

The synthesis, characterization and properties of cyclic poly ether ketones

Wu Zhongwen , Wang Junzuo, Chen Chunhai, Li Zhicheng
(Department of Chemistry, Jilin University, Changchun, China, 130023)

Abstract

In this work, a series of oligomers proved by IR, NMR, HPLC and GPC experiments to be cyclic poly aryl ether ketones were synthesized. Their crystal structure were studied by both X-ray diffraction and DSC measurements. It was found to have evident differences with that of linear poly aryl ether ketones, and it is expected to be an ideal matrix for ACM (Advanced Composite Materials).

Introduction

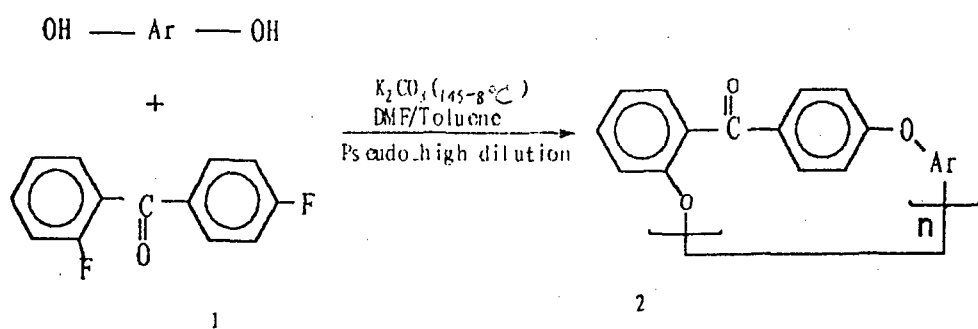
Low melt viscosity aromatic macrocyclic oligomers have been developed as unique intermediates for the synthesis of high performance engineering polymers in recent years^[1-8]. The in-situ transformation of the macrocyclic oligomers such as carbonates^[1], aryl ethers^[2,3,6,7], aramids^[4] and imides^[8] via a ring-opening polymerization route to high molecular weight polymers opens up the possibility of a wide range of applications for aromatic thermoplastics which are currently not accessible with the linear high molecular weight counterparts due to the inherent high melt viscosity. In particular, the low melt viscosity of cyclic oligomers permits applications of long or continuous fiber reinforced thermoplastics composites via processing methods such as compression molding, reaction injection molding and melt-pultrusion. The poly aryl ether ketones are getting into

wide spread applications as a high-performance thermoplastics composites. Because the poly aryl ether ketones don't solve in common organic solvents, the fabrication of the poly aryl ether ketones composites are by only melt processing. The high melt viscosity linear poly ether ketones is unavailable to the melting wet of long or continuous fiber. Thereby, the in-situ transformation of low melt viscosity aryl ether ketones cyclic oligomers via ring-opening polymerization route to high molecular weight polymers can solve this problem. In the area of cyclic(aryl ether)s, pioneering work has been reported by scientists from Imperial Chemical Industries (ICI)^[5], General Electric Co (GE)^[11]. In recently, Allan. S. Hay^[6,7] also reported the synthesized works of cyclic(aryl ether ketone)s oligomers by means of 1,2-bis(4'-fluorobenzoyl)benzene, 1,3-bis(4'-fluorobenzoyl)benzene, 4,4'-difluorobenzophenone. But, the cyclic (aryl ether ketone)s oligomers preparing by 2,4'-difluorobenzophenone, phenolphthalein have been not reported. In this paper, the synthesis, characterization, property and crystallinity of cyclic(aryl ether ketone)s oligomer synthesized by 2,4'-difluorobenzophenone, phenolphthalein will be discussed.

