

Novel Poly(ether ketone)arylates: Synthesis, Characterization and Properties

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ABSTRACT: In order to reduce the melt temperature (T_m) of the thermotropic crystalline polyarylate and improve its compatibility with poly(ether ether ketone) (PEEK), a series of poly(ether ketone)arylates (PEKARs) containing aryl ether ketone units (AEK) are synthesized through melt transesterification reaction from *p*-acetoxybenzoic acid, 1,3-bis(4'-carboxylphenoxy)benzene and 4,4'-bis(*p*-acetoxyphenoxy)benzophenone. The inherent viscosities of these polymers are in the range 0.35–0.81 dL/g. The morphologies and properties of PEKARs are characterized by polarized optical microscopy, wide-angle X-ray diffraction, differential scanning calorimetry, thermal gravimetric analysis, etc. The results show that all PEKARs are semi-crystalline polymers, and the introduction of AEK units can reduce the symmetry of the main chains, leading to decreasing the crystallizability and changing the crystalline form. The PEKARs with AEK less than 30% can exhibit thermotropic liquid crystalline state. The initial and the maximum decomposition temperatures increase with the increase in AEK content. These PEKARs are expected to act as processing agents for PEEK to reduce its processing viscosity. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2393–2398, 2013

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INTRODUCTION

Nowadays, it has been found that thermotropic liquid crystalline polymers (TLCPs) have excellent properties, including mechanical properties, chemical resistance, thermal stability, and so on. Therefore, they are widely used in many fields, such as membranes, fibers, and composites, etc.^{1–3}

There are a number of TLCPs shown in Table I. It is found that the melting temperature of the wholly aromatic thermotropic liquid crystalline polyarylate (PHB) is above 600°C which is higher than its decomposition temperature, which greatly restricts the development and application. In order to improve the processability, many researchers have made a lot of efforts and made some progress. It is well known that the rigid macromolecular chain and strong molecular interaction would cause the high melting point and bad solubility in common organic solvents.^{4,5} Therefore, the main idea is to increase the flexibility and reduce the symmetry of the main chains, including introducing the flexible chains,^{6–9} the side substituent,^{10–14} and spacer incorporation^{15–17} into main chains, for example, copolymerization of semi-flexible poly(ethylene terephthalate) (PET) with rod-like poly(4-hydroxybenzoic acid), polycondensation

of aliphatic dicarboxylic acids with mesogenic bisphenols, polycondensation of hydroquinones (HQs) (substituted or not) with α , ω -bisbenzoic acids (such as 4,4'-dicarboxy- α,ω -diphenoxyhexane) bearing the spacer molecule. Based on above studies, a lot of novel TLCPs have been synthesized, such as “X-7G”,⁴ “Xydar”, and “Vectra”.^{17,18} At the present time, Vectra is the only one industrial product of the polyarylate fiber.

In our previous work,²⁰ in order to reduce the melting temperature of TLCP with reserving thermotropic liquid crystalline state, a series of liquid crystalline copolyarylates containing *m*-aryl ether units were synthesized using *p*-acetoxybenzoic acid (PABA), 1,4-diacetoxybenzene (DAB), and 1,3-bis(4'-carboxylphenoxy)benzene [PMP(COOH)₂] by melt transesterification reaction. We considered blending those liquid crystalline copolyarylates with poly(ether ether ketone) (PEEK) to reduce the melt viscosity and improve the processability of PEEK. However, it was found that PEEK had very poor compatibility with those copolyarylates. Therefore, in present work, a novel monomer containing aryl ether ketone (AEK) groups, 4,4'-bis(*p*-acetoxyphenoxy) benzophenone (*p*-DAPBP), has been prepared by HQ and 4,4'-difluorobenzophenone firstly, then a series of novel

Table I. Chemical Structures and Melting Points of the Commercial TLCPs

| Trade Name | Company | Chemical structure | Melt point / °C |
|------------|-------------|--------------------|-----------------|
| PHB | Carborundum | | > 600 |
| X7G | Eastmman | | 228 |
| Xydar | Dartco | | 380 |
| Vectra | Celanese | | 270 |

polyarylates named as poly(ether ketone)arylates (PEKARs) containing AEK units have been synthesized by using the monomers of PABA, PMP(COOH)₂, and *p*-DAPBP through melt transesterification reaction. The introduction of aryl ether group is conducive to reducing the melt temperature of TLCPs; meanwhile, AEK units in PEKARs similar to the structure of PEEK are expected to improve the compatibility between PEEK and TLCP. So these thermotropic liquid crystalline PEKARs can be used as processing agents to improve the processability of PEEK by the effects of inducing orientation and reducing viscosity. The structure and properties of the monomers and polymers were characterized by Fourier transform infrared (FT-IR), ¹H Nuclear magnetic resonance (¹H NMR), polarizing microscope (POM), wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA).

