (DCDPS) is semi-crystalline but not soluble or thermally processable. Three bisphenols, 4,4′-isopropylidenediphenol (BPA), 4,4′-(hexafluoroisopropylidene)diphenol (BPAF) and 4,4′-dihydroxybiphenyl (BP), have been copolymerized with DHTP and DCDPS in order to study the effect of structure on crystallinity and processability. Both random and segmented copolymers containing different amounts of DHTP have been prepared via standard solution nucleophilic aromatic substitution polymerization technique. Only segmented polysulfone containing 50% BP and 50% DHTP was found to be semi-crystalline. This PAES had a melting temperature (T_m) 320 °C in the first heating cycle of a DSC measurement and the presence of crystallites was confirmed by wide angle X-ray diffraction (WAXS).

Keywords: Polysulfones; Semi-crystalline polymers; 4,4′-Dihydroxyterphenyl

1. Introduction

Poly(aryl ether sulfone)s (PAESs), with high glass transition temperatures (T_g), are amorphous aromatic tough thermoplastics and have unique high performance properties as engineering materials [1]. The synthesis and characterization of PAESs have been extensively investigated and well reviewed [2–7]. However, there are some undesirable features originating from their amorphous nature. They suffer from solvent sensitivity especially under stress and are subject to solvent cracking and they cannot form oriented film or fiber. The use temperature of PAES usually is about 30 °C lower than T_g. These shortcomings preclude their use when solvent resistance and high-temperature dimensional stability are required [8].

One way to overcome the above mentioned deficiencies of PAES is to make these polymers semi-crystalline [9]. For example, semi-crystalline thermoplastics such as poly(aryl ether ketone)s (PAEKs) exhibit good solvent resistance [10]. The crystalline phase also can act as physical crosslinks to enhance the high-temperature dimensional stability. Semi-crystalline engineering plastics such as polyesters have been used in temperatures much higher than their T_gs because they can be biaxially oriented and heat set. To achieve this goal, random or segmented copolymers poly(aryl ether ketone-*co*-sulfone)s (PAEKSs) have been widely explored to obtain high T_g semi-crystalline engineering thermoplastics [11–13]. Unfortunately such efforts are not very successful due to unwanted side reactions [14].

The ability of PAEKs to crystallize is generally ascribed to the close bond angles at aromatic ether (around 121°) and carbonyl groups (120–122°) leading to the linear chain geometry required for polymer crystallization [15]. Because the

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doi:10.1016/j.polymer.2007.08.036

bond angles at sulfonyl (around 106°) and aromatic ether (around 121°) groups are very different, the backbones of the PAESs have to adopt highly kinked conformations which interferes with the crystallization process [15]. The incorporation of terphenyl groups into the polysulfone backbone was shown to promote the crystallization but the polymers were highly insoluble with very high melting points thus nonprocessable [16]. In this study we synthesize random and segmented PAESs containing terphenyl group in the backbone and investigate the effect of terphenyl group on the thermal properties of the PAESs.

2. Experimental section

2.1. General considerations

All reagents were purchased from Aldrich and used as received unless otherwise noted. 4,4′-Dichlorodiphenylsulfone (DCDPS) was purchased from Aldrich and recrystallized from toluene. 4,4′-Difluorodiphenylsulfone (DFDPS, 99%+) and 4,4′-isopropylidenediphenol (BPA, 99%+) were purchased from Aldrich and used as received. 4,4′-Biphenol (BP) was obtained from Eastman Chemical and sublimed before use. 4,4′-(Hexafluoroisopropylidene)diphenol (BPAF), purchased from Aldrich, was purified by sublimation and dried under vacuum. NMR spectra were determined at 25 °C at 400 MHz with a Varian Unity spectrometer. The elemental analysis was done by Atlantic Microlab, Inc. (Norcross, Georgia).

