

One Step Synthesis and Rapid Ring-Opening Polymerization of Macrocylic (arylene thioether ketone) Oligomers

H. Yan,^{2,3} X. H. Li,¹ S. J. Wang,¹ Y. Z. Meng^{1,2}

¹State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

²Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, People's Republic of China

³Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

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ABSTRACT: Well-crystal macrocylic (arylene thioether ketone) oligomers were synthesized under high dilution condition by the reaction of Na₂S with bis(4-fluoro-phenyl)methanone in 1-methyl-pyrrolidone (NMP). The oligomers were fully characterized by Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS), high-pressure liquid chromatography (HPLC), gel permeation chromatography (GPC), ¹H NMR, ¹³C-NMR, and differential scanning calorimetry (DSC). According to DSC studies, uncatalyzed and rapid ring-opening polymerization (ROP) of the oligomers took place instantly when they were heated to melting point. Extracted by dichloro-methane, the

obtained polymer neither loses any weight nor dissolves in boiling 1-chloro-naphthalene. These facts indicated that there are no residual oligomers within the resultant polymer. The as-prepared oligomers could be potentially used as high-temperature hot-melt adhesive at a high temperature > 350°C, and matrices for high-performance composites and nanocomposites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 161–166, 2006

Key words: macrocylic; oligomers; ring-opening polymerization

INTRODUCTION

Macrocylic oligomers have attracted much attention in recent years as a reactive intermediate for both academic and industrial research because of their undergoing ring-opening polymerization (ROP) and forming high performance polymers.^{1–5} It is well known that macrocylics have many advantages. For example, they can undergo ROP without liberation of any byproducts, also they can be melt processed at a much lower temperature than the corresponding high molecular weight polymers due to their extremely low melting viscosities. These characteristics make them potentially applicable in the areas of high-temperature adhesives, and matrices for advanced thermoplastic composites. Various macrocycles can also be used as starting materials for the building of supramolecular

assemblies, which stimulated an additional interest in the field.

Moreover, the ROP of cyclic aromatic oligomers can offer numerous advantages over conventional methods, including the elimination of the used solvents, the absence of volatile byproduct, and the capability of achieving very high molecular weights in a short reaction time.⁶ Poly(butylene oxide), poly(iminoethylene), and nylon-6 have been commercialized using the same technique.^{7–9}

Many aromatic disulfide oligomers have been synthesized and their ROPs have been investigated extensively.^{10–19} Unfortunately there was a small amount of residual macrocylic oligomers remained in the resultant polymers after ROP, which in turn resulted in the poor mechanical properties for the resultant polymers. Furthermore, the resultant aromatic polydisulfides exhibited poorer thermal stabilities because of their disulfide bonds, when compared with those of the aromatic polysulfide.

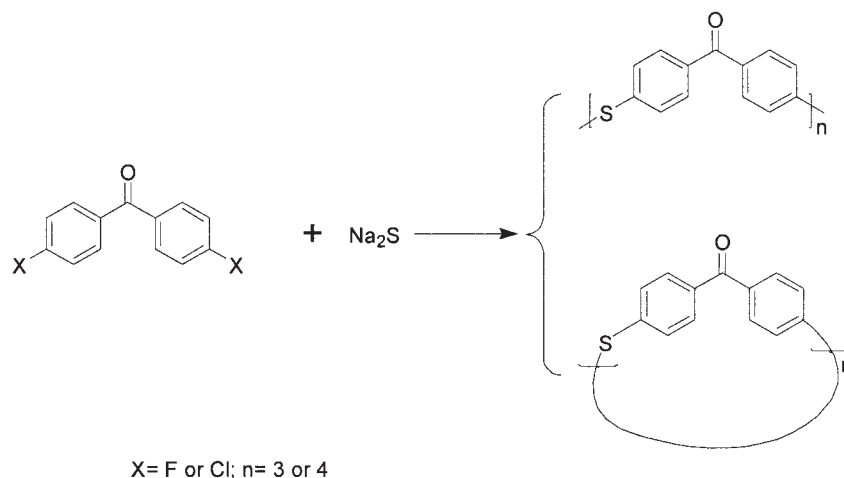
In this article, we report the synthesis of macrocylic (arylene thioether ketone) oligomers via one-step condensative polymerization and their cyclic structures. These oligomers ROP took place instantly upon being heated to their melting points > 400°C. The resultant polymer determined did not contain any residual macrocylic oligomers. The major merits of the

Correspondence to: Y. Z. Meng (mengyzh@mail.sysu.edu.cn).

