

# Rheological and Chemorheological Studies of Cyclic Aryl Ether Ketone and Aryl Ether Thioether Ketone Oligomers Containing the 1,2-Dibenzoylbenzene Moiety

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## SYNOPSIS

The melt stability, shear rate, and temperature dependence of steady-state shear viscosity of molten cyclic aryl ether ketone and thioether ketone oligomers containing the 1,2-dibenzoylbenzene moiety have been investigated. The isothermal chemorheology of the ring-opening polymerization of cyclic oligomers **4** and **9** in the presence of a nucleophilic initiator was also conducted. The cyclic aryl ether ketone oligomers are thermally stable in the melt, and their melt viscosity is several orders of magnitude lower than their high molecular weight linear counterparts. At a given temperature, the steady-state shear viscosity of the molten cyclics initially undergoes shear thinning as the shear rate increases, and once the shear rate is above  $10 \text{ s}^{-1}$ , the molten cyclic oligomers behave like Newtonian fluids. For the amorphous cyclic oligomers studied, the steady-state shear viscosity at  $100 \text{ s}^{-1}$  at a given temperature only depends on their glass transition temperature. The cyclic aryl thioether ketone oligomers are thermally unstable in the melt and undergo ring-opening polymerization in the absence of an initiator to form high molecular weight linear polymers with a concomitant rapid increase in viscosity. The rate of change in viscosity increases with temperature and is promoted by the addition of a catalytic amount of elemental sulfur or a disulfide such as 2,2-dithiobis(benzothiazole). It is hypothesized that the ring-opening polymerization is initiated by the *in situ* generated thiyl radical(s) and proceeds via a free-radical route. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Low melt viscosity aromatic macrocyclic oligomers have been developed as unique intermediates for the synthesis of high-performance engineering polymers in recent years.<sup>1-8</sup> The *in situ* transformation of the macrocyclic oligomers such as carbonates,<sup>1</sup> aryl ethers,<sup>2,3,6,7</sup> aramids,<sup>4</sup> and imides<sup>8</sup> via a ring-opening polymerization route to high molecular weight polymers opens up the possibility of a wide range of applications for aromatic thermoplastics that are currently not accessible with the linear high molecular weight counterparts due to the inherent high melt

viscosities. In particular, the low viscosity of cyclic oligomers permits applications of high-performance thermoplastics in the fabrication of long or continuous fiber reinforced thermoplastic composites via processing methods such as compression molding, reaction injection molding, and melt pultrusion. Because the processibility of the resin in any application will be largely dependent on its rheological properties, knowledge of the rheology of the cyclic oligomers and the viscosity profile during polymerization is, therefore, essential to the optimum design of the processing strategies.

We are currently studying the chemistry of cyclic aryl ether ketone oligomers containing the 1,2-dibenzoylbenzene moiety, which provide high molecular weight poly(aryl ether ketone)s upon ring-opening polymerization in the presence of a nucleo-

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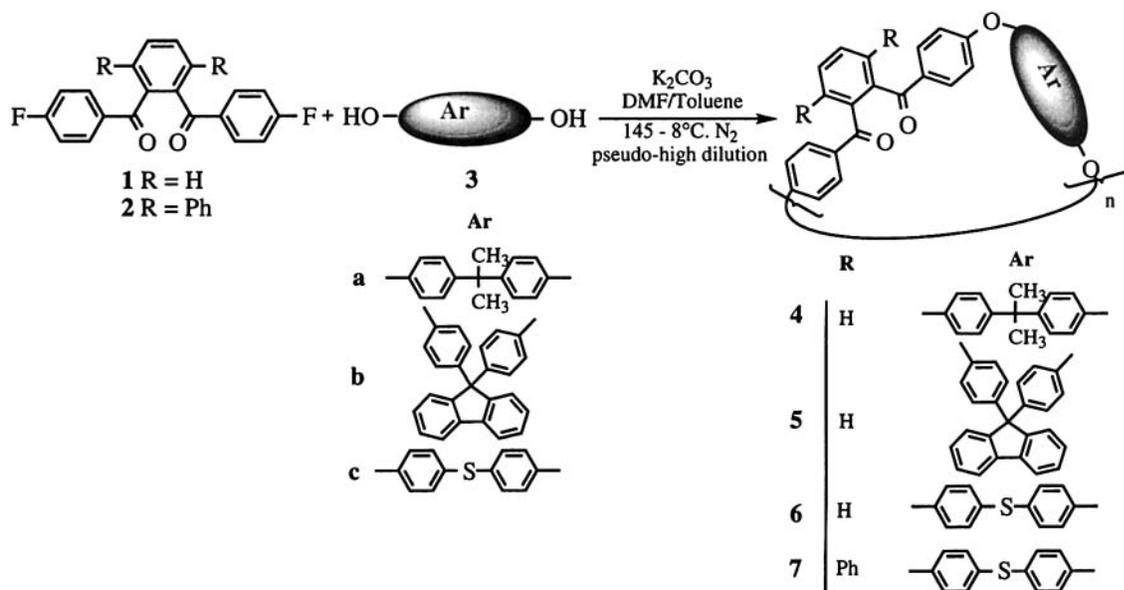
philic initiator. We have recently reported the efficient synthesis<sup>6,7</sup> and facile ring-opening polymerization<sup>9</sup> of these cyclic aryl ether ketone oligomers. Some preliminary results on the rheological and chemorheological studies of cyclic aryl ether ketone oligomers have also been reported.<sup>10</sup> As part of an on-going program, the work reported here was focused on the melt stabilities and rheological properties of cyclic aryl ether ketone and aryl ether thioether ketone oligomers, the viscosity-profile of the anionic ring-opening polymerization of the cyclic oligomers and chemorheological studies of the cyclic aryl ether thioether ketone oligomers in the presence of sulfur or an aromatic disulfide. The studies of the melt instability and chemorheology of the cyclic aryl ether thioether ketone oligomers has led to the discovery of a novel free-radical ring-opening polymerization of macrocyclic oligomers containing an aromatic sulfide linkage.<sup>11</sup>

## EXPERIMENTAL

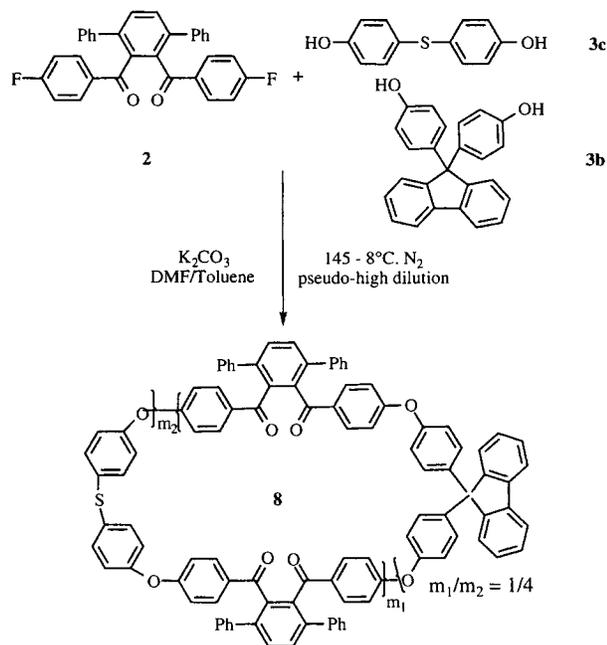
### Synthesis of Cyclic Oligomers

Reagent-grade solvents and chemicals were used without further purification. The cyclic oligomers 4–9 (Schemes 1–3) were prepared according to the procedure reported previously,<sup>6</sup> but on a larger

