

Crystallinity and Ring-opening Polymerization of Cyclic(Aryl Ether Ketone) Oligomers

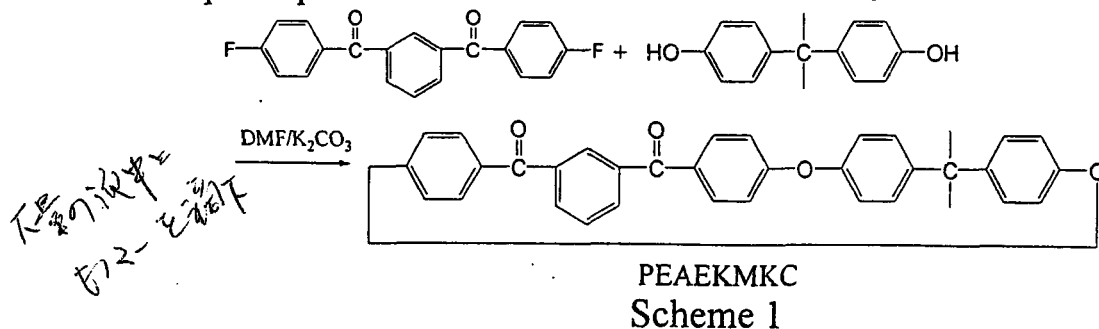
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In recent years, the advantages of using cyclic oligomers as precursors of thermalplastics have been well recognized. Ring-opening polymerization (ROP)⁽¹⁻⁶⁾ reactions have the advantages of converting low molecular weight cyclic monomers to high molecular weight polymers without release of volatile by-products. The installations of the ROP are much simpler than that of ordinary polymerization. They can be used to prepare high-quality carbon fiber or glass fiber composite materials. Recently, a lot of researchers have become interested in the preparations of those commercial resins, such as PI, PEEK, PES, by ring-opening polymerization.

By now, a large amount of research has been done about the ROP of the cyclic oligomers containing 1,2-bis(4'-fluorobenzoyl)benzene. When it comes to 1,3-bis(4'-fluorobenzoyl)benzene, little has been done due to the difficulty to synthesize the cyclic oligomers containing this monomer. The solubility of 1,3-bis(4'-fluorobenzoyl)benzene in many organic solvents is very low due to its particular structure. Therefore the crystallinity and ROP of the oligomers containing it have never been reported. However, we succeeded in preparing the cyclic oligomers containing it and studied their crystallinity and the ROP systematically.

Experimental Section

Macrocyclic oligomers containing 1,3-bis(4'-fluorobenzoyl)benzene and bisphenol-A were prepared successfully by using the pseudo-high dilution principal as shown blow⁽⁷⁾.



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Instruments Analyses

1. Differential Scanning Calorimetry (DSC) analyses were performed on a DuPout-2000 DSC in N₂ atmosphere at the temperature range from 200 °C to 380 °C .

2.X-ray spectra were obtained on a Riguku D/max-2B spectrometer.

Results and Discussion

—Polymorphism of the Purified Macrocyclic Oligomers

By varying the condition of the crystallization for example temperature , time of isothermal treatment and rate of cooling ,we got several crystals of the same oligomers .Figure 1 is the DSC traces of the different crystals. As can be seen from the traces, there are at least four stable crystals of the oligomers . Their X-ray spectra are shown in Figure 2. They can also prove that the four crystals to be different .What crystal system the four crystals are in is being studied.

