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Electrical and mechanical properties of poly(arylene disulfide)s derived from macrocyclic(arylene disulfide) oligomers

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Poly(arylene disulfide)s were prepared by thermo-initialized ring-opening polymerization (ROP) of macrocyclic(arylene disulfide) oligomers. These macrocyclic oligomers were synthesized by catalytic oxidation of 4,4′-oxybis(benzenethiol) with oxygen in the presence of a copper-amine catalyst. This is the first work to characterize and investigate the electrical and mechanical properties of the poly(arylene disulfide)s obtained via ring-opening polymerization. The surface resistance and volume resistance of the polyaromatic disulfides cured at 180–220°C were higher than 10^{14} ohm and 10^{16} ohm · cm, respectively. The results indicated that the as-made polymers exhibited superior dielectric properties. Both mechanical strength and electrical properties of these polymers varied according to ROP conditions. These properties demonstrated that the macrocyclic(arylene disulfide) oligomers derived from 4,4′-oxybis(benzenethiol) could be used to produce thermally curing insulating material to substitute epoxy resins. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

The study on the synthesis of high performance polymers via ring-opening polymerization of macrocyclic aromatic oligomers has attracted much attention in recent years [1–7]. The *in situ* transformation of macrocyclic oligomers such as cyclic aromatic carbonates, cyclic aromatic ethers, cyclic aramids, and cyclic imides into high molecular weight polyaromatics opened up the possibility of a wide range of applications for wholly aromatic thermoplastics, which are currently not accessible with the linear high molecular weight counterparts due to their inherent high melt viscosities.

The ring-opening polymerization of aromatic cyclic oligomers can offer many advantages over traditional methodologies, including the elimination of used solvents, the absence of volatile byproducts, and the capability of achieving very high molecular weights in a short reaction time. The low melt viscosities of cyclic aromatic oligomers permits the applications of high performance thermoplastics via simply processing methods such as compression molding, resin-transfer molding, melt pultrusion, and reaction injection molding etc.

Poly(arylene disulfide)s are a kind of polymer with many characteristic properties, for example, high resistance to environmental degradation, good adhesion to wood, metal, glass and concrete and excellent resistance to solvents, water, acids and bases. Poly(aliphatic disulfide)s have long been commercialized and have found many applications [8, 9], but the applications of poly(arylene disulfide)s have been limited by their processing problems that are mainly due to their poor solubility and high melt viscosity.

The synthesis of macrocyclic(arylene disulfide) oligomers has been performed since the first report by Marschalk 50 years ago [10]. Many macrocyclic(arylene disulfide) oligomers containing various functional groups, including sulfide, ketone, sulfone, biphenyl, methylene and isopropylidene, have been synthesized [11–15]. To produce high performance

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insulating material is a potential usage of the oligomers due to the absence of free charge carriers in disulfide polymers.

According to previous works [16, 17], the macrocyclic oligomers prepared from 4,4′-oxybis(benzenethiol) had particularly low melting temperatures ranging from 115 to 120°C, and were unique intermediates for the preparation of linear poly(arylene disulfide)s with high molecular weights. Upon heating over 150°C, the ring-opening polymerization can take place instantly without the presence of any initiator or catalyst.

The objective of this work is to synthesize and to perform ring-opening polymerization of macrocyclic(arylene disulfide) oligomers. In order to explore the potential applications of macrocyclic(arylene disulfide) oligomers as high-ranking insulating material, we focus herein on the investigation of electrical conductivities and dielectric properties of the polymers obtained under different conditions. The mechanical properties and thermal stability were also studied to predict the application threshold of the new material.