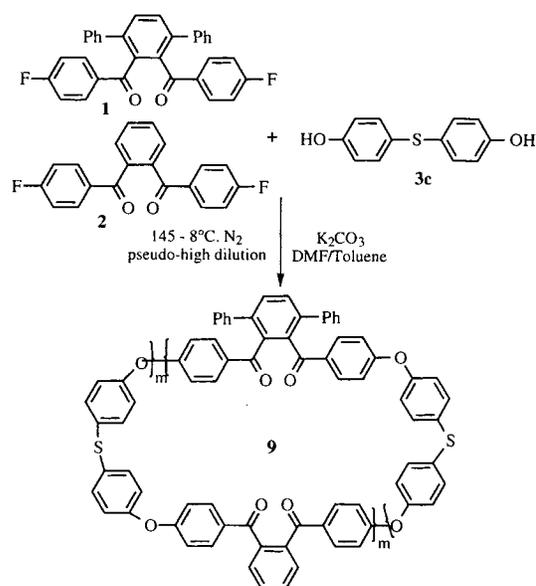
scale. A typical procedure is as follows. The cyclization reaction was conducted in a 12 L three-neck round-bottom flask that was equipped with a mechanical stirrer, Dean–Stark trap, condenser, N<sub>2</sub> inlet, and thermometer. The reaction vessel was charged with DMF (4.5 L), toluene (200 mL), and anhydrous potassium carbonate (55.28 g, 0.40 mol). The mixture was mechanically stirred and heated to reflux under Ar, and a small fraction (20 mL) of toluene was removed from the Dean–Stark trap in order to keep the refluxing temperature at 145°C. After refluxing at 145°C for 1 h, a solution of difluoro-monomer 1 (Scheme 1) (64.462 g, 0.200 mol) and bisphenol monomer 3a (49.658 g, 0.200 mol) in DMF (500 mL) was added at a rate of 1.20 mL/min over 8 h via a Perkin–Elmer HPLC pump series 10. After the addition, the resulting solution was kept at 145–8°C for another 8 h. The reaction mixture was cooled and filtered to remove salts. The solution was concentrated to 1.0 L under reduced pressure and added dropwise into 10 L of a vigorously stirring hydrochloric acid solution (0.20M) in deionized water. The desired oligomers precipitated, were collected by filtration, and washed with deionized water until acid free (checked with pH paper), and finally washed with methanol. The cyclic oligomers were dried at 160°C in a high vacuum oven for 24 h to give the desired oligomers 4 with a yield of 97%.



Scheme 1



Scheme 2



Scheme 3

### Characterization

GPC analyses were performed on a Waters 510 HPLC equipped with phenogel 5  $\mu$  columns (linear,  $3 \times 500 \text{ \AA}$ ) arranged in series with chloroform as solvent, and a UV detector set at 254 nm. Thermal analyses were conducted on a Seiko 220 DSC and 220 TGA/DTA instrument. Reverse phase HPLC analyses were performed on a DuPont Model 410 pump, ISS-100 autoinjector, and LC-235 diode array detector. Tetrahydrofuran/water gradient was used for the elution of cyclic oligomers on a C-8 reverse phase column ( $4.6 \times 256 \text{ mm}$ ) at a flow rate of 2.0 mL/min. The gradient program was; step 1, 60–80% THF over 17 min at exponent  $-2$ ; step 2, 84–100% THF over 1 min at exponent 1; step 3, 100% THF for 6 min; and step 4, 100–60% THF over 2 min (recycle).

### Rheological and Chemorheological Measurements

A Rheometrics System IV instrument was used, in a steady-state mode under a purge of nitrogen, to carry out the rheological and chemorheological characterization. A conical geometry was necessary for the rheological measurements of the cyclic oligomers because of the extremely low melt viscosity. The conical fixtures had a height of 17.5 mm, a diameter of 50 mm, and a cone angle of 0.0394 radians. The shear rate dependence of the steady-state shear viscosity of the cyclic oligomers was de-

termined over a temperature range of 230 to  $360^\circ C$  and in the shear rate range of 1 to  $500 \text{ s}^{-1}$ . Thermal stability of the molten cyclics were performed at  $100 \text{ s}^{-1}$  over a temperature range of 230 to  $390^\circ C$ . The effect of the thermal history on the composition of the cyclic mixtures was determined directly by GPC and HPLC analyses. The isothermal chemorheology of cyclic oligomers in the presence of a nucleophilic initiator or elemental sulfur and disulfide was carried out at a given temperature and a constant shear rate such as  $10 \text{ s}^{-1}$ . For the rheological tests, cyclic oligomers in powder form were dried in a vacuum oven at a temperature about  $50^\circ C$  higher than their  $T_g$  for 24 h prior to testing. For the chemorheological tests, the mixing of cyclic oligomers and initiator were carried out in the same manner as reported;<sup>9</sup> the mixture was also dried in a vacuum oven at a temperature about  $50^\circ C$  higher than their  $T_g$  for 24 h prior to testing. A typical procedure for the rheological measurement is as follows. The sample chamber was preheated to a given temperature and held at that temperature for 30 minutes to allow full expansion of the conical fixture, which was achieved by closing the two parts of the fixture and maintaining the torque at 0 and the gap meter at 0. The dried cyclic oligomers (3.2 g) were then added into the cylinder of the fixture as quickly as possible. It took 2 min for the sample chamber to reach the given temperature. After another 3 min, the distance of the two parts of the fixture was adjusted to allow

**Table I** Physical Properties of Cyclic Aryl Ether Ketone and Thioether Ketone Oligomers

| Cyclic Oligomers | Isolated Yield (%) | $M_n^a$ | $M_w^a$ | $T_g$ (°C) <sup>b</sup> | $T_m$ (°C) <sup>b</sup> |
|------------------|--------------------|---------|---------|-------------------------|-------------------------|
| 4                | 97                 | 1500    | 4800    | 154                     | 324                     |
| 5                | 95                 | 1700    | 5100    | 220                     | —                       |
| 6                | 96                 | 1300    | 3100    | 137                     | —                       |
| 7                | 95                 | 1900    | 5700    | 193                     | 385                     |
| 8                | 94                 | 2000    | 9000    | 232                     | —                       |
| 9                | 96                 | 1500    | 4800    | 161                     | —                       |

<sup>a</sup> Measured by GPC and calibrated against polystyrene standards.

<sup>b</sup> Measured by DSC under nitrogen atmosphere with a heating rate of 20°C/min.

a gap of precisely 50  $\mu\text{m}$ . The viscosity profile with shear rate change was measured.