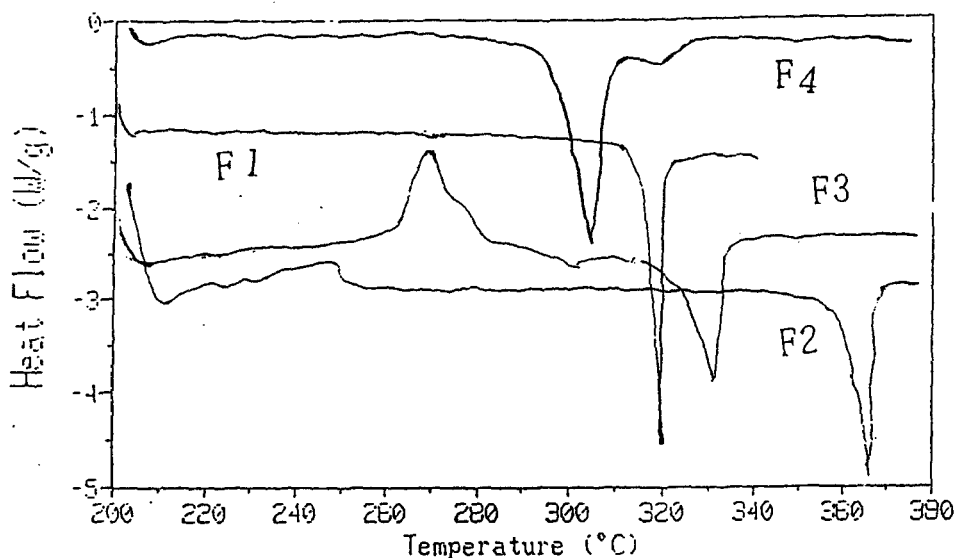


Fig.1 DSC traces of the four crystals

The means to get the different crystals are listed below.

1. Crystal F1 existed in the powder sample got from purification. It wouldn't turn to other crystals in the condition that the temperature of the heat treatment is below 240 °C.

2, If the oligomers were heated to 380 °C ,then treated isothermally at 340 °C for more than 30min after cooling, we could get crystal F2. But the rate of the cooling should be lower than 10 °C/min.

3.Crystal F3 would come up after the oligomers were heated to 380 °C, cooled rapidly ,treated at 290 °C for 30min then cooled rapidly.

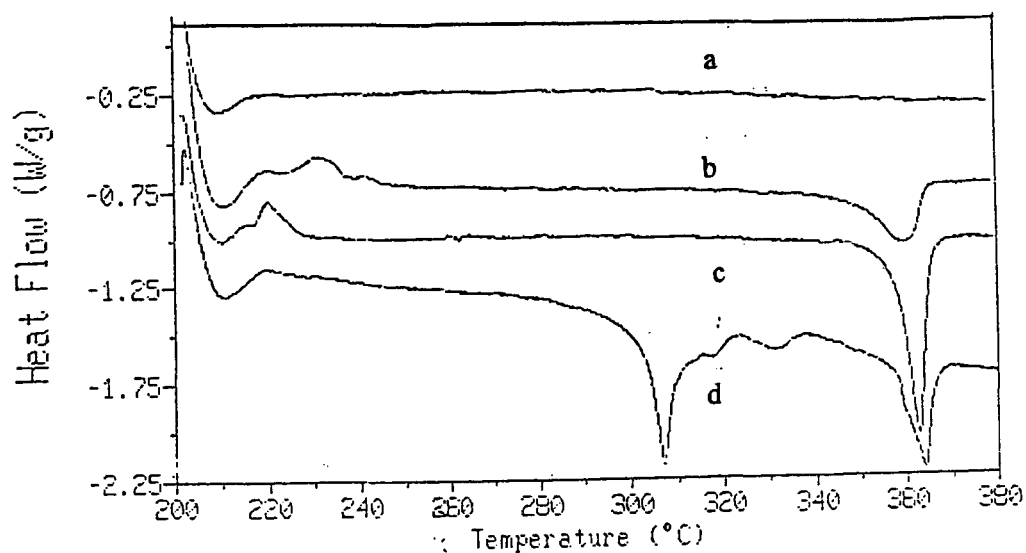


Figure.3 DSC traces of the ROP of the oligomers at different temperatures
a:400 °C b:380 °C c:355 °C d:340 °C

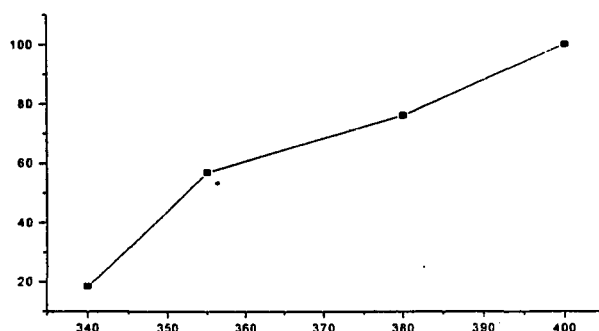


Figure4 .Conversion of the ROP as a function of temperature
2. Effect of CsF on the ROP of the Macrocylic Oligomers
a. Influence of the Weight Ratio of CsF

When the effect was investigated, the reaction temperature was kept at 340 °C for 10min. As can be seen in Figure 5, the ratio of the initiator had great influence on polymerization. The rate of the ROP increased with the ratio of initiator.

