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Cyclic Oligomers of Phenolphthalein Polyarylene Ether Sulfone (Ketone): Preparation Through Cyclo-depolymerisation of Corresponding Polymers

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Abstract: Cyclic oligomers of phenolphthalein polyarylene ether sulfone(ketone) were prepared through cyclo-depolymerisation of corresponding polymers using CsF as the catalyst in dipolar aprotic solvent DMAc and DMF, and a family of macrocycles containing from dimer up to at least heptamer were confirmed by GPC, HPLC and MALDI-TOF-MS. The yields of cyclics get as high as 86.3% and 87.9% respectively.

Keywords: Cyclic oligomer, phenolphthalein polyether sulfone(ketone) , cyclodepolymerisation, cesium fluoride.

The advantages of using cyclic oligomers as macrocyclic precursors for the preparation of high performance polymers by ring-opening polymerisation(ROP) have been well recognized. It could produce a revolutionary change in the preparation of advanced thermoplastic composite , and it has very important use in the polymerisation process to get polymers such as reinforced reactive injection mode(RRIM) and resin transfer mode (RTM) *etc*. Cyclo-depolymerisation(CDP) is such a novel technique for the preparation of macrocyclic polyarylethers. Compared with the conventional method of pseudo-high-dilution, CDP reaction makes the concentration of reactant increase greatly, and achieves chemical recovery and recycling of high-performance aromatic polymers . Especially it presents an intelligent method for the recycling polymers in contrast to energetic recycling(incineration) and pyrolytic recycling.

There was some research on the CDP of polyether sulfone(PES)[1,2]. In these experiments[2] PES (M_w=43000,M_n=23000) was cyclo-depolymerized, and the highest yield of cyclic dimer to octamer was 74%. Here for the first time we report the CDP of amorphous phenolphthalein polyether sulfone(PES-C)**1a** and phenolphthalein polyether ketone(PEK-C)**1b**. **1a** and **1b** with wide molecular weight distribution undergo catalytic transetherification (**Scheme 1**) at elevated temperature in the presence of fluoride ion, a strong nucleophile (**Scheme 2**) in dipolar aprotic solvent DMAc and DMF for 50 hours,

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and convert in good yields to macrocyclic oligomers(**Table 1)**.

The cyclic oligomer components of product are confirmed by GPC, HPLC(**Table 1**) and MALDI-TOF-MS(**Figure 1**). In **Figure 1 2a** and **2b** reveal cyclic oligomers from dimer up to at least heptamer with reasonable signal to noise ratio. The MS spectrum of **2a** shows two signals for each oligomer. For example, the signals for cyclic trimer are located at 1597.4 and 1619.4 Da. The signal at 1597.4Da corresponds to the protonated molecular ion peak, that at 1619.4Da is due to the adduct of the trimer with a sodium cation. Spectrum of **2b** gives one signal for each oligomer corresponding to the protonated peak. HPLC data show that the yields of cyclics were 86.3% and 87.9% respectively, higher than the result of PES, because the cardo rings on the side chains lead to easy bend to form cyclos after the breakage of ether linkages.

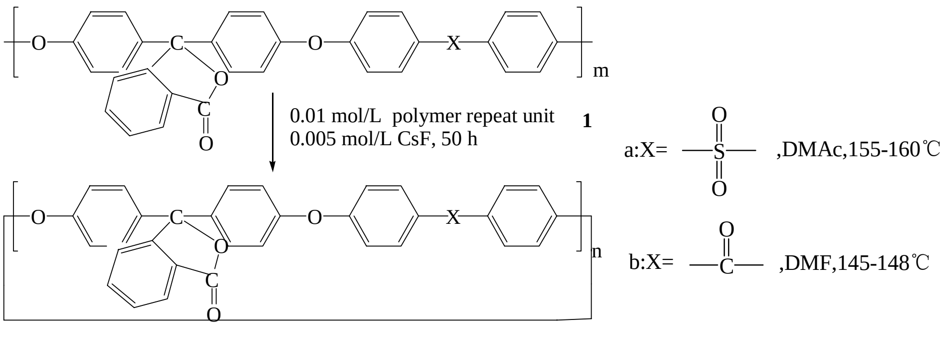
Table 1 Change of molecular weight and distribution of cyclic oligomers formed in the CDP reaction

	1[a]		**2**[b]			mole percentages of cyclic oligomers(%)②						
	M_w (*10^4)	M_n (*10^4)	M_w (*10^3)	M_n (*10^3)	Yield (%)	n=2	n=3	n=4	n=5	n=6	n=7	n>=8
a	12.7	2.4	3.2	1.3	86.3	19.7	24.2	15.9	10.4	6.6	4.5	5.0
b	15.5	2.0	7.6	2.1	87.9	45.4	20.8	10.0	5.6	3.7	2.4	—

a GPC data, PS standard.

b Reverse phase gradient HPLC data, THF and water as the solvents.

Scheme 1 CDP reaction of PES-C and PEK-C



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Scheme 2 Transetherification mechanism at the presence of F⁻

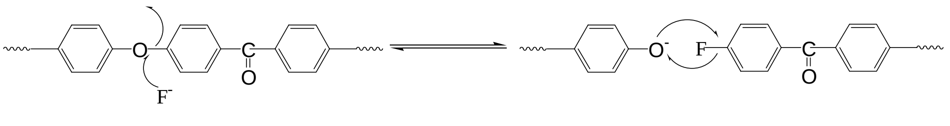
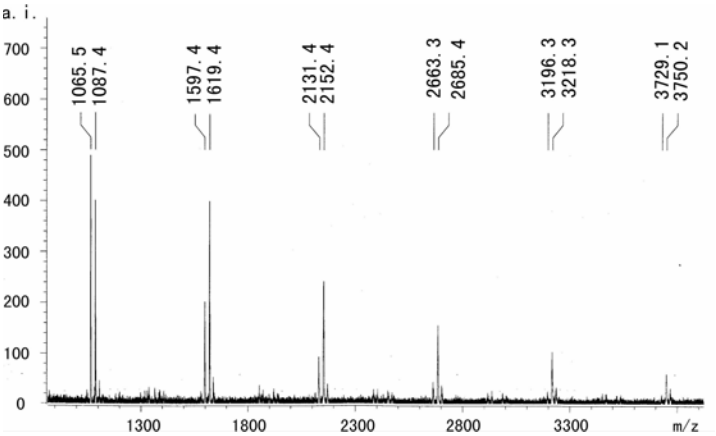
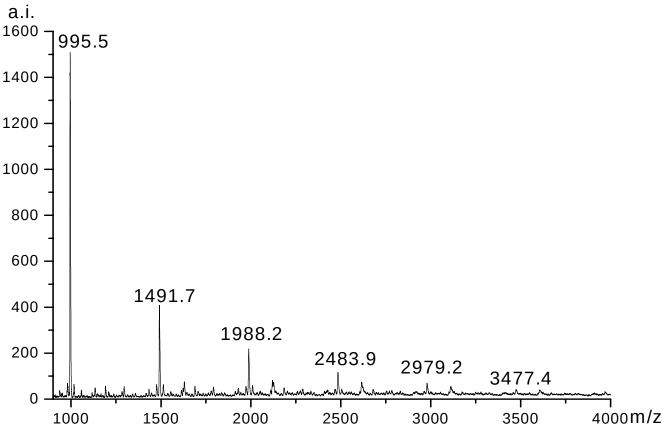


Figure 1 MALDI-TOF-MS spectrum of **2a** and **2b**



2a



2b

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