2.1.1. Size exclusion chromatography (SEC)

Molecular weights of synthesized polymers were determined using size exclusion chromatography (SEC) using a Waters 717 Autosampler equipped with three in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector. The d*n*/d*c* values were determined online using the calibration constant for the RI detector and the mass of the polymer sample. SEC measurements were performed at 40 °C in tetrahydrofuran at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer was eluted from the column during the measurement.

2.1.2. TGA and DSC

Thermogravimetric analysis (TGA) was conducted under nitrogen, from 25 to 800 °C at a heating rate of 10 °C using a TA Instrument TGA 295. Glass transition temperatures were determined using a TA Q1000 DSC at a heating rate of 10 °C/min under nitrogen.

2.1.3. Wide angle X-ray diffraction (WAXS)

Photographic flat plate WAXS studies were conducted using a Philips PW 1720 X-ray diffractometer emitting Cu Kα radiation (1.54 Å wavelength), operating at a voltage of 40 kV and tube current of 20 mA. The sample to film distance was set to 47.3 mm for all samples. Direct exposures (4 h) were made in a Warhus camera using Kodak Biomass MS film in an evacuated sample chamber. The sample thickness was in the range of 12–14 mils.

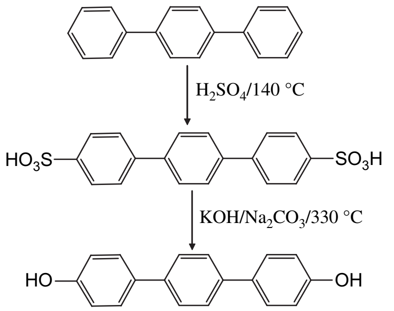
2.2. Preparation of 4,4′-dihydroxyterphenyl (DHTP)

The synthetic procedure of 4,4′-dihydroxyterphenyl (DHTP) is shown in Scheme 1 [17]. Concentrated sulfuric acid of 130 g was heated to 110 °C, and 40 g of terphenyl were added. The temperature was raised to 140 °C and maintained for 4 h. After cooling down to 100 °C, 120 mL of water was added dropwise, and the mixture was allowed to cool and then filtered with suction, giving a crude product which was used directly in the next stage.

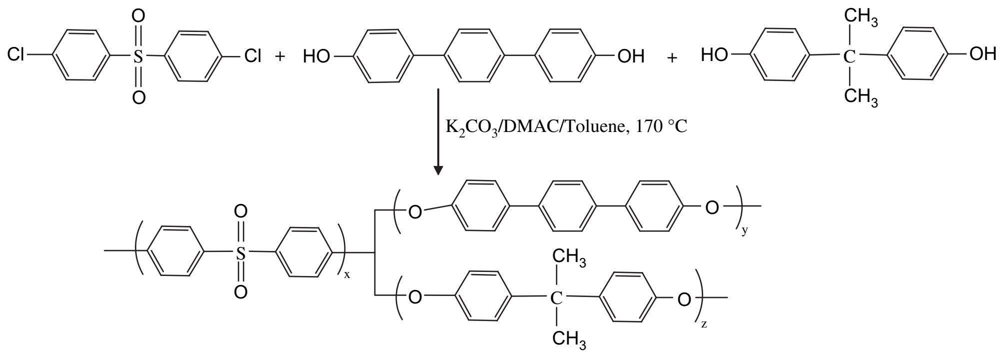
The stainless steel vessel in a Parr reactor was charged with 170 g of potassium hydroxide, 17 g of sodium carbonate and 70 g of the crude product described above. The temperature was raised to 330 °C and the mixture was stirred for 3 h under argon. The mixture was then cooled down to 100 °C and the pressure was released by opening the valve. The reaction mixture was transferred out by the addition of 1 l of water and the crude product precipitated out was filtered with suction. The crude product was suspended in 2 l of water, acidified with concentrated hydrochloric acid, heated to 90 °C and filtered with suction while still hot. The crude product was dried and recrystallized twice from *N*,*N*′-dimethylacetamide (DMAc). Yield: 85% as a white powder. ^{1}H NMR (DMSO-d_6, 100 MHz) δ ppm: 7.56 (s, 4H, Ar-H), 7.46 (d, 4H, Ar-H), 6.80 (d, 4H, Ar-H). ^{13}C NMR (DMSO-d_6, 400 MHz) δ ppm: 157.10, 138.14, 130.50, 127.54, 126.31, 115.78. Elemental analysis calculated C, 82.42; H, 5.38; O, 12.20. Found: C, 82.37; H, 5.52; O, 12.08.