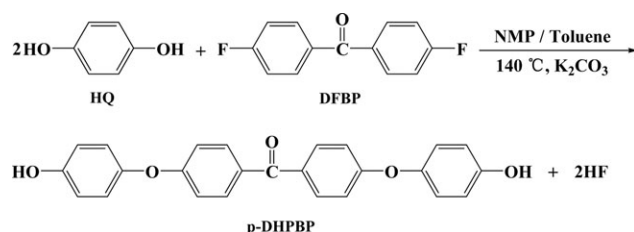
EXPERIMENTAL SECTION

Materials

HQ, *m*-dihydroxybenzene, potassium carbonate, *N*-methyl-2-pyrrolidone (NMP), 4-hydroxybenzoic acid, toluene, ethanol, acetic anhydride, sulfuric acid, *p*-hydroxybenzoic acid (PHBA), zinc acetate, diantimony trioxide, dimethyl sulfoxide (DMSO) (all from Chengdu Ke Long Co.), and 4,4'-difluorobenzophenone (DFBP, from Wuhan XinHuayuan chemical Co.) were analytically pure and used as received. 1,3-bis(4'-carboxylphenoxy)benzene [PMP(COOH)₂] was prepared in our laboratory and the synthesis route was reported by our previous work.²⁰

Monomer Synthesis

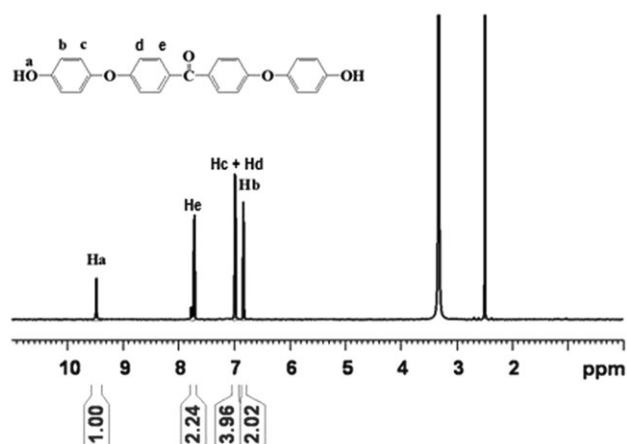
Synthesis of the 4,4'-bis(*p*-hydroxyphenoxy)benzophenone (*p*-DHPBP). *p*-DHPBP was synthesized from DFBP and excess HQ by nucleophilic substitution (shown in Scheme 1). The detailed procedure of synthesis is shown as follows: 55.06 g (0.5 mol) of HQ, 43.64 g (0.2 mol) of DFBP, 69.10 g (0.5 mol) of

**Scheme 1.** Synthetic route of *p*-DHPBP.

potassium carbonate dissolved in 300 ml NMP and 40 ml toluene in a 500 ml three-neck round-bottom flask equipped with a stirring bar, a gas inlet and a drying tube. An oil bath was used to keep desired reaction temperatures. The flask was slightly heated to 140°C for 7 h, and then the temperature was increased to 160°C for 1 h to remove toluene. At last, the product was cooled to the room temperature and poured into distilled water for precipitation. The pH value of the product was adjusted to 3–4 through adding hydrochloric acid, and then filtered under negative-pressure to obtain the crude product. The crude product was washed repeatedly by distilled water until the filtrate was nearly neutral, and finally dried at 80°C under vacuum. Taupe powder of *p*-DHPBP was obtained with the yield above 70%.