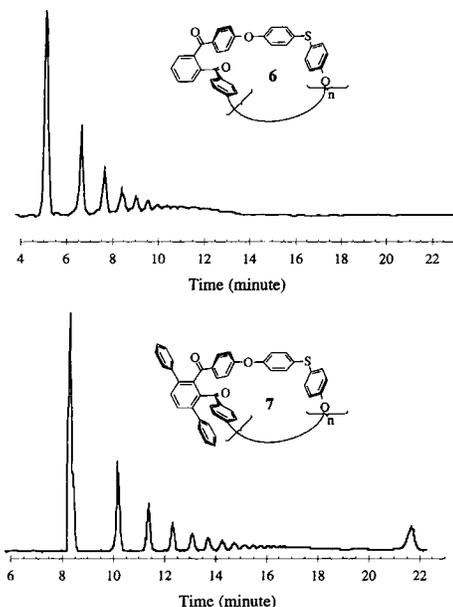
## RESULTS AND DISCUSSIONS

### Cyclic Aryl Ether and Thioether Ketone Oligomers

The cyclic oligomers containing the 1,2-dibenzoylbenzene moiety were prepared by an aromatic nucleophilic substitution reaction of difluoro-monomers **1** and **2** with the potassium salts of bisphenols **3** (Schemes 1–3) according to the procedure previously reported.<sup>6</sup> The characterization of these cyclics has been reported,<sup>7</sup> and some physical properties of the cyclics are listed in Table I. The cyclization of difluoro-monomer **1** with bisphenols under pseudohigh dilution conditions affords essentially a quantitative yield of cyclic aryl ether oligomers without formation of high molecular weight linear polymers. On the other hand, the cyclization of difluoro-monomer **2** with bisphenols generally leads to the formation of cyclics that are contaminated with 5% high molecular weight linear polymers. Typical reverse phase gradient HPLC traces of cyclic oligomers **6** and **7** are shown in Figure 1. The cyclics contaminated with high molecular weight linear polymers can be purified by soxhlet extraction using ethyl acetate as solvent.

### Rheology of Cyclic Aryl Ether Ketone Oligomers

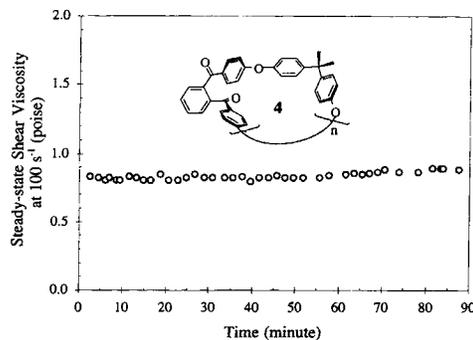
The cyclic aryl ether ketone oligomers are thermally stable in the melt. A typical melt stability measurement of cyclic oligomers **4** is shown in Figure 2. The



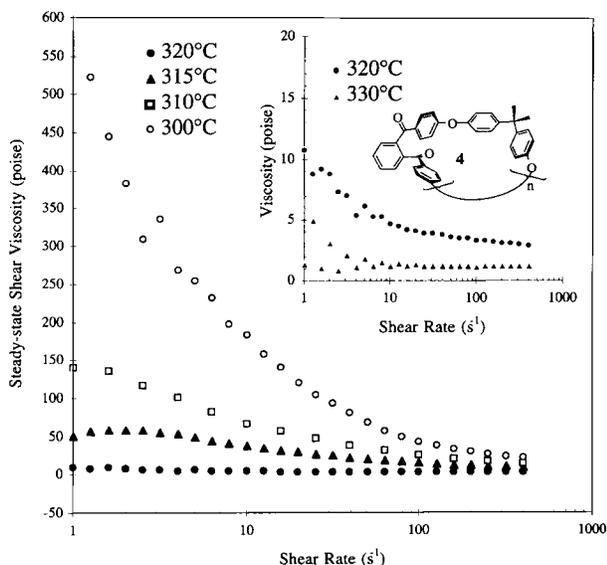
**Figure 1** Reverse-phase gradient HPLC traces of cyclic aryl ether thioether ketone oligomers **6** and **7**.

melt viscosity of cyclic oligomers **4** at 350°C is stable during the test period (90 min); this suggests that the cyclic oligomers are essentially salt free, as the salt residues in a cyclic aryl ether sulfone<sup>2c</sup> initiate the ring-opening polymerization and result in the melt instability of the cyclic aryl ether sulfone. GPC and reverse-phase gradient HPLC analyses of the cyclic oligomers before and after melt stability measurements indicate no change of the composition of the cyclic oligomers.

The shear rate and temperature dependence of the steady-state shear viscosity of cyclic oligomers **4** is shown in Figure 3. The steady-state shear viscosity of the cyclic oligomers at a given temperature



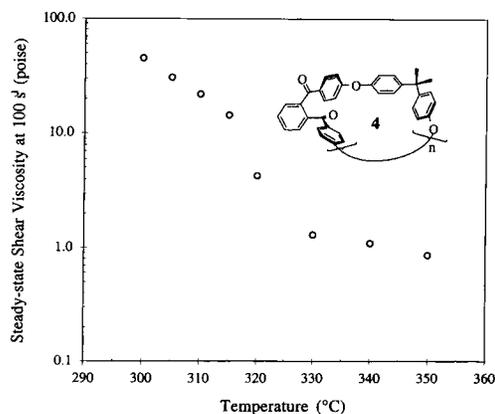
**Figure 2** Steady-state shear viscosity as a function of time for cyclic aryl ether ketone oligomers **4** at 350°C and 100  $\text{s}^{-1}$  under nitrogen.



**Figure 3** Shear rate and temperature dependence of the steady-state shear viscosity for cyclic aryl ether ketone oligomers **4**.

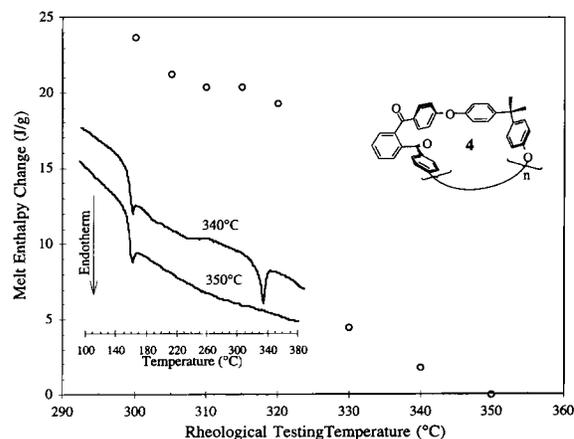
decreases monotonically as the shear rate increases. However, the shear rate dependence decreases dramatically as the testing temperature increases. Once the testing temperature reaches 320°C, which is close to the melting temperature ( $T_m$ ) of the cyclic oligomers, the viscosity is essentially independent of the shear rate. This is much more obvious when the testing temperature was increased to 330°C (see the insertion in Fig. 3). This implies that above  $T_m$ , the molten cyclic oligomers behave like Newtonian fluids. It should be pointed out that at higher temperature (e.g., 330°C), the viscosity of the molten cyclic oligomers is so low that the torque generated at lower shear rate (e.g., below 10  $s^{-1}$ ) is below the detection limit of the rheometer used. In most cases, the melt viscosity of the cyclic oligomers is independent of shear rate once the testing shear rate is above 10  $s^{-1}$ . Therefore, as a matter of consistency and simple comparison, in this article the melt viscosity of the molten cyclics is taken at a shear rate of 100  $s^{-1}$ .