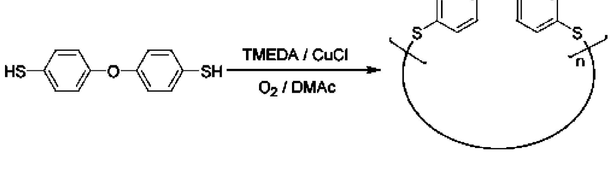
2. Experimental

2.1. Materials

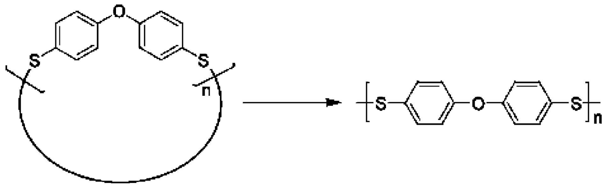
All the chemicals used were of analytical reagent grade and were used without further purification. Diphenyl ether were obtained from commercial sources and used as received. 4,4′-oxybis(benzenethiol) was fabricated according to the procedure described in the our previous paper [17].

2.2. Synthesis of macrocyclic(arylene disulfide) oligomer

Iodine and dimethyl sulphoxide (DMSO) have been frequently used as oxidant to prepare disulfides or polydisulfides from thiols [18–20]. Hay found that dithiols can be transformed into polydisulfides by reacting with oxygen in the presence of a mixture of tertiary amine and a copper salt [21]. Ding further demonstrated that catalytic oxidation of arenedithiols is an effective way to synthesize macrocyclic(arylene disulfide) oligomers [22]. In this work, the macrocyclic oligomers were synthesized in a relatively larger scale by catalytic oxidation of 4,4′-oxybis(benzenethiol) under pseudo high dilution condition (Scheme 1). To a 3L three-neck flask equipped with an oxygen inlet and a mechanical stirrer were charged with 3.0 g of CuCl, 6.0 g of N,N,N′,N′-tetramethylethylenediamine (TMEDA) and 2×10^{-3} m^3 N,N-dimethylacetamide (DMAc). The reaction mixture was vigorously stirred for 10 min while oxygen was bubbled in. Then 40.0 g 4,4′-oxybis(benzenethiol) dissolved in 250×10^{-6} m^3 DMAc was drop-wise added to the reaction mixture over 3–4 h. The resulting mixture was stirred for another hour to ensure the completion of oxidation and then filtered. The filtrate was treated with 2×10^{-3} m^3 5% dilute HCl and stirred for 1 h to remove the copper salt. The precipitates were collected by filtration, washed with methanol twice and dried at 50°C under vacuum for 24 h. The yield was 89%.



Scheme 1 Synthesis of macrocyclic(arylene disulfide) oligomers by copper catalytic oxidation reaction.



Scheme 2 Ring-opening polymerization of macrocyclic(arylene disulfide) oligomers.

2.3. Sample preparation via ring-opening polymerization

The samples used for characterization, as described below, were fabricated by reactive molding, according to the reaction depicted in Scheme 2 using a hydrostatic compression molding machine. The macrocyclic(arylene disulfide) oligomers derived from 4,4′-oxybis(benzenethiol) were firstly heated to melt (~120°C) followed by pressing to exclude the air, and then the resulting small disks were compression molded under a pressure of 20 MPa at 180, 200 and 220°C, respectively. A mold residence time of 30 min was performed and the as-molded samples were cooled to room temperature rapidly upon an existing cooling and pressure-keeping equipment under the pressure of ~20 MPa. The samples for tensile tests and dynamic mechanical analyses were prepared by cutting the molded pieces into the desired shapes.

2.4. Instrumentation

The static tensile properties were measured at 23°C and relative humidity of 50% using an Instron Model 5566 tensile tester. The cross-head speed was set at 2 mm min^{-1}. Five specimens of each sample were tested, and the average results are reported. Dynamic mechanical analyses (DMA) were carried out with a Du Pont DMA (Model 983) in dual cantilever mode at a fixed frequency of 1 Hz and an oscillation amplitude of 0.1 mm. The dimension of the specimens used was $30 \times 10 \times 2$ mm^3. The temperature profile of the measurement employed ranged from −20 to 170°C at a heating rate of 3°C/min.