In Figure 6, the gradient is smaller when the ratio of CsF is below 0.25%.It means that the conversion of the ROP increased slowly at low ratio. Then the conversion of the macrocylic oligomers increased with the ratio of the initiator rapidly after 0.25%.The conversion is about 100% when the ratio is 1.00% or bigger.

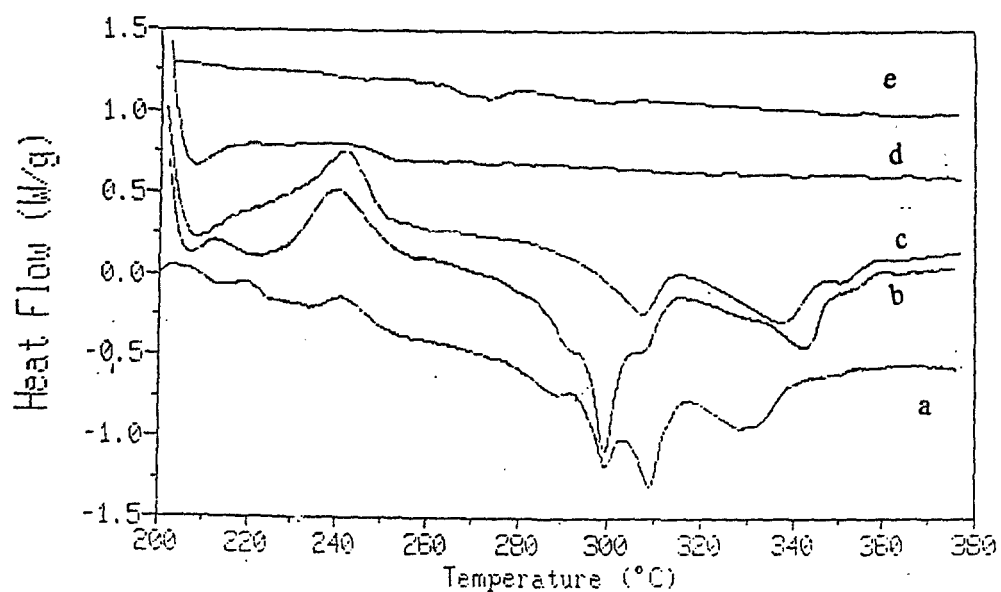


Figure 5 Effect of the ratio of the initiator on the ROP
 a:0.1% b:0.25% c:0.5% d:1% e:2%

Table 2 .Effect of the ratio of the initiator on the ROP

	a	b	c	d	e
Ratio of initiator (wt%)	0.1	0.25	0.5	1	2
Crystalline enthalpy (J/g)	77.81	73.90	47.50	0	0
Conversion of the ROP (%)	6.5	11.2	42.9	100	100

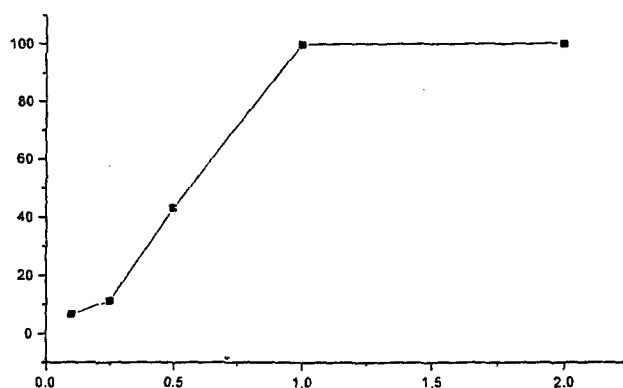


Figure 6 Conversion of the ROP as a function of the ratio of the initiator

b. Effect of Reaction Time on the Conversion of the ROP

Figure 7 shows the conversion vs time relationships for the ROP of

macrocyclic oligomers at 340 °C in the presence of 0.5wt% CsF. The process of the ROP can be seen in the Figure 7 clearly . The conversion increased from 30% to 100% when the time is increased from 5min to 20 min. In Figure8 ,the conversion of the ROP increases slowly with time between 5min and 10min. We think the period between 5min and 10min was the induction period . The rate of the reaction after 15min increased rapidly. And it was probably the increasing period.