The ¹H NMR and FT-IR spectra of *p*-DHPBP are shown in Figures 1 and 2, respectively. ¹H NMR (600 MHz, DMSO-*d*₆, δ, ppm): 9.470 (s, 2H, H_a), 7.750 (d, 4H, H_d), 6.989 (d, 8H, H_c), 6.823 (d, 4H, H_b). IR (KBr): 3550~3200 cm⁻¹ (—OH, ν_{O—H}), 1644 cm⁻¹ (—CO—, ν_{C=O}), 1599~1467 cm⁻¹ (—Ar—, ν_{C=C}), 1234 cm⁻¹ and 1098 cm⁻¹ (δ_{C—O—C}).

4,4'-bis(*p*-acetoxyphenoxy)benzophenone (*p*-DAPBP) and *p*-Acetoxybenzoic acid (PABA). Due to hydroxyl can be oxidized easily at high temperature, it is necessary to be acetylated before polymerization. The procedures of acetylation of *p*-DHPBP and PHBA are similar, so the acetylation of *p*-DHPBP is taken as an example to illustrate the general procedure. In a 500 ml round-bottom flask, 395.18 g (1 mol) of *p*-DHPBP with excess

**Figure 1.** ¹H NMR spectrum of the *p*-DHPBP.

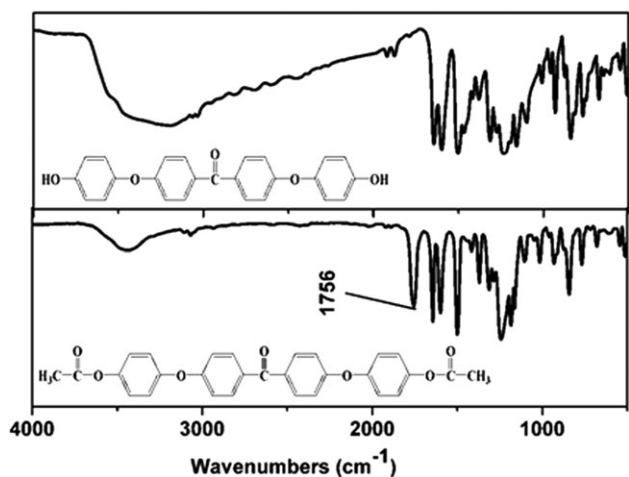


Figure 2. FT-IR spectra of *p*-DHPBP and *p*-DAPBP.

of 300 ml of acetic anhydride and three drops of 98% sulfuric acid reacted at 60°C for 3–5 h. Then the mixture was slowly poured into ice water for precipitation. The precipitate was filtered and washed repeatedly until the filtrate was nearly neutral, and then dried at 105°C under vacuum. The taupe powder of *p*-DAPBP was obtained with the yield of 90.2%, and the melting point is 174°C (determined by DSC at a heating rate of 5°C/min). As shown in Figure 2, after acetylation, the IR absorption peak of the hydroxyl disappeared completely (the absorption peak around 3400 cm^{-1} should be attributed to the absorption of the moisture in KBr); meanwhile, a characteristic absorption band of C=O stretching vibration for ester carboxyl can be found around 1756 cm^{-1} in the FT-IR spectrum. In Figure 3, the ^1H NMR absorption peak of the hydroxyl disappeared completely at 9.470 ppm, and a characteristic peak of methyl could be found at 2.28 ppm. So we can confirm that the acetylation has been completely finished.

Polymerization

All polymers were synthesized by melt transesterification process (shown in Scheme 2). The synthesis of PEKAR-1 was taken as an example to illustrate the general synthetic procedure. 42.03 g of PABA, 24.12 g of *p*-DAPBP, 17.52 g of PMP(COOH) $_2$, 0.0785 g of Zinc acetate, and 0.2055 g of antimony oxide were placed in a 2 L high temperature and high pressure polymeriza-