2.3. Preparation of random PAESs

The copolymerization procedures were similar for all random DHTP containing PAESs (Scheme 2) [18]. A typical copolymerization for DHTP–BPA random copolymer is described below. First, 1.918 g (7.31 mmol) of DHTP, 3.000 g (10.45 mmol) of DCDPS, and 0.716 g (3.13 mmol) of BPA were added to a three-necked flask equipped with an overhead mechanical stirrer, an argon inlet, and a Dean–Stark trap. Potassium carbonate (13.7 mmol, 1.92 g) and sufficient DMAc (35 mL) were introduced to afford a 20% (w/v) solid concentration. Toluene (17 mL; usually, DMAc/toluene = 2/1 v/v)



Scheme 1. The synthesis of 4,4′-dihydroxyterphenyl.



Scheme 2. The synthesis of DHTP–BPA random PAES copolymer.

was used as an azeotroping agent. The reaction mixture was refluxed at 145 °C for 4 h to dehydrate the system. The temperature was raised slowly to 170 °C by the controlled removal of the toluene. The reaction was allowed to proceed for 24 h. The solution was cooled to room temperature and the copolymer was precipitated out in acidic water. The precipitated copolymer was washed with deionized water and then vacuum dried at 120 °C for 24 h.

2.4. Preparation of segmented PAESs

The copolymerization procedure was similar for all the segmented terphenyl containing PAESs. A typical copolymerization for the segmented copolymers is described below. First, 1.419 g (7.62 mmol) of BP and 2.115 g of DFDPS (8.32 mmol) were added to a three-necked flask equipped with an overhead mechanical stirrer, an argon inlet, and a Dean–Stark trap. Potassium carbonate (1.263 g, 3.13 mmol) and 20 g of diphenylsulfone were introduced to afford a 20% (w/v) solid concentration. Toluene (15 mL) was used as an azeotroping agent. The reaction mixture was refluxed at 145 °C for 4 h to dehydrate the system. The temperature was raised slowly to 175 °C by the controlled removal of the toluene. The reaction was allowed to proceed for 24 h. To the same reaction flask described previously, 2.000 g (7.62 mmol) of 4,4′-dihydroxyterphenyl, 1.762 g (6.93 mmol) of DFDPS, 1.263 g (3.13 mmol) of potassium carbonate, and 15 g of diphenylsulfone were introduced. Toluene (20 mL) was used as an azeotroping agent. The reaction mixture was refluxed at 145 °C for 4 h to dehydrate the system. The temperature was raised slowly to 170 °C by the controlled removal of the toluene. The reaction was allowed to proceed at 175 °C for 1 h, 200 °C for 1 h, 250 °C for 1 h, and at 300 °C for 2 h. At the final stage of the polymerization, the polymerization solution would climb up the stirring rod indicating the high molecular weight of the polymer. The solution was cooled to room temperature and the copolymer was taken out by breaking the reaction flask. The solid was heated and swelled in boiling DMAc three times to remove the diphenylsulfone. After that the solid was successively rinsed with hot acetone, hot water and hot ethanol to clean the polymer and then vacuum dried at 120 °C for 24 h.