The electric strength, dielectric property and electrical resistivity measurements of the poly(arylene disulfide)s were respectively performed at room temperature on a high voltage tester (Shanghai Electric China, model HT-100) using 25/75 mm brass electrodes, Schering Bridge (Tettex Switzerland, model 2821) and high resistance meter (Shanghai Electric China, model ZC36). The dimensions of used samples were 2 mm in thickness and 80 mm in diameter.

Thermogravimetric analysis (TGA) of the samples was performed in a Perkin Elmer TGA-6 under a

TABLE I Tensile properties for the poly(arylene disulfide) polymers obtained at varying ROP temperatures

ROP temperature (°C)	180	200	220
Tensile modulus (MPa)	884.0 ± 32	1081 ± 54	1208 ± 153
Maximum tensile strength (MPa)	18.95 ± 2.84	19.56 ± 1.86	18.29 ± 4.30
Elongation (%)	1.82 ± 0.32	2.82 ± 1.05	1.55 ± 0.54

nitrogen protective atmosphere (100×10^{-6} m^3/min). The temperature used ranged from 30 to 1000°C with a heating rate of 20°C/min. Prior to these analyses, the samples were dried in a vacuum oven at 60°C for 36 h.

3. Results and discussion

3.1. Mechanical properties

Table I lists the static tensile properties for the poly(arylene disulfide)s obtained at varying temperatures by ring-opening polymerization (ROP). It can be seen that both tensile strength and modulus increased with increasing ROP temperature. The tensile modulus increased from 884 ± 32 to 1208 ± 153 MPa when increasing the ROP temperature from 180 to 220°C. Presumably, this was resulted from the higher molecular weights of resulting polymers cured at higher temperature. No obvious improvements were observed for the tensile strength and strain at break with increasing ROP temperature, implying that the further increase in molecular weight does not change these properties. We have previously reported that the ROP can be completed and high molecular weight polymers can be afforded in a very short time (several minutes) [16].

Dynamic mechanical analysis (DMA) is a commonly used method to examine the time-dependent deformation behaviour of a sample under periodic sinusoidal deformation force with very small amplitudes. It can give the temperature dependence of Young's modulus E' (storage modulus) and loss modulus E'' as well as the mechanical loss factor tan δ (damping). Fig. 1 shows the storage modulus E' of the poly(arylene disulfide)s cured at 180, 200, and 220°C, respectively. Similarly with the constant strain rate measurements, the storage modulus E' increased with increasing ROP temperature. The storage modulus for poly(arylene disulfide)s cured at 220°C is about 300 MPa higher than that cured at 180°C. It is also evident that from Fig. 1 that the strength of as-made polymers was very sensitive to temperature change around their glass transition temperature (T_g). The polymers lost their strength completely at temperatures higher than their $T_g s$, indicating that these new polymers can only be used at temperatures lower than their $T_g s$. The increase in the application temperature for the new polymer could be achieved by the cross-linking of the polydisulfide, which has been disclosed in previous work [11]. In this connection, these new polymers could be used as a hot-melt adhesive, immersion coating in insulating areas. The application involves the ROP followed by annealing (cross-linking).

The loss modulus E'' and tanδ curves of the poly(arylene disulfide)s are shown in Figs 2 and 3, respectively. The peaks appearing in the two figures clearly indicate the relaxation process of these polymers. The $T_g s$ (obtained from Fig. 3) of the polymers cured at 180, 200, and 220°C are 86, 92 and 100°C, respectively. The obvious increase in $T_g s$ also demonstrated the increase in the molecular weight