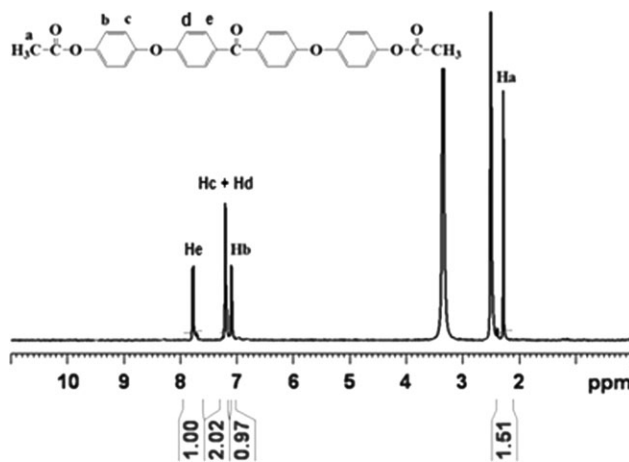


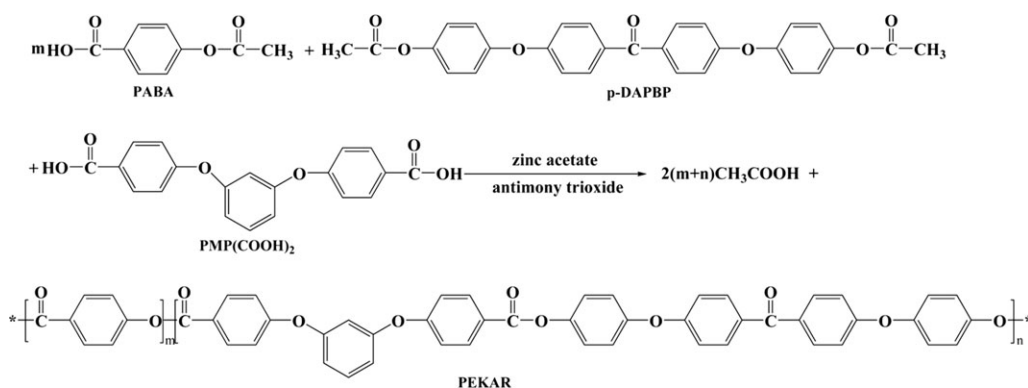
Figure 3. ^1H NMR spectrum of the *p*-DAPBP.

tion reactor equipped with a gas outlet and a vacuum inlet. Nitrogen was used to maintain an inert environment. Under the pressure of 1.0 MPa and a constant stirring rate of 50 rpm, the temperature was slightly heated to 180°C for 2 h. Then the temperature was increased to 240°C under the pressure of 1.0 MPa for 2 h and 280°C under the pressure of 0.5 MPa for 1 h. At last the temperature was 300–310°C under vacuum ($P = -0.098$ MPa) for 0.5 h. Once the reaction was over, the product was cooled to room temperature. The obtained polymer was crushed into powder and washed repeatedly with DMSO/ethanol (v/v=3:7), and then dried at 105°C under vacuum. ^1H NMR spectrum of the product could not be carried out because PEKAR cannot dissolve in common deuterium reagents. But the structure was confirmed by IR spectrum (shown in Figure 4). IR (KBr): 1737 cm^{-1} ($-\text{COO}-$, $\nu_{\text{C=O}}$), 1647 cm^{-1} ($-\text{CO}-$, $\nu_{\text{C=O}}$), 1595~1498 cm^{-1} ($-\text{Ar}-$, $\nu_{\text{C=C}}$), 1158 cm^{-1} and 1055 cm^{-1} ($\delta_{\text{C-O-C}}$).

All polymers were prepared by a similar procedure described as above. These polyarylates were symbolized as PEKAR-1, PEKAR-2, PEKAR-3, and PEKAR-4 according to the different monomer ratios (shown in Table II).

Measurements

Infrared spectra were recorded from KBr pellet with a Nicolet 560 FT-IR spectrometer. ^1H NMR spectra were obtained through a Bruker 600 MHz Ultra Shield NMR spectrometer in



Scheme 2. Synthetic route of the PEKARs.

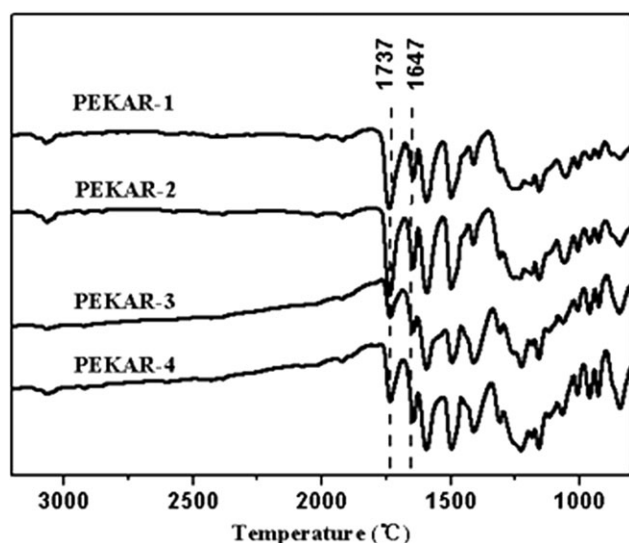


Figure 4. FT-IR spectra of the PEKARs.