3. Results and discussions

3.1. Synthesis of polymers

Polycondensations of bisphenols with stoichiometric amounts of DCDPS or DFDPS were carried out in the presence of excess potassium carbonate as base in aprotic polar solvents such as DMAc, sulfolane or diphenylsulfone depending on the solubility of the polymers (see Section 2 for details). A representative example of the synthesis of random polysulfone copolymers using BPA, DHTP and DCDPS is shown in Scheme 2. For the synthesis of random polysulfone copolymers, only DCDPS was used. Very good conversions and high molecular weights were obtained as indicated by the SEC data shown in Table 1. The percentages of the DHTP in the copolymer were verified by the ^{1}H NMR and were very close to the monomer feed ratios. When the copolymerization contained 70% DHTP (since the mole ratio of phenol to DCDPS was always kept to 1:1, the percentage mentioned here is the mole percentage of DHTP to the total amount of bisphenols), sulfolane was used as the solvent to keep the polymers soluble during the polymerization.

For the synthesis of segmented copolymers, the BPA or BP containing fluorine terminated oligomers ($M_n = 5$k) were synthesized first. Because the oligomer synthesized from DHTP and DCDPS or DFDPS is insoluble in organic solvents, we could not synthesize the segmented copolymers by connecting the two different oligomers directly [19]. To overcome the solubility problem, the BPA or BP containing fluorine terminated

Table 1
Compositions, molecular weights and molecular weight distributions of the random polysulfone copolymers

Compositions			M_n (g/mole)	M_w/M_n
BPA, 100%	DHTP, 0%	DCDPS, 100%	28,200	2.90
BPA, 90%	DHTP, 10%	DCDPS, 100%	49,500	2.61
BPA, 70%	DHTP, 30%	DCDPS, 100%	29,200	1.94
BPA, 50%	DHTP, 50%	DCDPS, 100%	48,100	2.23
BPAF, 100%	DHTP, 0%	DCDPS, 100%	29,200	2.82
BPAF, 90%	DHTP, 10%	DCDPS, 100%	36,500	2.92
BPAF, 70%	DHTP, 30%	DCDPS, 100%	22,600	2.33
BPAF, 50%	DHTP, 50%	DCDPS, 100%	26,900	2.14

oligomers were mixed with the DHTP and DFDPS for the second polycondensation step. The BPA or BP containing fluorine terminated oligomers were enchained by the DHTP DFDPS oligomers formed in situ. A representative example for the synthesis of random polysulfone copolymers using BP, DHTP and DFDPS is shown in Scheme 3. We found that the BPA or BP containing chlorine terminated oligomers were not reactive enough to form high molecular weight segmented polymer. So only DFDPS was used for the synthesis of segmented polysulfone copolymers. The segmented PAES copolymers show big differences in solubility and appearance from the random ones with the same composition. Although we can not exclude the occurrence of trans-etherification during the polymerization to make segmented PAES copolymers, such possible trans-etherification can be reduced greatly by using the much more reactive DFDPS instead of the DCDPS [20].