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Scheme 1 Synthesis of macrocyclic (arylene thioether ketone) oligomers.

method in this article fall on (1) that higher yield can be afforded by one step reaction; (2) The synthesized crystalline cyclic oligomers undergo ROP instantaneously in melt in a few minutes, without any cyclic oligomers remaining in the resultant polymer.

EXPERIMENTAL

Materials

All the chemicals used were reagent grade and purified by standard methods. Bis-(4-fluoro-phenyl)-methanone was purchased from commercial source and used after recrystallization twice in absolute ethanol. Sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$), 1-methyl-pyrrolidone (NMP), toluene, methanol, tetrahydrofuran (THF), and chloroform were also obtained from commercial sources and used as received.

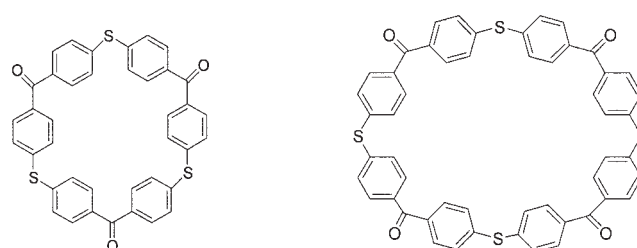
Instrumentation

Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS) were recorded on a Bruker MALDI-III TOF instrument with a maximum laser output of 6 mW at a wavelength of 337 nm (N_2 laser light, 3 ns pulse width, 100 mm diameter spot). The MALDI-TOF instrument was operated in a positive reflection mode. The ions produced from each laser shot were accelerated to 25 keV into a 1-m drift region. The matrix used for all experiments was 2,5-dihydroxy benzoic acid (Aldrich). NMR spectra were recorded at 400 MHz on a Bruker DRX-400 NMR instrument and the chemical shifts were listed in parts per million downfield from tetra-methylsilane. High-pressure liquid chromatography (HPLC) analysis was carried out on a Milton Roy CM4000 multiple solvent delivery system with a C_{18} Prime Sphere $4.6 \times 200 \text{ mm}^2$ column with, THF as eluent solvent, and a UV

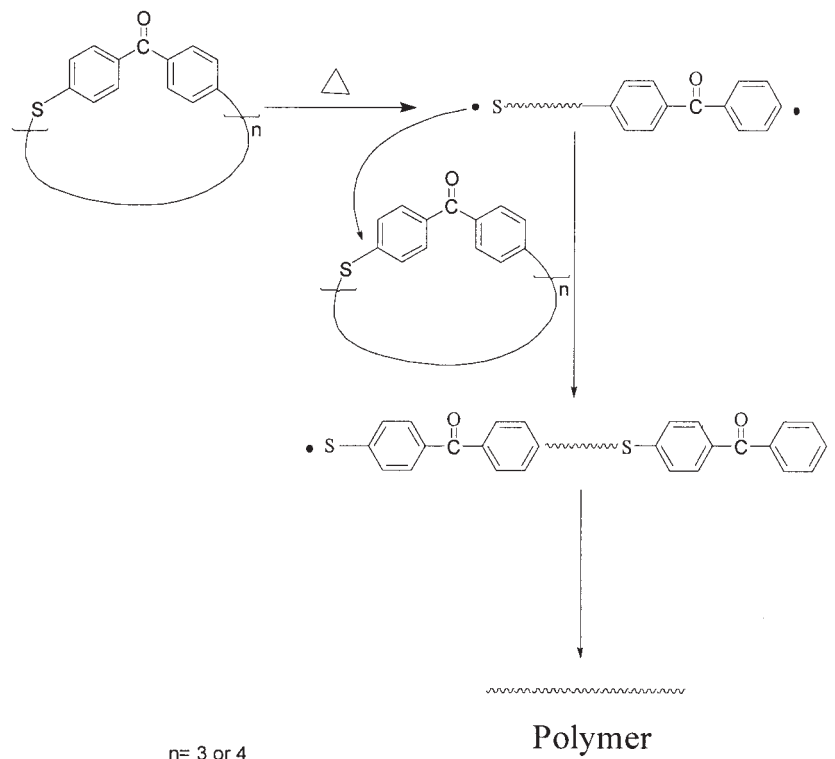
detector operated at 254 nm. Gel permeation chromatography (GPC) analysis was performed using a Waters 510 GPC instrument equipped with 5 mm Phenogel columns (linear, 3500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. Differential scanning calorimetry (DSC) scans were obtained using a Perkin-Elmer DSC-7C instrument at a heating rate of $20^\circ\text{C min}^{-1}$ in N_2 (20 mL min^{-1}) atmosphere. Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) were performed on a Perkin-Elmer TG/DTA 6300 instrument at a heating rate of $20^\circ\text{C min}^{-1}$ in N_2 (300 mL min^{-1}) atmosphere.