The temperature dependence of the steady-state shear viscosity of cyclic **4** is shown in Figure 4. The steady-state shear viscosity of the molten cyclics at 100  $s^{-1}$  decreases from 46 poise to 1.0 poise as the testing temperature increases from 300 to 330°C, and there is a sharp change of the melt viscosity in the temperature range of 310–330°C. However, the steady-state shear viscosity remains essentially constant in the temperature range of 330 to 350°C.

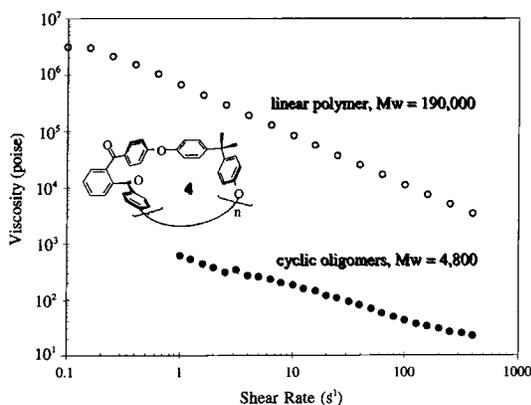


**Figure 4** Temperature dependence of the steady-state shear viscosity at 100  $s^{-1}$  for cyclic aryl ether ketone oligomers **4**.

This is due to the fact that in the temperature range of 300 to 330°C the crystalline cyclic oligomers were not fully melted and the crystalline solids act as particle fillers. The fraction of crystalline solids in the molten cyclics decreases as the testing temperature increases. Once the temperature reaches 330°C, the crystalline cyclics were essentially completely melted and, therefore, the melt viscosity should approach its minimum. After the melt stability tests, the cyclic oligomers were cooled and analyzed by DSC. The DSC results show that the cyclic oligomers are still crystalline even when treated at 340°C for 90 min, but they are amorphous after treatment at 350°C for 90 min (see the insertion in Figure 5). The effect of melt stability testing tem-



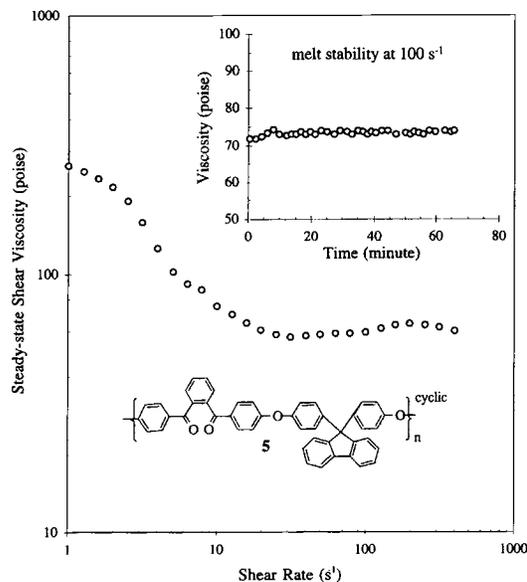
**Figure 5** Effect of rheological testing temperature upon the melt enthalpy change of cyclic aryl ether ketone oligomers **4** after rheological measurements. The insertion is the DSC trace of cyclic **4** after rheological measurements at 340 and 350°C.



**Figure 6** Shear rate dependence of the melt viscosity at 300°C for cyclic aryl ether ketone oligomers **4** and its high molecular weight linear counterparts.

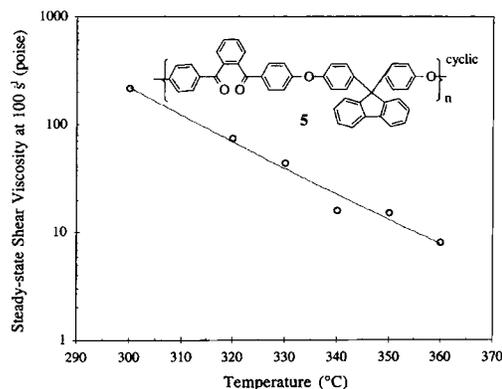
perature on the melting enthalpy change of the cyclic oligomers **4** is shown in Figure 5. Figure 5 shows that the cyclic oligomers after treatment at temperatures below 330°C are still highly crystalline, but after treatment at temperatures above 330°C the crystallinity is reduced dramatically, and when treated at 350°C, the cyclic oligomers are completely amorphous. We believe that at temperatures below 330°C there is significant amounts of cyclic oligomers in the form of crystalline solids, which act as nuclei for rapid recrystallization upon cooling; therefore, there is little change in the crystallinity. Above 330°C, the fraction of crystalline solids present in the molten cyclic oligomers is dramatically decreased as the testing temperature approaches the off-set melting temperature (342°C) of the cyclic oligomers and there are fewer nuclei to initiate the recrystallization upon cooling. Once the testing temperature reaches 350°C, the cyclic oligomers were completely molten and there are no nuclei remaining to initiate recrystallization of the cyclic oligomers upon cooling. The melt viscosity of the cyclic oligomers **4** at 300°C is three orders of magnitude lower than that of the linear polymers, although there are still a certain amount of cyclics remaining as crystalline solids (Fig. 6). This lower viscosity offers potential advantages in composite fabrication relative to the corresponding high molecular weight polymers.

The shear rate and temperature dependence of the steady-state shear viscosity of cyclic oligomers **5** are shown in Figures 7 and 8. The cyclic oligomers **5** are thermally stable in the melt (see the insertion in Fig. 7); and at a given testing temperature, the melt viscosity of the cyclic oligomers **5** initially de-

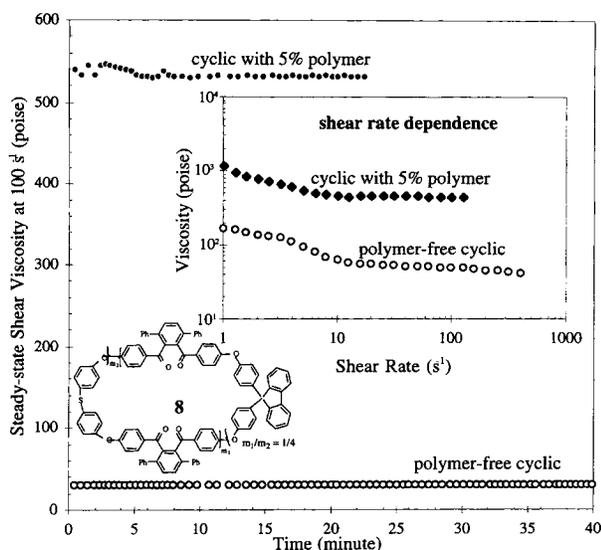


**Figure 7** Shear rate dependence of the steady-state shear viscosity at 320°C for cyclic aryl ether ketone oligomers **5**. The insertion is the steady-state shear viscosity as a function of time for cyclic aryl ether ketone oligomers **5** at 320°C and 100 s<sup>-1</sup> under nitrogen.

creases monotonically as the shear rate increases; however, once the shear rate reaches 10 s<sup>-1</sup> the melt viscosity is independent of the shear rate (Fig. 7). This suggests that the cyclic oligomers initially experience shear thinning, and once the shear rate is above 10 s<sup>-1</sup>, the cyclic oligomers behave like Newtonian fluids. Figure 8 shows that the steady-state shear viscosity of the amorphous cyclic **5** at 100 s<sup>-1</sup> decreases monotonically as the testing temperature increases from 300 to 360°C, and there is a linear



**Figure 8** Temperature dependence of the steady-state shear viscosity at 100 s<sup>-1</sup> for cyclic aryl ether ketone oligomers **5**.