deuteriochloroform using tetramethylsilane (TMS) as the internal standard. Inherent viscosities of the TLCPs were measured in 1,1,2,2-tetrachloroethane (TCE)/phenol (v/v = 4:6) at 30°C at a concentration of 0.25 g/dL with an Ubbelohde capillary viscometer. DSC data were obtained on a Netzsch DSC 204F1 under a nitrogen flow with both heating and cooling rates of 10°C/min. Before the equipment running, the temperature and heat enthalpy were calibrated with indium standard. TGA was performed with a TA SDT Q600 thermal analyzer using a heating rate of 10°C/min in nitrogen at a flow rate of 100 cm³/min. Wide-angle X-ray diffraction (WXR) was conducted with an X'Pert Pro X-ray diffractometer. The scanning rate was 12°/min over a scattering angle range of $2\theta = 5\text{--}50^\circ$. The dried polymer powder was used for WXR measurements. Texture observations were carried out on a Leica DMLP POM with a Linkam heating stage.

RESULTS AND DISCUSSION

Preparation of Polymers

PEKARs are random copolymers synthesized by transesterification; the structures and the properties can be controlled by adjusting the molar ratios of the monomers. The actual contents of AEK units in the polymers can be calculated approximately using the integration area of ketone and ester groups in

FT-IR spectrum (shown in eq. (1)). The theoretical content of AEK units is defined as shown in eq. (2). The results can be found in Table II. With the molecular weight of polymers increasing, the content of unesterified end groups decrease; meanwhile, the actual values are more close to the theoretical value. Due to PEKARs could not dissolve in common solvent such as THF, their molecular weights could not be characterized by gel permeation chromatography (GPC). The influence of copolymerization ratios on molecular weight was characterized by inherent viscosities as shown in Table III. When the content of *p*-DAPBP was less than 25%, the yield was above 90% and the inherent viscosity was in the range 0.7–0.8 dL/g; however, when the content of *p*-DAPBP was more than 33%, the yield and the inherent viscosity lowered because *p*-DAPBP was easy to sublimate resulting in the breakdown of equimolar ratio of the monomers. Therefore, the actual content of AEK units was far more than the theoretical value.

$$\omega_{(\text{act})} = \frac{A_{1737\text{cm}^{-1}}}{A_{1647\text{cm}^{-1}}} \times 100\% \quad (1)$$

where $\omega_{(\text{act})}$ represents the actual content of aryl ether ketone, and A is integration area;

$$\omega_{(\text{the})} = \frac{N_1}{N_2} \times 100\% \quad (2)$$

where $\omega_{(\text{the})}$ represents the theoretical content of aryl ether ketone; N_1 represents molar number of aryl ether ketone units; and N_2 represents molar number of ester units.

Texture Structure of Polymers

The texture structure of TLCPs was observed by the hot stage POM. It is seen from Figure 5 that PEKAR-1 exhibits a characteristic bright texture in its melted state owing to the birefringence at 320°C. It was also observed that the birefringent texture of PEKAR-2 was stable at 260°C. When the temperature was heated to 360°C, the texture structure of PEKAR-2 disappeared and the melt of PEKAR-2 became transparent, suggesting its phase state become isotropic at this temperature. PEKAR-3 and PEKAR-4 were melted partly at 280°C. The typical liquid crystalline texture was not present. The results demonstrate that the introduction of the AEK units is not conducive to the formation and stabilization of the liquid crystalline state because the symmetry of the molecular chain was destroyed.

Table II. Content of Aryl Ether and Ketone Units, the Inherent Viscosities and Yields of PEKARs

| Polymers | PABA:PMP(COOH) ₂ : <i>p</i> -DAPBP | Theoretical value ^a (%) | Actual value ^b (%) | $[\eta]^c$ (dL/g) | Yield (%) |
|----------|---|------------------------------------|-------------------------------|-------------------|-----------|
| PEKAR-1 | 70:15:15 | 15 | 19.36 | 0.72 | 90.16 |
| PEKAR-2 | 60:20:20 | 20 | 29.00 | 0.81 | 92.31 |
| PEKAR-3 | 50:25:25 | 25 | 42.24 | 0.69 | 90.37 |
| PEKAR-4 | 33:33:33 | 33 | 51.76 | 0.35 | 88.73 |

^adetermined by equation 2.