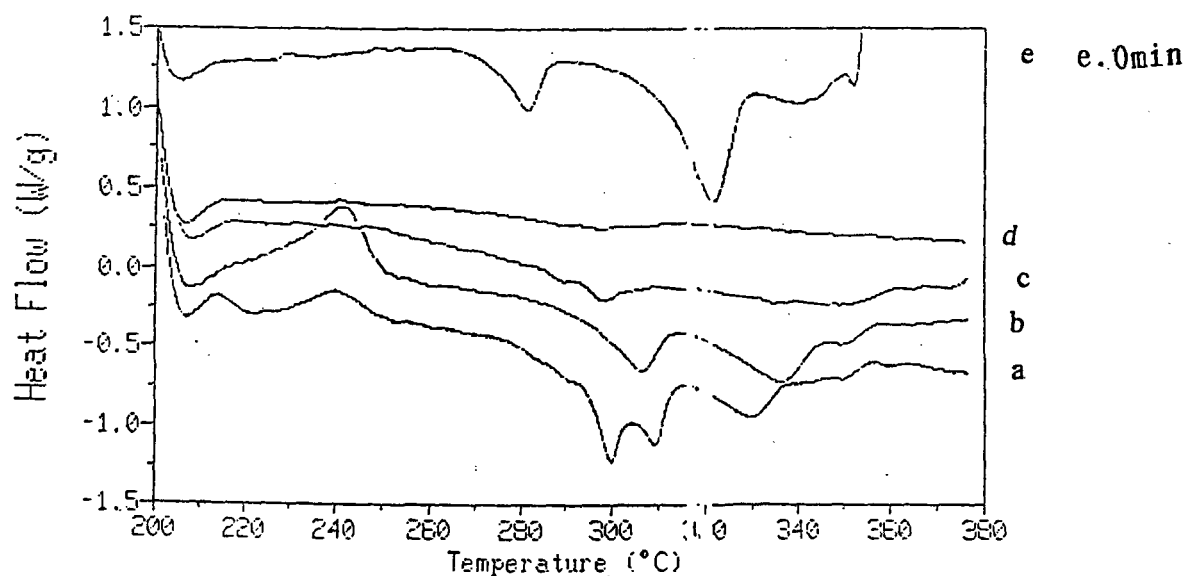


Figure 7.DSC traces for the ROP at different reaction time

Table 3. Effect of the reaction time on the conversion of the ROP.

	a	b	c	d
Time (min)	5	10	15	20
Crystalline enthalpy(J/g)	56.91	47.50	37.19	0
Conversion of the ROP(%)	31.6	42.9	55.3	100

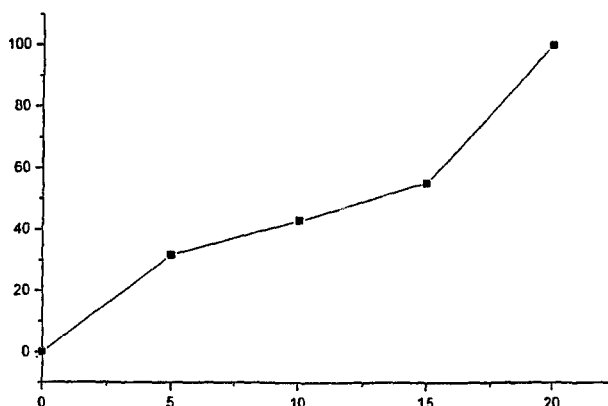


Figure 8. Conversion of the ROP as a function of time .

The ROP of the cyclic (aryl ether ketone) oligomers was studied by DSC to decide the optimum conditions. The conversion of the ROP increases with reaction temperature ,reaction time and the weight ratio of the initiators. As for the particular oligomers , CsF is a more efficient initiator than K_2CO_3 .The ROP has an induction period relying on initiators, ratio of initiators and temperature.

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