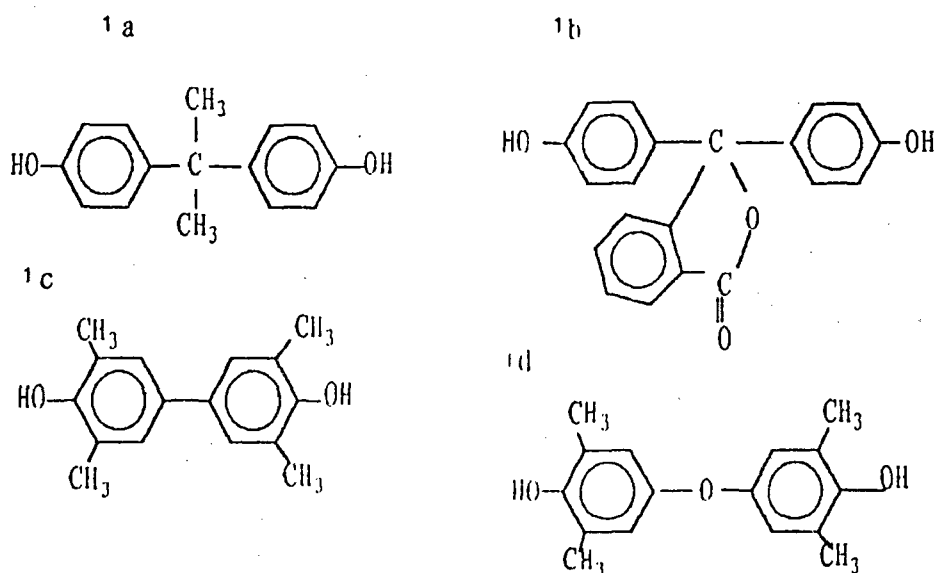
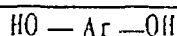
Results and discussion

1. Synthesis and characterization of cyclic (aryl ether ketone)s from 2,4'-difluorobenzophenone.

Cyclic(aryl ether ketone)s can be prepared by the aromatic nucleophilic substitution route utilizing a AA+BB approach. We have prepared a series of cyclic (aryl ether ketone)s from 2,4'-difluorobenzophenone and monomer 1 (scheme 1).



Scheme 1



The preparation route of cyclic (aryl ether ketone)s was used by the pseudo-high dilution principle^(1,6,7). The final products were isolated and purity. The HPLC patterns of cyclic oligomers were shown in Figure 1. The separated peaks in HPLC patterns proved that the products were cyclic oligomers. The cyclicity by the reaction of 1a, 1b and 2,4-difluorobenzophenone were better than that of 1c, 1d and 2,4'-difluorobenzophenone by the comparison of the separated peaks' shape. The peaks of the curve 1 in Figure 1 were very well separated, however, the peaks of the curve 3 and curve 4 in Figure 1 were not strictly distinguished and showed wide molecular weight

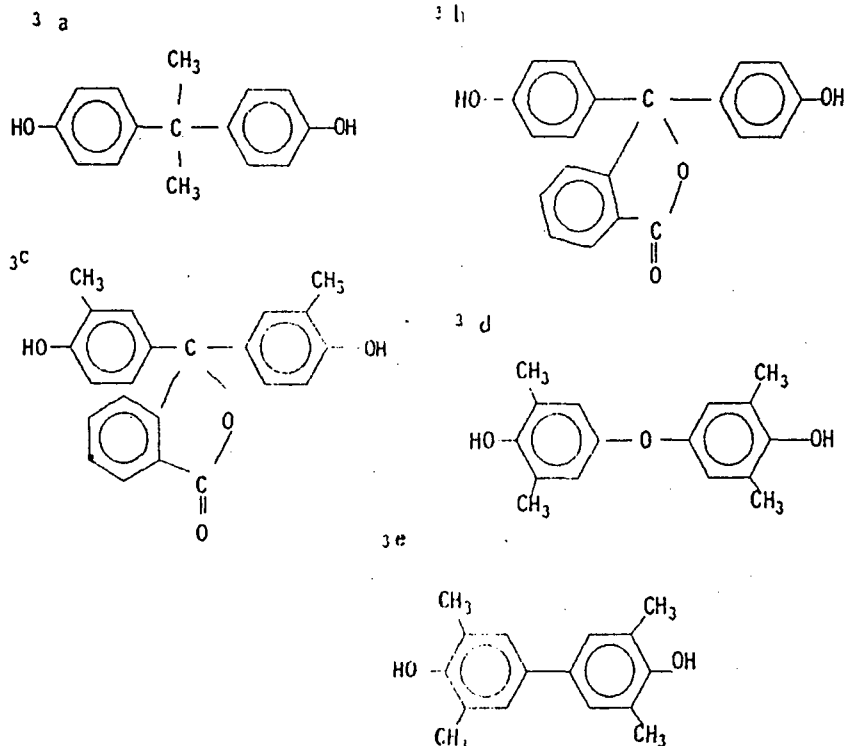
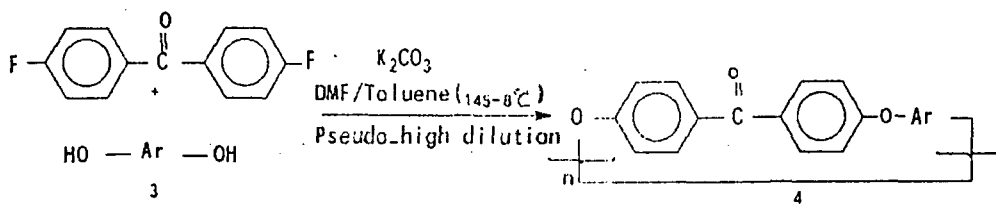
distribution. 2,4'-difluorobenzophenone is easy to form cyclo-oligomers when considering the conformation condition. However, the introduction of the substitute group in ortho position of bisphenol such as 1c, 1d produces a strong repelling force with the neighbour atoms and hinders the formation cyclo-oligomers of 2c, 2d.