3.2. Solubility of polymers

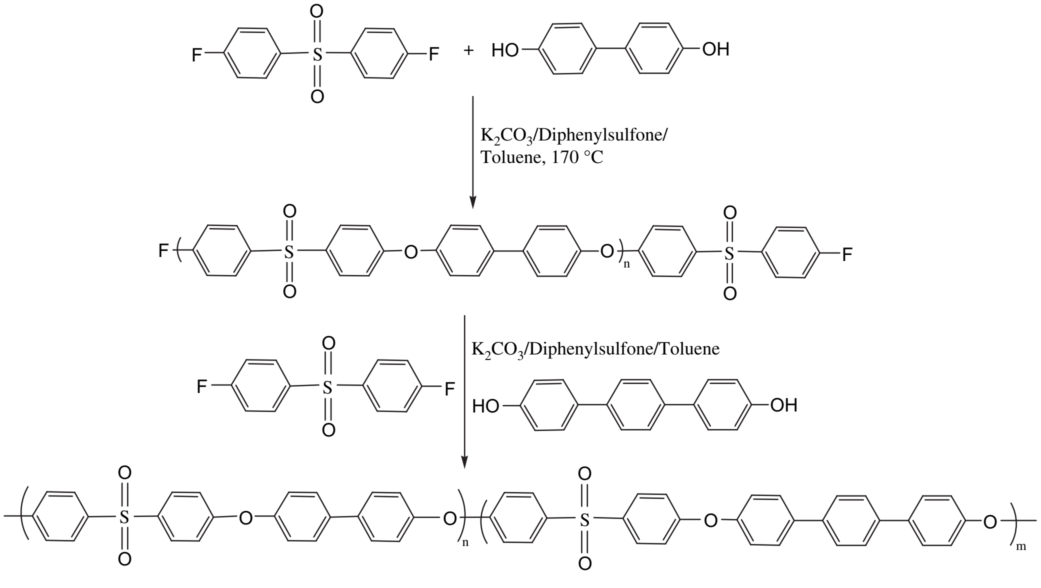
The incorporation of DHTP decreased the solubility of the polysulfone copolymers. The polysulfone copolymer synthesized only from DHTP and DCDPS is insoluble in any organic solvents. During the polymerization the polymer precipitated out quickly from sulfolane in the powder form. This is likely just low molecular weight oligomer. For random copolymers synthesized from BPA or BPAF with DHTP, the polymers are soluble in THF, chloroform and DMAc at room temperature when the molar percentage of DHTP is lower than 70%. For random copolymers synthesized from BP and DHTP, the polymers are soluble in hot DMAc or NMP when the molar percentage of DHTP is lower that 70%. The solubility of the segmented copolymers is significantly lower than that of the random copolymers. The segmented copolymer from BPA and DHTP is only soluble in hot DMAc. The segmented copolymer containing BP is only slightly swelled in boiling DMAc.

3.3. Polymer crystallization

These polysulfone copolymers demonstrated excellent thermal stability with a 5% weight loss between 490 and 500 °C in nitrogen. For the DHTP–DCDPS polysulfone copolymers, glass transition temperature T_g and melting temperature T_m were 250 and 370 °C, respectively, close to the reported values [16]. This indicates that the terphenyl group does straighten the polymer chain and facilitate the packing of the polymer chains to form crystallites. Since this polymer is non-processable, BPA, BPAF and BP were incorporated to lower the glass transition temperature and the melting temperature.

However, even containing 70% DHTP, the synthesized random copolymers are non-crystalline and exhibit no crystallization or melt transition in DSC measurements. The glass transition temperatures increase with the increased amount of incorporated DHTP in a BPA copolymer and are summarized in Fig. 1. Similar results were obtained when incorporating BPAF or BP. These random copolymers exhibit considerably higher T_g values than the corresponding PAESs without terphenyl groups. This is attributed to the more rigid polymer backbone of these polymers because of the presence of the terphenyl groups [21]. It seems that the terphenyl groups have to be concentrated to induce chain crystallization.

For the segmented PAES containing 50% BPA and 50% DHTP, no well-defined crystallization or melt transition was observed in DSC measurements. Crystallization was clearly shown in the first heating cycle of the DSC measurement of segmented PAES containing 50% BP and 50% DHTP (Fig. 2). The formation of crystallites was also confirmed by the wide angle X-ray diffraction (Fig. 3). The melting temperature is 320 °C which is low enough for processing. However, no crystallization or melt transition was observed in the second heating cycle (Fig. 2), even when the sample was annealed at 300 °C for 30 min. Although we cannot totally rule out re-equilibration of the segmented copolymer in the



Scheme 3. The synthesis of DHTP–BP segmented PAES copolymer.

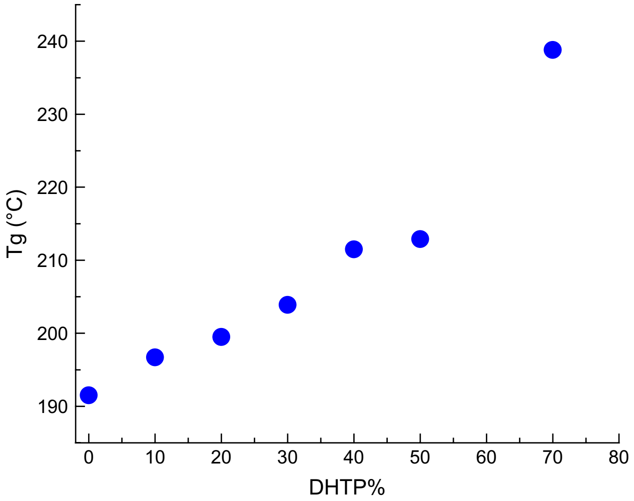


Fig. 1. Glass transition temperatures of the random BPA–DHTP polysulfone copolymers containing different amounts of DHTP.