^bdetermined by equation 1.

^cMeasured at a polymer concentration of 0.25 g/dL in TCE/phenol (v/v = 4:6) at 30°C.

Table III. The TGA Data of PEKARs

| Polymers | $T_{id}^{a/}$ °C | $T_{md}^{b/}$ °C | Char yield ^c /% |
|----------|------------------|------------------|----------------------------|
| PEKAR-1 | 406.2 | 456.88 | 56.95 |
| PEKAR-2 | 411.1 | 458.99 | 55.49 |
| PEKAR-3 | 419.9 | 454.33 | 52.63 |
| PEKAR-4 | 420.9 | 461.22 | 52.21 |

^{a,b} T_{id} and T_{md} represent the initial (5% loss weight) and the maximum decomposition temperature, respectively.
^cResidual weight percentage at 800°C in nitrogen.

Crystallization Behaviors of Polymers

The WXR patterns show that all proposed PEKARs are semi-crystalline polymers (shown in Figure 6). There are obvious crystalline diffraction peaks at 18.71°, 19.64°, 20.74°, 23.02°, and 29.05° in PEKAR-1 and PEKAR-2. But the diffraction peaks of 19.64°, 20.74°, and 29.05° nearly disappear in PEKAR-3 and PEKAR-4 while a new diffraction peak can be found at 35.47°, suggesting that the crystal form of PEKARs changes with the increase of the content of AEK units.

Thermal Properties of Polymers

The thermal properties of PEKARs were studied by DSC. It can be noted from Figure 7 that there are no glass transitions but obvious endothermic peaks in DSC curves of the PEKARs. Two

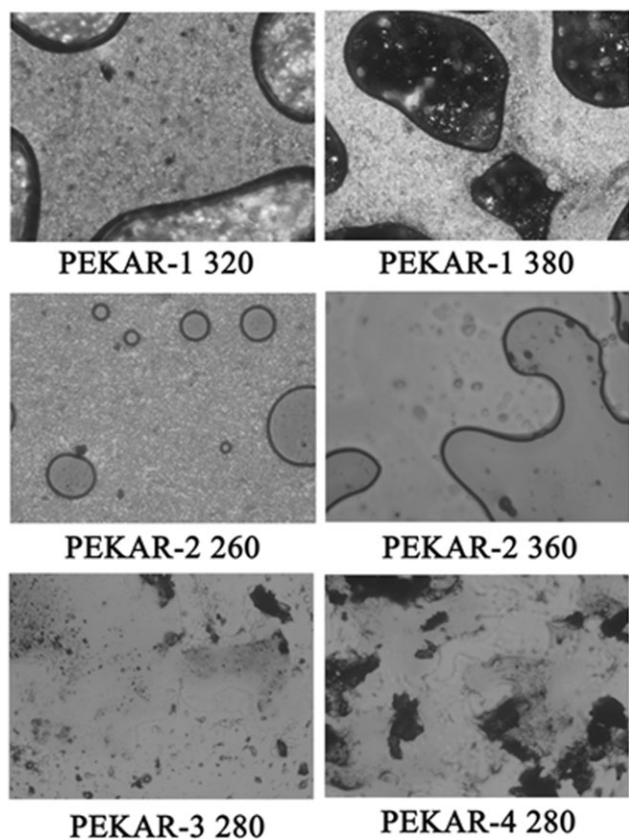


Figure 5. POM micrographs of PEKARs at different temperatures.