Synthesis of macrocyclic (arylene thioether ketone)s

Macrocyclic (aromatic thioether ketone) oligomers were prepared under high dilution condition as depicted in Scheme 1. The main products are shown in Scheme 2. A 500-mL flask equipped with a Dean-Stark trap, a condenser, and a nitrogen inlet was charged with 250 mL of NMP, 2 mL of toluene, and 7.20 g (0.03 mol) of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. The mixture was kept refluxing at 150°C under N_2 for 30 min to remove produced water



Scheme 2 Macroscopic (arylene thioether ketone) trimer and tetramer.



Scheme 3 Free radical ring-opening polymerization of macrocyclic oligomers.

entirely. Then the solution of 6.54 g anhydrous bis(4-fluoro-phenyl)-methanone (0.03 mmol) in 50 mL NMP was introduced into the reaction flask over a period of 5 h, using a syringe pump. After finishing the addition, the reaction mixture was kept refluxing for another 2 h. The resulting mixed solution was cooled down and then 1000 mL H₂O was added. After 20 min vigorously stirring, the produced macrocyclics were precipitated out by adding 20 mL of 5% HCl. The precipitates were collected by filtration and washed consecutively with water, followed by washing twice thoroughly with ultrasound stirring using methanol. The resultant powders were extracted with dichloromethane for 12 h. After evaporating, 2.16 g dark gray powder was obtained. The macrocyclic oligomers were dried in a vacuum oven at 80°C for 24 h. Upon recrystallizing twice from chlorobenzene, a mixture of macrocycles was produced. Their identities were confirmed by DSC, MALDI-TOF MS analysis, and NMR spectroscopy.

ROP procedure for synthesized macrocyclics

As depicted in Scheme 3, the ROP of macrocyclics was performed in the melt. A typical ROP procedure is given as follows: macrocyclic oligomers samples (~10 mg) were placed in DSC aluminum pans and measurements were made from 90°C to 360–480°C at a scanning rate of 20°C min⁻¹ under nitrogen atmosphere. Second and third scans were performed on

some samples by heating to desired temperature after quenched cooling below 100°C before analysis.