2. Crystallinity of cyclic (aryl ether ketone)s from 2,4'-difluorobenzophenone.

The WAXD patterns of cyclo-oligomers were shown in Figure 2. The very weak diffraction peaks in Figure 2 proved the crystallizability of the cyclic (aryl ether ketone)s oligomers preparing from 2,4'-difluorobenzophenone is very bad. This condition is similar to the high molecular weight linear polymers containing ortho linkage^[9]

3. Synthesis and characterization of cyclic(aryl ether ketone)s from 4,4'-difluorobenzophenone.

A series of cyclic (aryl ether ketone)s oligomers from 4,4'-difluorobenzophenone and bisphenol were prepared and listed in Scheme 2.



All cyclic (aryl ether ketone)s oligomers have not hydroxyl because of no absorption around 3450cm^{-1} in IR measurement. F-NMR showed no fluoro-end in all cyclic (aryl ether ketone)s. The GPC patterns of cyclo-oligomers were shown in Figure 3, from the Figure 3, the cyclicity by the reaction of 4,4'-difluorobenzophenone and bisphenol (shown in Scheme 2) is very well. The molecular weight correction by means of the standard polystyrene showed that cyclic 4a to 4d consist of macrocycles with repeating units from 1 to 3. The cyclic dimer is

dominant. However, there are some high molecular weight linear polymers or higher repeating units (above 3) in cyclo-oligomer 4d, 4e because of a shoulder peak in the cyclic trimer absorption peak. This also deduces that the cyclicity of 3d, 3e is less than that of 3a, 3b, 3c. This is maybe due to methyl substitution in 3d, 3e monomer strong repelling force with neighbour atoms inhibiting the formation of cyclo-oligomers.

4. Crystallinity of cyclic (aryl ether ketone)s from 4, 4'-difluorobenzophenone

The WAXD patterns of 4a, 4b, 4e were shown in Figure 4. Many sharp diffraction peaks suggested that the cyclic (aryl ether ketone)s oligomers from 4, 4'-difluorobenzophenone were very well to crystallize. This is different from the cyclic aryl ether ketones oligomers from 2, 4'-difluorobenzophenone and linear high molecular weight amorphous polymers with same structure⁽¹⁰⁾.

5. The thermal properties of cyclic (aryl ether ketone)s from 4, 4'-difluorobenzophenone

The thermal properties of cyclic-oligomers from 4, 4'-difluorobenzophenone were listed in Table 1

Table 1. Thermal properties of cyclo-oligomers from 4, 4'-difluorobenzophenone

cyclic oligomer	T _g ^a (°C)	T _m ^a (°C)	Exotherm Tonset (°C)	T _d ^b (°C) (5%)
4a	133	384	---	489
4c	---	---	no change below 450 (°C)	
4c	195	---	400	
4d	192	---	320	

Notes: a: measurement in DSC at 20 °C/min heating rate, N₂ atmosphere. b: measurement in TG at 20 °C/min, N₂ atmosphere.