**Figure 9** Steady-state shear viscosity as a function of time at 320°C and 100 s<sup>-1</sup> for cyclic aryl ether ketone oligomers **8** before and after removing the high molecular weight linear polymer. The insertion is the corresponding shear rate dependence the steady-state shear viscosity at 320°C.

relationship between the logarithm of the viscosity and the temperature.

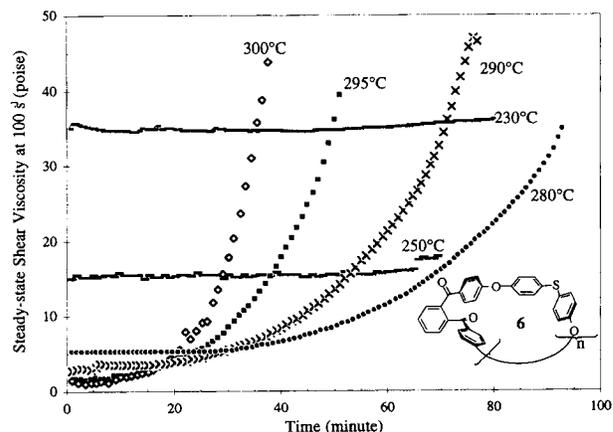
As was pointed out earlier, the cyclic oligomers based on monomer **2** normally contain ca. 5% high molecular weight linear polymers. It would be interesting to compare the melt viscosity of the cyclic oligomers contaminated with linear high molecular weight polymers with that of polymer-free cyclic oligomers. Cyclic oligomers **8**, contaminated with 5% high molecular weight linear polymers, was chosen for this experiment, and the linear polymer was removed by soxhlet extraction using ethyl acetate as solvent over 48 h. After extraction the cyclic oligomers were confirmed to be free of polymer by reverse-phase gradient HPLC analysis. The effect of the presence of a few percentage of high molecular weight linear polymers upon the melt viscosity of the cyclic oligomers is profound. With only 5% high molecular weight linear polymers, the steady-state melt viscosity of the cyclic mixture is increased by more than one order of magnitude (Fig. 9). There is considerable evidence in the literature that indicates that, in cyclic and linear polymer mixtures, the linear molecules will thread through the cyclic rings.<sup>12-15</sup> McKenna et al.<sup>14,15</sup> have found a strong viscosity enhancement upon the addition of small amounts of linear polystyrene to cyclic polystyrene, which they attribute to the threading of the cyclic

rings by the linear polymer. Some threading would be expected to occur for the contaminated cyclic oligomers **8**. This threading would result in a strong viscosity enhancement of the rheological properties of the cyclic/linear mixture. This demonstrates that removing the high molecular weight linear polymers from the cyclic oligomers is crucial in order to reap the processing advantage of the low viscosity of cyclic oligomers.

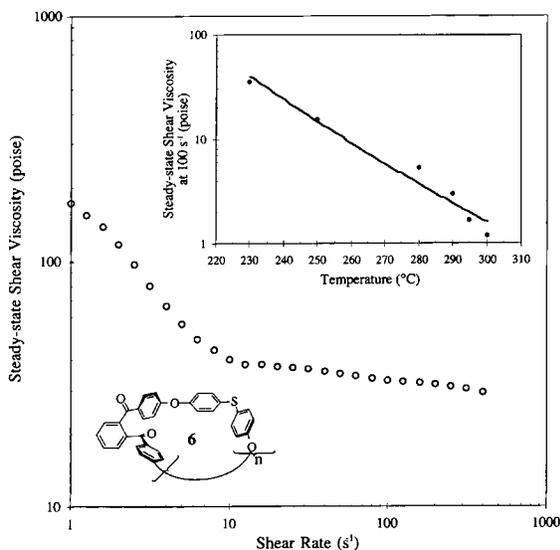
### Rheology of Cyclic Aryl Ether Thioether Ketone Oligomers

So far we have demonstrated that cyclic aryl ether ketone oligomers are thermally stable in the melt, and the molten cyclic oligomers have very low melt viscosities and behave like Newtonian fluids at a shear rate above 10 s<sup>-1</sup>. However, cyclic aryl thioether ketone oligomers are thermally unstable in the melt and undergo melt polymerization to form high molecular weight linear polymers.

The temperature dependence of the steady-state shear viscosity of cyclic oligomers **6** at a shear rate of 100 s<sup>-1</sup> is shown in Figure 10. The initial melt viscosity decreases dramatically as the testing temperature increases, and the melt viscosity remains low at temperatures below 250°C. Above that temperature the melt viscosity increases rapidly with time. Also, the rate of increase in viscosity increases rapidly as the testing temperature increases. The shear rate dependence of the steady-state shear viscosity of cyclic oligomers **6** at 230°C (Fig. 11) shows that the viscosity initially decreases dramatically as the shear rate increases; however, once the shear



**Figure 10** Steady-state shear viscosity as a function of time for cyclic aryl thioether ketone oligomers **6** at 100 s<sup>-1</sup> under nitrogen.



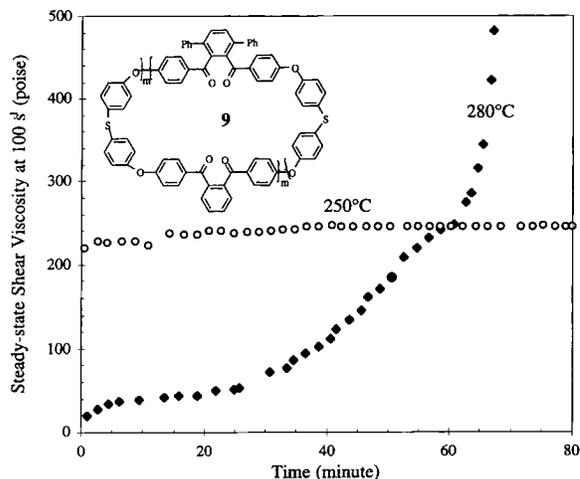
**Figure 11** Shear rate dependence of steady-state shear viscosity for cyclic aryl thioether ketone oligomers **6** at 230°C. The insertion is temperature dependence of the initial steady-state shear viscosity at 100 s<sup>-1</sup> for cyclic **6**.

rate reaches 10 s<sup>-1</sup>, the melt viscosity is essentially independent of the shear rate, implying the molten cyclics behave like Newtonian fluids. The temperature dependence of the initial steady-state shear viscosity at 100 s<sup>-1</sup> (see the insertion in Fig. 11) shows a similar trend as that for cyclic oligomers **5**.

Figure 12 shows a stable steady-state shear viscosity of cyclic oligomers **9** at 250°C, but the viscosity is not stable at 280°C and increases dramatically with time. Cyclic oligomers **7** are also thermally unstable and undergo rapid ring-opening polymerization to form high molecular weight linear polymer at 390°C under a shear rate of 10 s<sup>-1</sup> (Fig. 13). The melt ring-opening polymerization led to the formation of ultra-high molecular weight polymers, having a  $M_w$  of 602,000 (against polystyrene standards) and  $M_n$  of 26,000, compared to  $M_w$  of 5700 and  $M_n$  of 1900 for the initial cyclic oligomers.