RESULTS AND DISCUSSION

Synthesis of macrocyclic (arylene thioether ketone) oligomers

The macrocyclic (arylene thioether ketone) oligomers were synthesized via the reaction of bis-(4-fluoro-phenyl)-methanone with sodium sulfide. For this kind of reaction, the kinetic studies in literature have proved to be an SNR reaction.²⁰ However, the reaction is not a simple nucleophilic substitution reaction by a sulfur anion. The solvent NMP plays an extremely important role. It functions as a catalytic reactant, transforming Na₂S into a soluble nucleophile. The empirical formula Na₂S NMP H₂O or sodium 4-(*N*-methylamino) butanoate-NaSH has been proposed for the nucleophile.²⁰

As known, any polycondensation reaction toward a high molar mass generally affords not only linear polymers, but also a homologous series of macrocyclic oligomers in amounts that are dependent both on the polymer system involved and on the reaction conditions.^{21,22} Under high dilution conditions, the probability of intramolecular reactions is significantly greater than that of intermolecular ones, and therefore, cyclic oligomers are predominant products. Two different methods are generally adopted to afford

TABLE I
Physical Properties of Macrocylic (arylene sulfide) Oligomers

Yield (%)	34
Melting point ^a (°C)	409
	446
TGA (-5%, N ₂) (°C) ^b	536

^a Measured under N₂ protection; at a heating rate of 20°C/mm.

^b 5% weight loss temperature obtained in N₂ at a heating rate of 20°C/min.

high-dilution or pseudohigh-dilution condition. The first one is to perform the cycloenclosure reaction directly in high dilution condition. However, only very low concentration of produced macrocylic can be obtained by using this method. The second one is to carry out the cyclization by adding the reactants very slowly during the reaction. In this case, relatively high cyclic oligomer concentration can be reached. In this regard, the latter method was used in this work to synthesize the macrocylics.

By using aforesaid method, a mixture of low molecular weight oligomers was readily synthesized, as described in Scheme 1. The mixture of these macrocylic oligomers is very soluble in organic solvents such as methylene chloride, chlorform, *N,N'*-dimethyl formamide (DMF), *N,N'*-dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), and THF.

The physical properties of the mixture of these macrocylic oligomers were shown in Table I. It can be seen that high yields of these macrocylic oligomers were achieved.

Molecular structure of synthesized macrocylics

The MALDI-TOF-MS spectrum of the oligomers is shown in Figure 1. Clear signals that indicated exactly

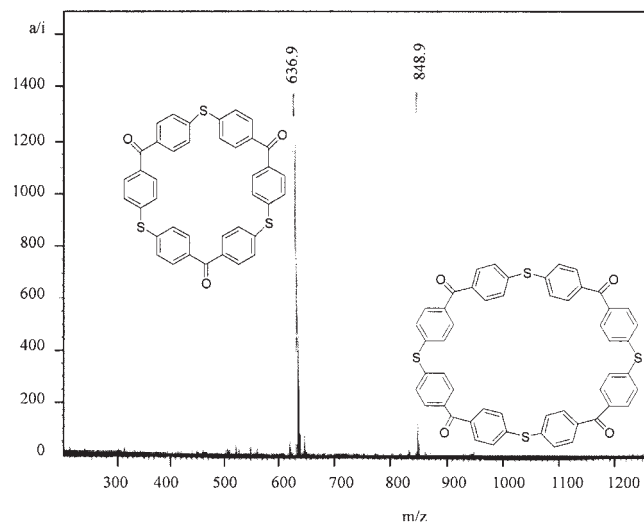


Figure 1 MALDI-TOF-MS spectrum of macrocylic (arylene thioether ketone) oligomers.

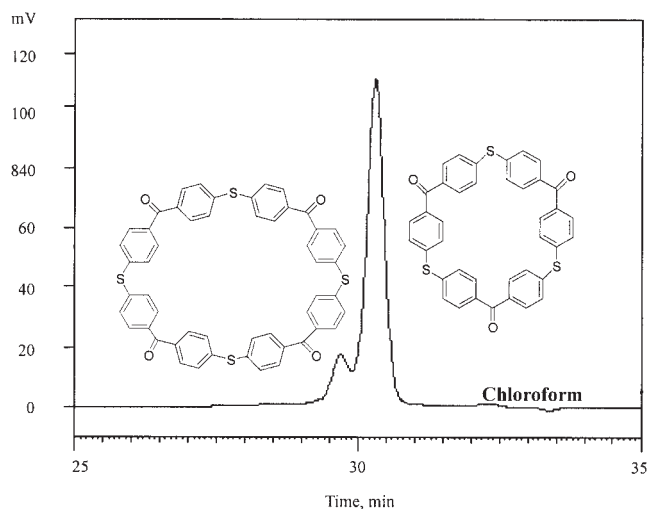


Figure 2 GPC trace of macrocylic (arylene thioether ketone) oligomers.