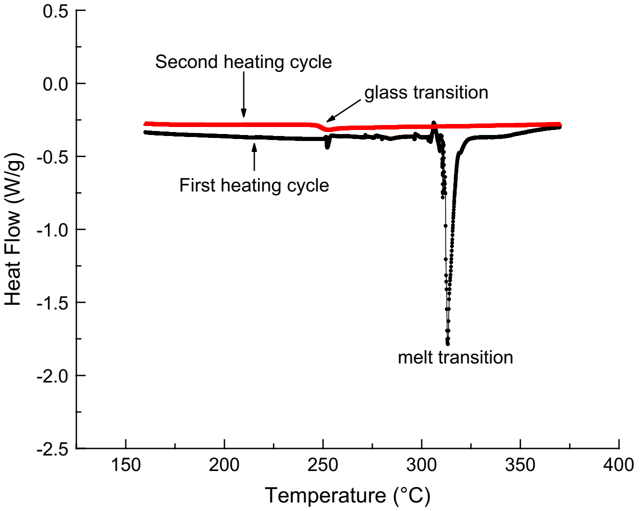


Fig. 2. DSC curves (first and second heating cycles) of the segmented PAES containing 50% BP and 50% DHTP, obtained at a heating rate of 10 °C/min.

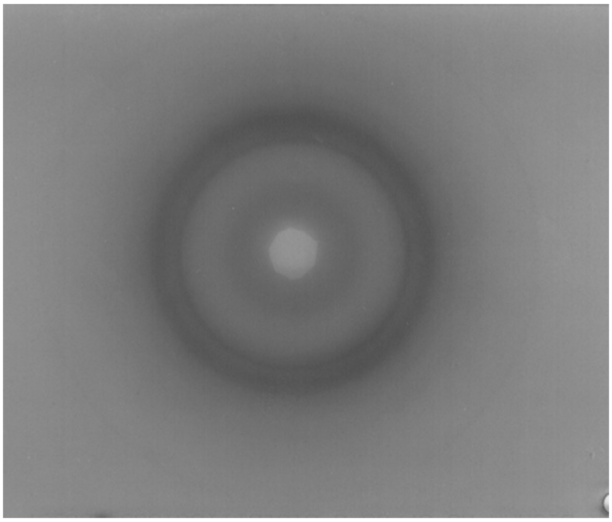


Fig. 3. WAXS pattern of the segmented PAES containing 50% BP and 50% DHTP.

DSC measurement, such crystallization behavior is similar to polycarbonate which undergoes solvent-induced crystallization and shows very slow crystallization rate in the melt state [22].

4. Conclusions

In this study 4,4′-dihydroxyterphenyl has been incorporated into the backbone of conventional PAESs to make them semi-crystalline. The more linear and rigid terphenyl groups can induce the formation of crystallites for the segmented PAES containing 50% BP and 50% DHTP. The semi-crystalline segmented PAES copolymer showed a melting temperature 320 °C in the first heating cycle of DSC measurement. The formation of crystallites was confirmed by the WAXS. No crystallization was observed in the second heating cycle of the DSC measurement likely due to the slow crystallization rate of the copolymer in the melt state.

Acknowledgment

This work was supported by the start-up funding from Department of Chemistry at Virginia Tech and partial support from Solvay Advanced Polymers. We thank Professor Timothy Long's group for the help on the GPC, TGA and DSC measurements and Prof. Herve Marand for helpful discussions.

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