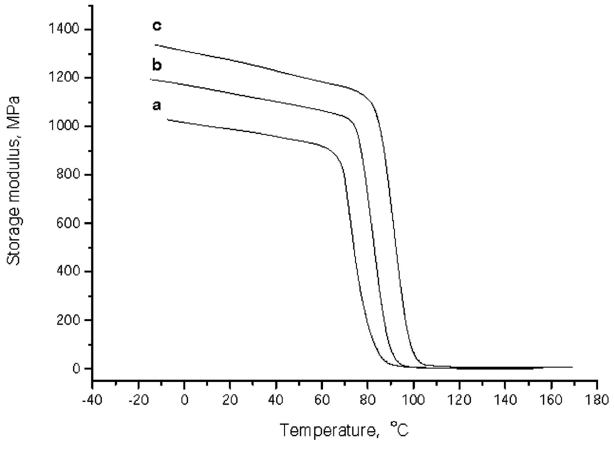


Figure 1 Storage modulus versus temperature for the poly(arylene disulfide)s derived from macrocycli(4,4′-oxybis(benzenethiol)): (a) polymers prepared by ROP at 180°C, (b) at 200°C, and (c) at 220°C.

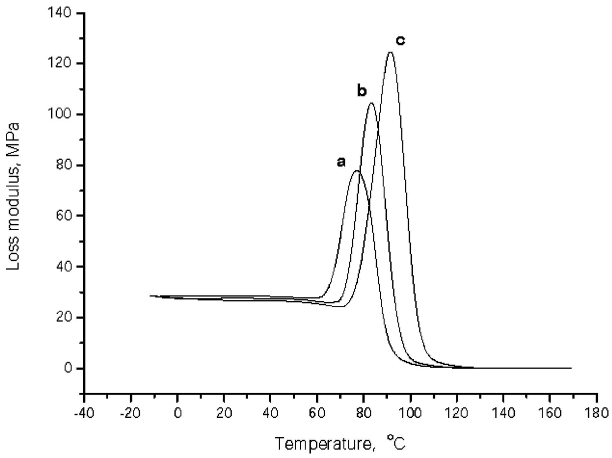


Figure 2 Loss modulus versus temperature for the poly(arylene disulfide)s derived from macrocycli(4,4′-oxybis(benzenethiol)): (a) polymers prepared by ROP at 180°C, (b) at 200°C, and (c) at 220°C.

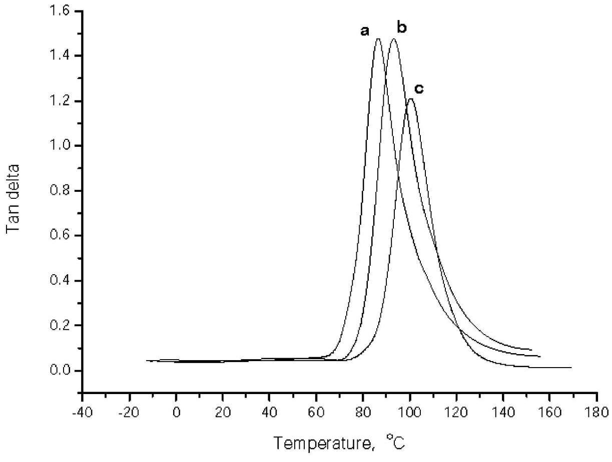


Figure 3 Loss factor versus temperature for the poly(arylene disulfide)s derived from macrocycli(4,4′-oxybis(benzenethiol)): (a) polymers prepared by ROP at 180°C, (b) at 200°C, and (c) at 220°C.

TABLE II Electrical and dielectric properties for the poly(arylene disulfide) polymers obtained at varying ROP temperatures

ROP temperature	180°C	200°C	220°C
Dielectric constant at 50 Hz	3.62 ± 0.08	3.66 ± 0.02	3.72 ± 0.05
Dissipation factor at 50 Hz	0.0059 ± 0.0004	0.0054 ± 0.0010	0.0068 ± 0.0006
Surface resistivity (ohm)	$2.9 \pm 0.9 \times 10^{14}$	$3.2 \pm 2.3 \times 10^{14}$	$6.1 \pm 2.1 \times 10^{14}$
Volume resistivity (ohm · cm)	$4.4 \pm 1.1 \times 10^{16}$	$3.3 \pm 2.4 \times 10^{16}$	$2.4 \pm 0.9 \times 10^{17}$
Electric breakdown strength		>24 kV/mm	

for poly(arylene disulfide)s with increasing ROP temperature.