the macrocylic oligomers of trimer and tetramer were observed. Moreover, the spectrum is with good signal-to-noise ratio. The figure shows that there were only two oligomers with molecular weights of 636.9 (trimer) and 848. (tetramer), respectively. No linear oligomers were observed.

GPC curve of the oligomers is shown in Figure 2. As can be seen from the figure, the oligomers with elution time of 29.8 min and 30.2 min were the predominant components of the product (eluent time 32.7 min was solvent). Considering the deviation caused by calibrating standard, the two peaks should be cyclic trimer and tetramer. Trimer appeared to be the main product of the macrocylics. HPLC curve of the oligomers is shown in Figure 3. Similarly, there were two components observed in the oligomers. Macrocylic trimer is the main component with a content of >99%.

The ¹H NMR and ¹³C NMR of the macrocylic oligomers are showed in Figure 4 and Figure 5, respec-

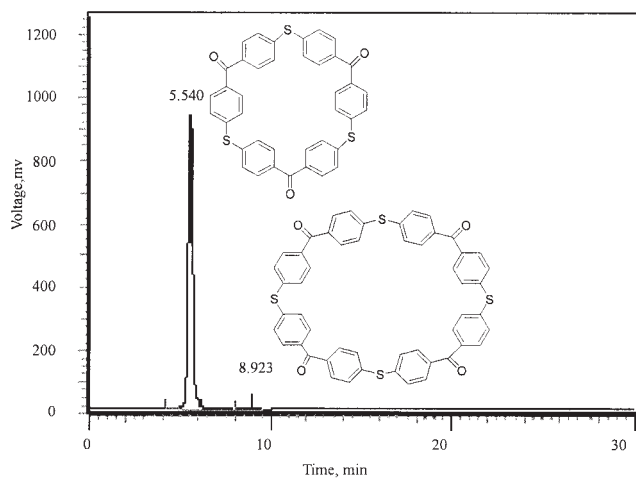


Figure 3 HPLC trace of macrocylic (arylene thioether ketone) oligomers.

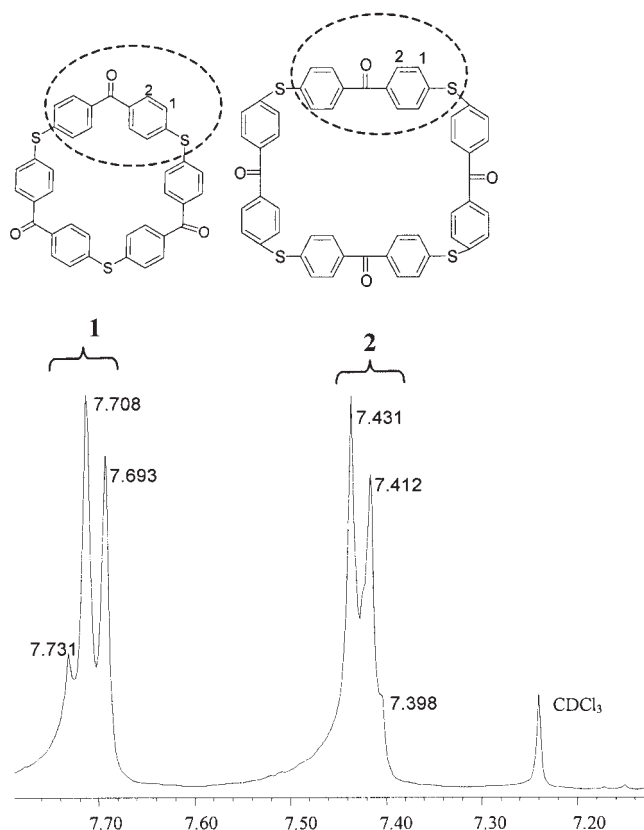


Figure 4 ^1H NMR for macrocyclic (arylene thioether ketone) oligomers.

tively. According to the analysis of these oligomers, the expected trimer and tetramer were obtained under the specified reaction condition described in this article.