#### Temperature Dependence of the Steady-State Shear Viscosity of Cyclic Oligomers at 100 s<sup>-1</sup>

In the preceding sections, we have shown that the temperature dependence of the melt viscosities of amorphous cyclic oligomers and semicrystalline cyclic oligomers are different, and that there is a linear relationship between the logarithm of the melt viscosity and the testing temperature for the amorphous cyclic oligomers (see Figs. 8 and 11). Replotting the logarithm of the steady-state shear vis-

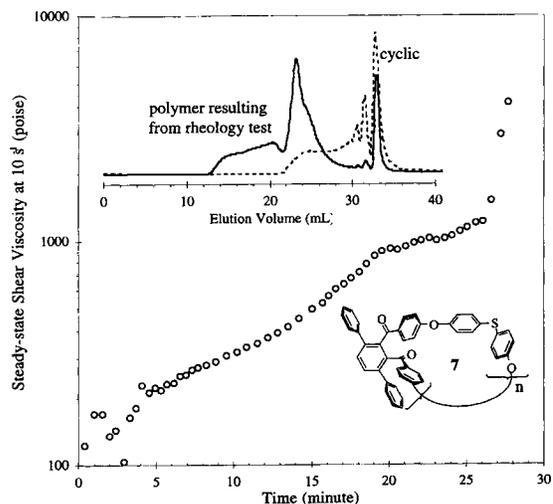


**Figure 12** Steady-state shear viscosity as a function of time for cyclic aryl thioether ketone oligomers **9** at 100 s<sup>-1</sup> under nitrogen.

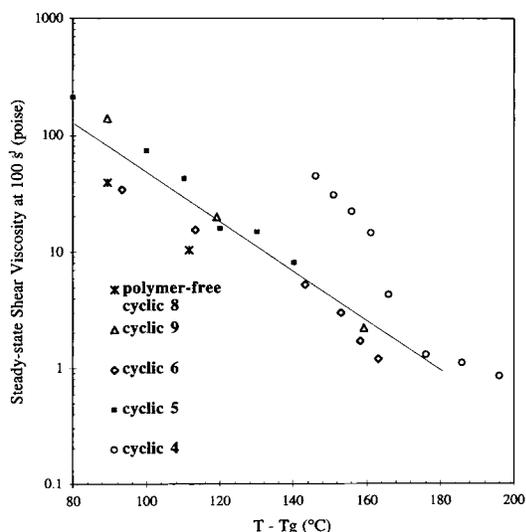
cosity at 100 s<sup>-1</sup> against the temperature difference ( $T - T_g$ ) of the testing temperature ( $T$ ) and the  $T_g$  of cyclic oligomers (Fig. 14), shows that there is a reasonably simple linear relationship for all the amorphous cyclic oligomers which can be expressed as

$$\ln(\eta_{100}(T)) = 9.118 - 0.0528(T - T_g) \quad (1)$$

where  $\eta_{100}(T)$  is the steady-state shear viscosity (poise) at 100 s<sup>-1</sup> as a function of temperature,  $T$



**Figure 13** Steady-state shear viscosity as a function of time for cyclic aryl thioether ketone oligomers **7** at 390°C and 10 s<sup>-1</sup> under nitrogen. The insertion is GPC traces for cyclic oligomers **7** and the material resulting from the rheological test at 390°C.



**Figure 14** Steady-state shear viscosity at  $100 \text{ s}^{-1}$  as a function of the temperature difference between the testing temperature ( $T$ ) and glass transition temperature ( $T_g$ ) for the cyclic oligomers.

( $^{\circ}\text{C}$ ), and  $T_g$  is the glass transition temperature of the cyclic oligomers.

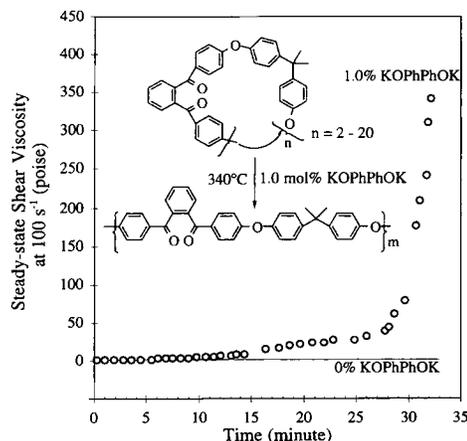
The melt viscosity of the semicrystalline cyclics **4** at temperatures below their melting temperature is far above the linear relationship; however, once the testing temperature is above the  $T_m$ , the melt viscosity falls into the linear relationship. This demonstrates that for the amorphous cyclic oligomers the temperature dependence of the melt viscosity is only affected by the glass transition temperatures of the cyclic oligomers. The relationship in Figure 14 may be taken as a master curve for the temperature dependence of the melt viscosity of the amorphous cyclic oligomers. Once the  $T_g$  of a particular cyclic oligomers is determined, one could approximately calculate the steady-state shear viscosity of the cyclic oligomers at a particular temperature.

### Chemorheology of Cyclic Oligomers **4** and **9** in the Presence of a Nucleophilic Initiator

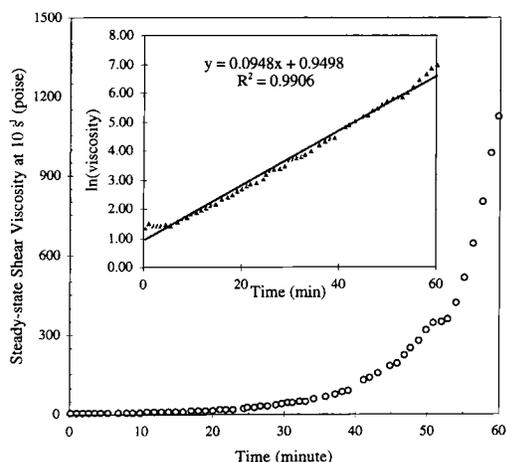
In the preceding section we have demonstrated the low viscosity of the cyclic oligomers. In a previous article<sup>9</sup> we have shown that the cyclic aryl ether ketone oligomers in the melt undergo a facile ether exchange reaction in the presence of a nucleophilic initiator to form high molecular weight linear polymers in a short period of time (ca. 30 min). This rapid polymerization and the low melt viscosity of

the cyclic oligomers offer the potential of reactive processing of high-performance poly(aryl ether)s. An important aspect of reactive processing is the dramatic increase in viscosity during the reaction. The nature of the change in viscosity of the reactive media during the formation of the polymer is determined both by an increase in the molecular weight of the polymer being formed and by an increase in the concentration of the polymer in the reaction media. As we have shown,<sup>9</sup> the ring-opening polymerization of the cyclic aryl ether ketones proceeds via a chain-growth mechanism and involves a transesterification between linear and cyclic oligomers; therefore, the viscosity change will mainly depend on the concentration of the polymer being formed during the reaction.