Cyclo-oligomer 4c, 4d had started to decompose or cross before reaching the melting temperature, therefore, they don't fit for melting processing. T_g, T_m were not able to be found below 450 °C because of high crystallinity of cyclo-oligomer, it isn't suitable for ring-opening polymerization above melting temperature. While, T_m of the cyclo-oligomer 4a is 384 °C, the temperature which starts to decompose is 454 °C. It provides a processing temperature window [70 °C] which allows the fabrication and ring-opening polymerization of cyclic oligomer.

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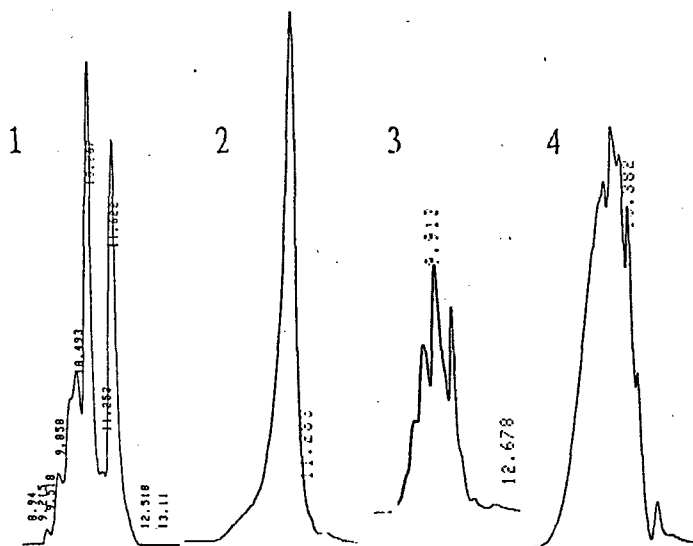


Figure 1. HPLC trace of cyclic oligomers from 2,4'-fluorobenzophenone
 1. cyclic oligomer 2a 2. cyclic oligomer 2b
 3. cyclic oligomer 2c 4. cyclic oligomer 2d

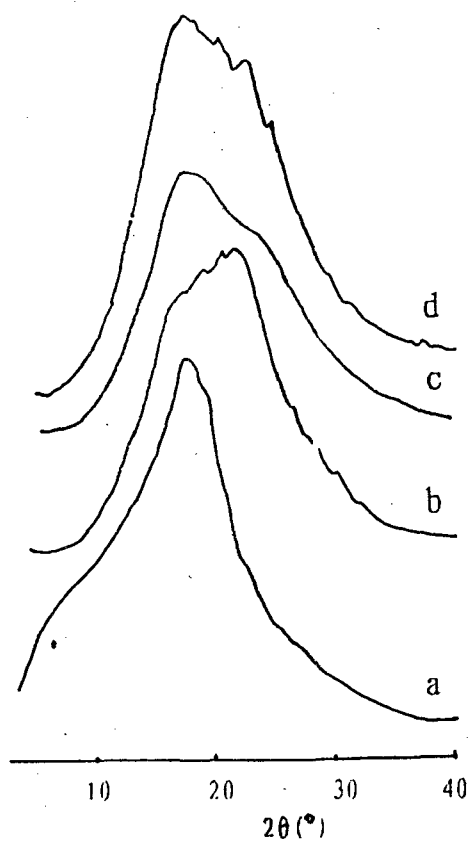


Figure 2. WAXD patterns of cyclic oligomers from 2,4'-fluorobenzophenone
 a. cyclic oligomer 2a b. cyclic oligomer 2b
 c. cyclic oligomer 2c d. cyclic oligomer 2d