ROP of macrocyclic oligomers

On the basis of the previous study,²³ the ROP of macrocyclic disulfide oligomers was generally performed in

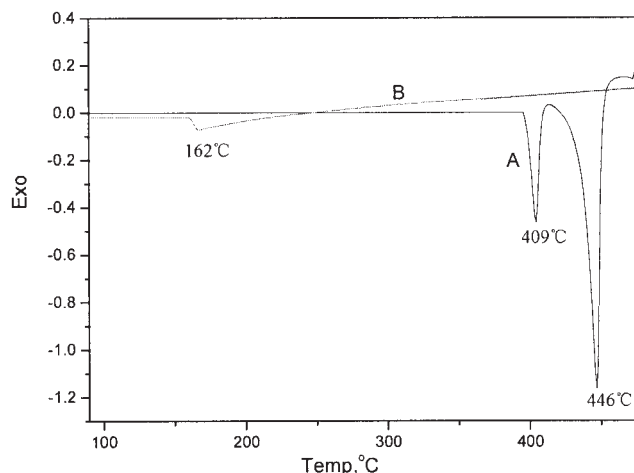


Figure 6 DSC curve of macrocyclic (arylene thioether ketone) oligomers.

the melt. To study the ROP of the macrocyclic monosulfide oligomers, DSC analysis was used and the scan traces were shown in Figure 6. There were two endothermic peaks in the first scan to 480°C, indicating that there were two melting points. Two melting points corresponded to two kinds of oligomers with two different crystalline cells. When the oligomers were heated to 480°C again, both endothermic peaks disappeared indicating the complete disappearance of the oligomers. From the second scan B, we can see that there was one glass transition temperature of 162°C observed. Compared to the literature, no melting point at about 335°C was detected,²⁴ implying that the resultant polymer may have a crosslinking structure.

Another sample was used to study the ROP in detail using DTA method (Fig. 7). After being heated to 430°C followed by quenching to below 100°C, there was one endothermic peak at 409°C observed. When heated to 450°C again, the endothermic peak at 409°C

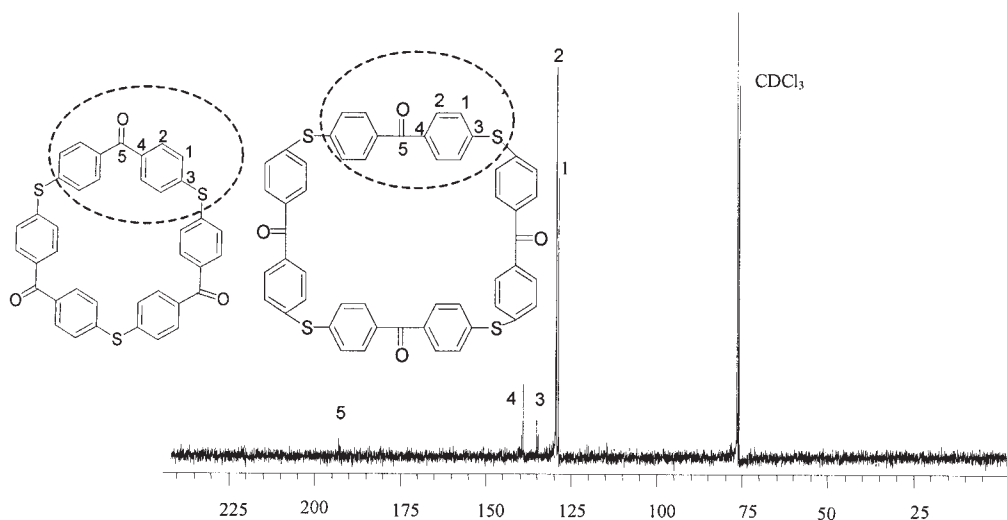


Figure 5 ^{13}C NMR for macrocyclic (arylene thioether ketone) oligomers.

disappeared and there was only one endothermic peak at 446°C, indicating the completion of ROP and the formation of high molecular weight polymer at once in the melt at temperature >400°C.