The isothermal viscosity profiles for the ring-opening polymerization of cyclic oligomers **4** in the melt at  $340^{\circ}\text{C}$  under a shear rate of  $100 \text{ s}^{-1}$  in the presence of 1.0 mol % potassium 4,4-biphenoxide (KOPhPhOK) are shown in Figure 15. Figure 15 shows the flat viscosity profile (i.e., no reaction) exhibited by the cyclic oligomers in the absence of an initiator, in strong contrast to the rapid increase of the viscosity observed when KOPhPhOK was used to initiate the polymerization. Potassium carbonate is also an effective initiator for the ring-opening polymerization, as shown by the viscosity change during the polymerization of cyclics **4** (Fig. 16). As the conversion of cyclic oligomers to polymer increases, there is an exponential rate of increase in viscosity, and as the conversion of cyclic oligomers to polymer approaches completion, the viscosity tends to ap-



**Figure 15** Isothermal steady-state shear viscosity profile for the cyclic aryl ether ketone oligomers **4** in the presence of 1.0 mol % potassium 4,4-biphenoxide (KOPhPhOK) at  $340^{\circ}\text{C}$  and  $100 \text{ s}^{-1}$  under nitrogen.

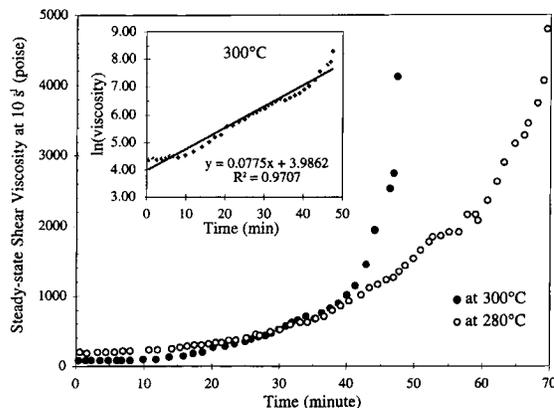


**Figure 16** Isothermal steady-state shear viscosity profile for the cyclic aryl ether ketone oligomers **4** in the presence of 1.0 mol % potassium carbonate at 340°C and 10 s<sup>-1</sup> under nitrogen. The insertion is the semi-log plot of the viscosity against time.

proach an infinite value. The semi-log plot of the viscosity profile (see the insertion in Fig. 16) shows a very good linear relationship between the logarithm of the viscosity and the reaction time. The isothermal viscosity profiles can be expressed as

$$\ln \eta(t) = \ln \eta_0 + kt \quad (2)$$

where  $\eta(t)$  is the viscosity as function of time,  $t$ ,  $\eta_0$  is the zero-time viscosity, and  $k$  is the apparent kinetic factor that is related to the rate of polymerization. Therefore, the value of  $k$  can be used for relative comparison of the rate of polymerization of cyclic oligomers initiated by different initiators and at different reaction temperatures. The  $k$  value obtained from the least squares analyses and the linear square coefficient  $R$  are tabulated in Table II. The  $k$  value clearly shows that KOPhPhOK is much



**Figure 17** Isothermal steady-state shear viscosity profiles for the cyclic aryl ether thioether ketone oligomers **9** in the presence of 1.0 mol % potassium potassium 4,4-biphenoxide (KOPhPhOK) at 10 s<sup>-1</sup> under nitrogen. The insertion is the semi-log plot of the viscosity against time at 300°C.

more effective than K<sub>2</sub>CO<sub>3</sub> as the initiator for the ring-opening polymerization of cyclics **4**. It should be pointed out that the linear high molecular weight counterparts of cyclics **4** are thermally unstable and tend to form a crosslinked network,<sup>9</sup> and the viscosity change during the ring-opening polymerization might also be affected by this possible cross-linking reaction. Nevertheless, the  $k$  value should give us an indication of the relative reactivity of different initiators.

Figure 17 shows the isothermal viscosity profiles of the ring-opening polymerization of cyclic oligomers **9** in the presence of 1.0 mol % KOPhPhOK at 280 and 300°C. As the reaction temperature increases, the rate of the increase in viscosity increases, and the time for the viscosity to approach an infinite value decreases. The values of  $k$  and  $R$  for eq. (2) were obtained from the least squares analyses and are listed in Table II.

**Table II** Parameters of Eq. (2) for the Isothermal Viscosity Profiles of Ring-Opening Polymerization of Cyclic Oligomers **4** and **9** in the Presence of a Nucleophilic Initiator

| Cyclic Oligomers | Initiator                      | Temperature (°C) | $k \times 10^2$ (min <sup>-1</sup> ) <sup>a</sup> | $R^b$ |
|------------------|--------------------------------|------------------|---|-------|
| <b>4</b>         | KOPhPhOK                       | 340              | 15.72   | 0.98  |
| <b>4</b>         | K <sub>2</sub> CO <sub>3</sub> | 340              | 8.28  | 0.99  |
| <b>9</b>         | KOPhPhOK                       | 280              | 4.72  | 0.99  |
| <b>9</b>         | KOPhPhOK                       | 300              | 7.75  | 0.98  |

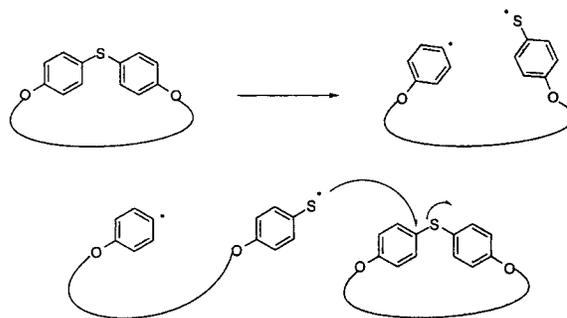
<sup>a</sup>  $k$  is the apparent kinetic factor for eq. (2).

<sup>b</sup>  $R$  is the linear square coefficient from the least squares analyses.

### Chemorheology of Cyclic Oligomers **6** and **9** in the Presence of a Disulfide or Elemental Sulfur

As demonstrated in the previous sections, in contrast to the cyclic ether ketone oligomers **4** and **5**, cyclic aryl thioether ketone oligomers **6**, **7** and **9** are thermally unstable in the melt and the melt viscosity increases rapidly as testing time progresses in the absence of an initiator. It is known<sup>16</sup> that aryl sulfides [eq. (3)] undergo a thermal disproportionation reaction via a radical route and the reaction can be promoted by the addition of diphenyl disulfide. The diphenyl disulfide undergoes thermolysis at high temperatures to give diphenyl sulfide and elemental sulfur<sup>17</sup> [eq. (4)], and the reverse reaction has also been demonstrated.<sup>18</sup> We suspected that the thioether ketone oligomers would undergo similar thermal cleavage of the S—C bond to form thiyl radical(s) that would initiate the polymerization to generate high molecular weight polymers (Scheme 4). By the addition of elemental sulfur or disulfide, a disulfide linkage could also be formed in the cyclic

oligomers. The disulfide moiety formed would undergo thermolysis to form thiyl radical(s), which could promote the polymerization. Indeed, by the addition of a catalytic amount of elemental sulfur or 2,2-dithiobis(benzothiazole) (DTB) disulfide, the rate of increase in viscosity of thioether ketone oligomers increases rapidly under an isothermal curing condition.