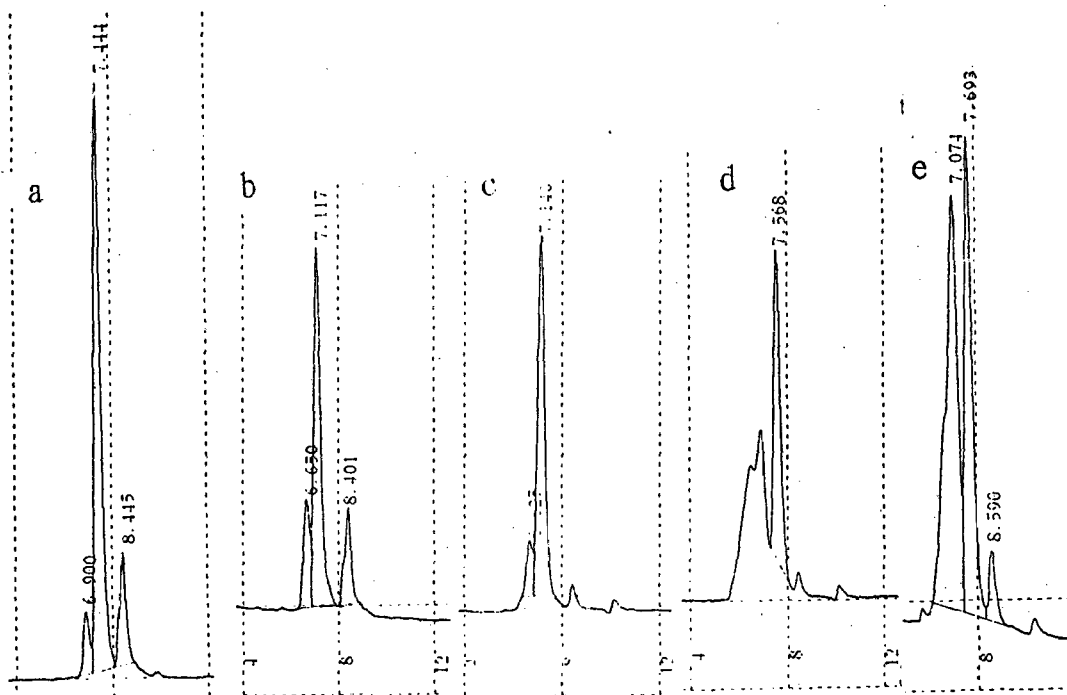


Figure 3. GPC trace of cyclic oligomers from 4,4'-difluorobenzophenone

- a. cyclic oligomer 4a
- b. cyclic oligomer 4b
- c. cyclic oligomer 4c
- d. cyclic oligomer 4d
- e. cyclic oligomer 4e

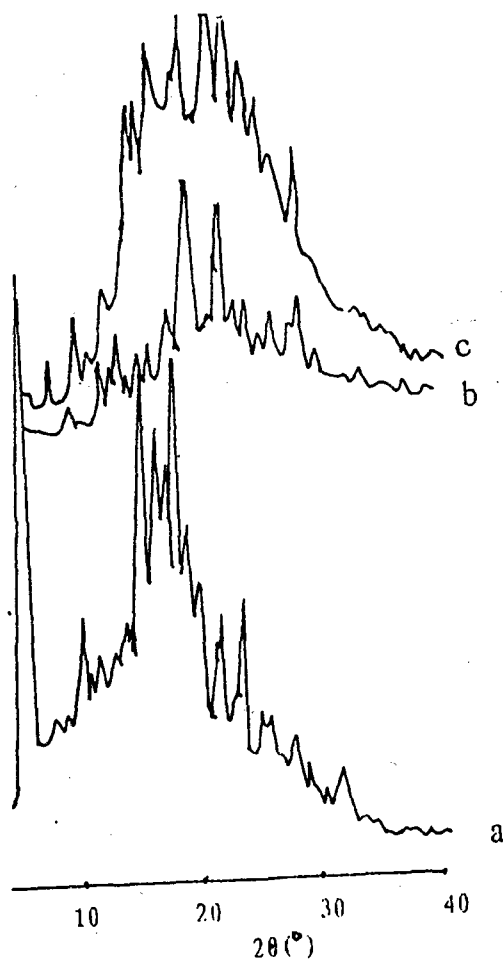


Figure 4. WAXD curves of cyclic oligomers from 4,4'-difluorobenzophenone

- a. cyclic oligomer 4a
- b. cyclic oligomer 4b
- c. cyclic oligomer 4c