Thermal properties of macrocyclic oligomers

Figure 8 shows the thermogravimetric traces of the synthesized oligomers. It can be seen that the 5% weight loss temperature is higher than 536°C, demonstrating that the polymer derived from the macrocyclics exhibits superior thermal stability. Presumably, the polymer was instantly produced upon heating the macrocyclics over 400°C. Moreover, the resultant polymer, after extracted with methylene chloride for 24 h, did not lose any weight. This means there is a complete conversion of macrocyclics into high molecular weight polymer that is insoluble in boiling 1-chloro-naphthalene.

CONCLUSIONS

Well crystalline macrocyclic (arylene thioether ketone) oligomers can be synthesized by the reaction of bis(4-fluoro-phenyl)-methanone with Na₂S under pseudohigh-dilution condition via one step reaction. These macrocyclic oligomers can readily undergo free radical ROP instantly in the melt without any catalyst, affording linear, high molecular weight poly(arylene thioether ketone) (PASK) without any residual oligomers. The resultant PASK exhibited highly thermal stability and a high glass transition temperature of about 162°C. The polymer also has a melting point indicating its semicrystalline structure. These macrocyclic oligomers show potential applications of PASK as matrix for fabricating long or continuous fiber reinforced thermoplastic composites via facile processing methods such as compression molding, and reaction injection molding etc.

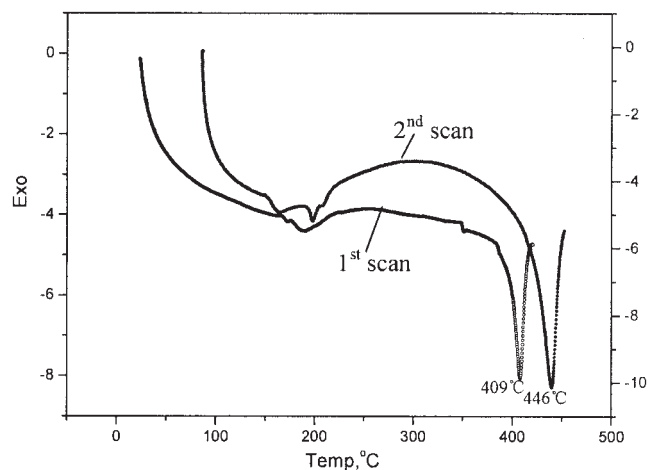


Figure 7 DTA curve of macrocyclic (arylene thioether ketone) oligomers.

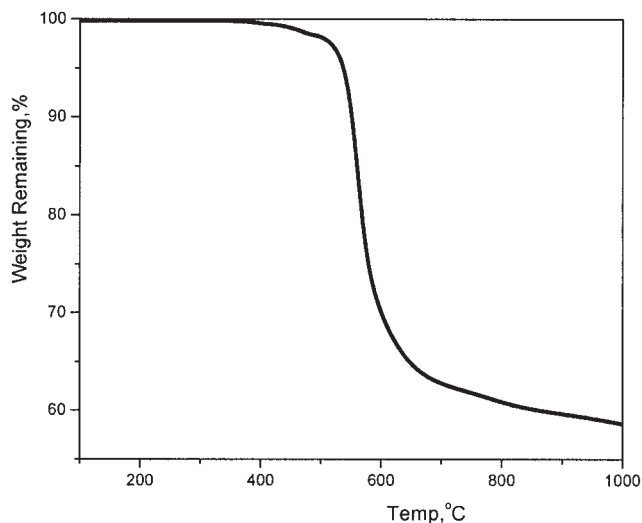


Figure 8 TG curve of macrocyclic (arylene thioether ketone) oligomers.

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