Scheme 4

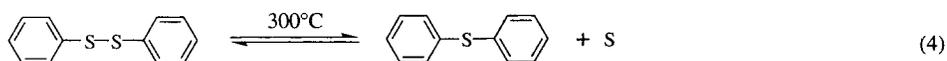
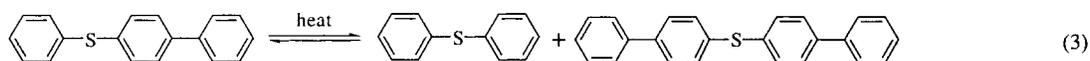


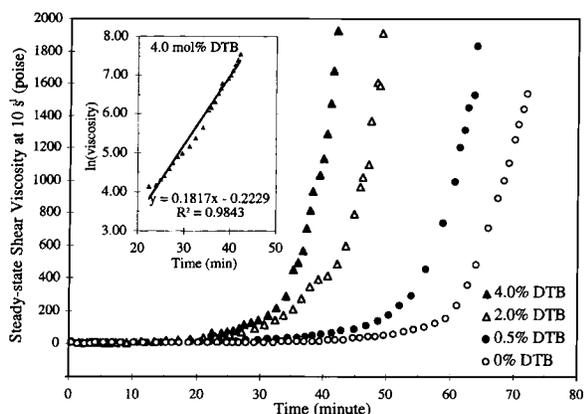
Figure 18 shows the isothermal viscosity profiles of cyclic oligomers **6** at 295°C under a shear rate of 10 s<sup>-1</sup> in the presence of 0–4.0 mol % disulfide DTB. It clearly demonstrates that the time for the viscosity to approach an infinite value decreases as the amount of disulfide DTB added increases. The semi-log plot of the viscosity profile (see the insertion in Fig. 18) shows a very good linear relationship between the logarithm of the viscosity and the reaction time. The isothermal viscosity profiles can also be expressed as eq. (2). The *k* value obtained from the least squares analyses and the linear square coefficient *R* are tabulated in Table III. If we take the *k* value as the relative rate of polymerization, with the addition of 0.5 mol % of DTB the polymerization rate was doubled. In the presence of higher levels of DTB (e.g., 4.0 mol %), the relative polymerization rate was increased by five times.

Figure 19 shows the isothermal viscosity profiles of cyclic oligomers **9** at 300°C in the presence of 0–3.0 mol % elemental sulfur. The *k* and *R* values obtained from the least squares analyses are listed in

Table III. Elemental sulfur is also an effective catalyst for the polymerization of the thioether ketone oligomers, and the relative rate of polymerization increases with increasing sulfur content. In the absence of any catalyst, the relative rate of the polymerization (i.e., the value of *k*) for cyclic oligomers **6** at 295°C and **9** at 300°C is approximately the same. This indicates that the thermolysis of the S—C bond and the reactivity of the thiyl radical(s) generated are identical in both oligomers.

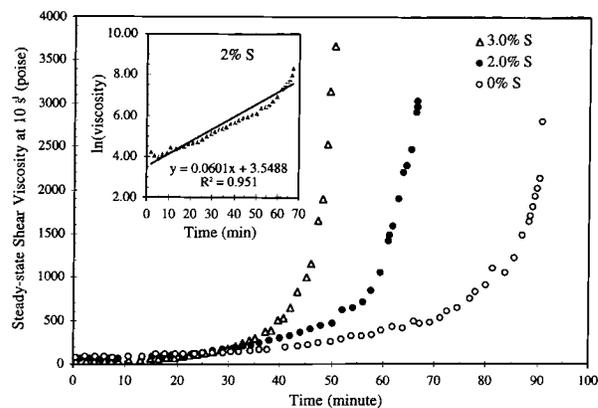
### CONCLUSIONS

The melt stability and rheological properties of cyclic aryl ether ketone and thioether ketone oligomers containing the 1,2-dibenzoylbenzene moiety were investigated. The cyclic aryl ether ketone oligomers are thermally stable in the melt and their melt viscosity is several orders of magnitude lower than their high molecular weight linear counterparts. At a given temperature, the steady-state shear



**Figure 18** Isothermal steady-state shear viscosity profiles for the cyclic aryl ether thioether ketone oligomers **6** at 295°C and 10 s<sup>-1</sup> under nitrogen in the presence of 0 to 4.0 mol % DTB. The insertion is a semi-log plot of the viscosity against time.

viscosity of the molten cyclics initially undergoes shear thinning as the shear rate increases; however, once the shear rate reaches 10 s<sup>-1</sup>, the steady-state shear viscosity is independent of the shear rate and the molten cyclic oligomers behave like Newtonian fluids. The lower limit of the shear rate for the molten cyclics to behave like Newtonian fluids decreases as the testing temperature increases. For the amorphous cyclic oligomers studied, the steady-state shear viscosity at 100 s<sup>-1</sup> at a given temperature only depends on their glass transition temperature. The cyclic aryl thioether ketone oligomers are thermally unstable in the melt and undergo ring-opening polymerization in the absence of an initiator to form high molecular weight linear polymers with a concomitant rapid increase in the viscosity. The rate of change in viscosity increases with temperature.



**Figure 19** Isothermal steady-state shear viscosity profiles for the cyclic aryl ether thioether ketone oligomers **9** at 300°C and 10 s<sup>-1</sup> under nitrogen in the presence of 0 to 3.0 mol % S. The insertion is a semi-log plot of the viscosity against time.

Melt polymerization of cyclic oligomers **4** and **9** in the presence of a nucleophilic initiator such as KOPhPhOK was studied by monitoring the isothermal viscosity profiles of the reaction medium. The rate of polymerization increases as the reaction temperature increases. For the thioether ketone oligomers **6** and **9**, the addition of elemental sulfur or a disulfide such as DTB effectively promotes the thermally induced free-radical polymerization. The rate of polymerization increases with increasing the amounts of sulfur or DTB added. This preliminary work has led to the discovery of a novel free radical polymerization of macrocyclic oligomers containing an aromatic sulfide linkage.<sup>11</sup> Detailed studies of the free radical ring-opening polymerization of cyclic aryl thioether ketone oligomers **7** will be presented

**Table III** Parameters of Eq. (2) for the Isothermal Viscosity Profiles of Ring Opening Polymerization of Cyclic Oligomers **6** and **9** in the Presence of Sulfur and Disulfide DTB

| Cyclic Oligomers | Initiator | Temperature (°C) | $k \times 10^2$ (min <sup>-1</sup> ) <sup>a</sup> | $R^b$ |
|------------------|-----------|------------------|---|-------|
| <b>6</b>         | None      | 295              | 3.47  | 0.93  |
| <b>6</b>         | 0.5% DTB  | 295              | 6.60  | 0.94  |
| <b>6</b>         | 2.0% DTB  | 295              | 10.83   | 0.99  |
| <b>6</b>         | 4.0% DTB  | 295              | 18.17   | 0.99  |
| <b>9</b>         | none      | 300              | 3.71  | 0.97  |
| <b>9</b>         | 2.0% S    | 300              | 6.01  | 0.98  |
| <b>9</b>         | 3.0% S    | 300              | 9.23  | 0.98  |

<sup>a</sup>  $k$  is the apparant kinetic factor for eq. (2).

<sup>b</sup>  $R$  is the linear square coefficient from the least squares analyses.

in another article (Wang, Chan, and Hay, in preparation).

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