3.2. Electrical and dielectric properties

The surface resistance, volume resistance, dielectric constant, dissipation factor and electric strength of poly(arylene disulfide)s derived from macrocyclic(4,4′-oxybis(benzenethiol)) measured at 50 Hz are tabulated in Table II. The surface resistance and volume resistance for all the polymers are greater than 10^{14} ohm and 10^{16} ohm · cm, respectively. Little increase of these values was observed with the increase in ROP temperature from 180 to 220°C. The increase is believed to result from the higher molecular weight obtained at higher ROP temperature.

Dielectric constant, also referred to as the specific inductive capacity (SIC), is a measure of an insulator's ability to store electrical energy, and dissipation factor represents the ability to generate heat during service. The dielectric constant and dissipation factor of the poly(arylene disulfide)s measured at 50 Hz are 3.6–3.7 and $5.4\text{–}6.8 \times 10^{-3}$, respectively. No obvious change was observed with increasing the ROP temperature. Such low dielectric constant and dissipation factor values are beneficial for use as insulating material.

3.3. Thermal stability

The thermal properties of the poly(arylene disulfide)s were determined using thermogravimetric analysis (TGA) method. The TGA curves of the polymers synthesized at 180, 200 and 220°C are shown in Fig. 4, respectively. All the decomposition traces are almost the same. The polymers exhibited highly thermal stability with 95% weight remaining at 340°C, and 34% weight remaining at a temperature as high as 1000°C. This indicated that these new polymers are good flame retardant materials.

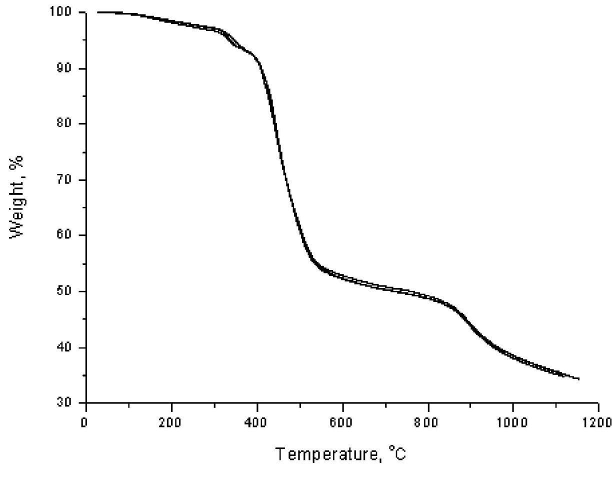


Figure 4 TGA curve versus temperature for the poly(arylene disulfide)s derived from macrocycli(4,4′-oxybis(benzenethiol)): (a) polymers prepared by ROP at 200°C and (b) at 220°C.

4. Conclusion

Poly(arylene disulfide)s can be simply prepared via ring-opening polymerization (ROP) of macrocyclic(4,4′-oxybis(benzenethiol)), and their electrical and mechanical properties were accordingly investigated. It was found that the new polymers have high surface ($>10^{14}$ ohm), high volume resistivity ($>10^{16}$ ohm · cm), low dielectric constant (<3.72) and dissipation factor ($<7 \times 10^{-3}$). The static and dynamic mechanical analyses of these polymers indicated that the tensile modulus is greater than 1.0 GPa. Both electrical and mechanical properties can be improved by increasing the ROP temperature. With the superior mechanical and electrical properties, the poly(arylene disulfide)s showed potential applications as hot-melt adhesive, immersion coating in insulating areas.

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