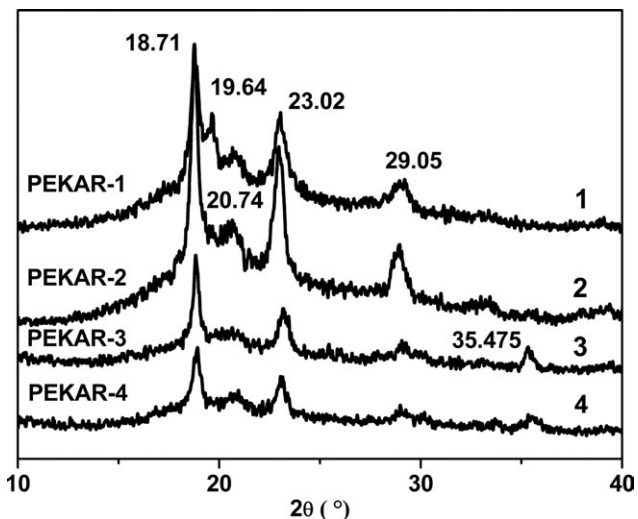


Figure 6. The WAXD patterns of PEKARs.

broad endothermic peaks could be found in the curve of PEKAR-1. Combined with the analytical result of POM, the melting endothermic peak is at 319.2°C. Referring to some papers,¹⁹ this is a common phenomenon of thermotropic liquid crystal polymers, because polymers have different perfection of crystallization in different stages of crystallization. In addition, clear point cannot be observed below 390°C, which corresponds to the result of POM. In the curve of PEKAR-2, there are two endothermic peaks far from each other. The former peak is broad and has a high heat enthalpy, which corresponds to the melting process. The later peak is sharp and has a low heat enthalpy, which is the typical clear point of liquid crystalline polymer. Melting endothermic peaks were observed nearly at 280°C in the heating curve of PEKAR-3 and PEKAR-4. Figure 8 also shows that with the content of AEK groups increasing, the melting temperature does not change monotonously, and a minimum value can be found. The reason is that the

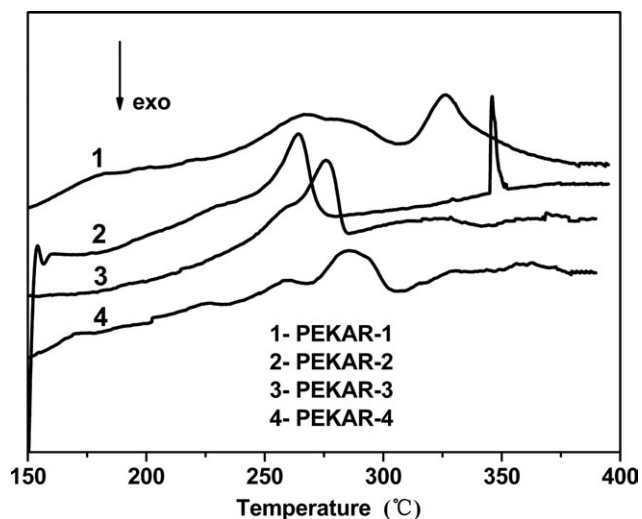


Figure 7. The DSC curves of the PEKARs.

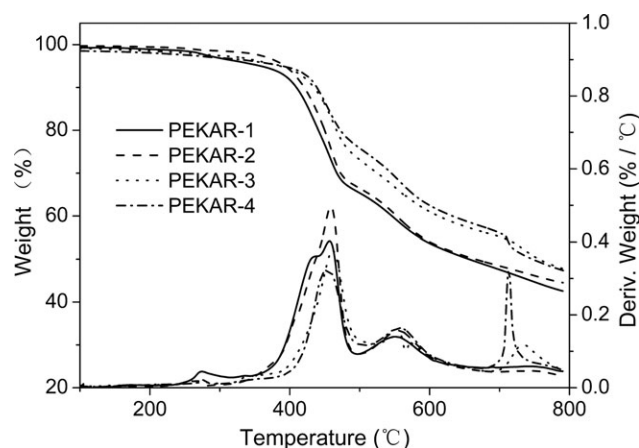


Figure 8. The TGA-DTG curves of PEKARs.

introduction of AEK destroys the symmetry of the molecular chain, which makes entropy change (ΔS) increases, but the strong polarity of AEK group can make the intermolecular forces stronger leading to the increase of enthalpy change (ΔH). So the melting temperature of PEKAR is the result of the competition between the two kinds of effects.

Thermal Decomposition of Polymers

The thermal decomposition of the synthesized PEKARs was investigated in nitrogen atmosphere by TGA. TGA curves show that there are two decomposing stages at 460°C and 555°C, respectively. The weight of polymers decreased 30% at 460°C, which is the main decomposing stage. The initial decomposition temperatures (T_{id} 5% weight loss), the maximum decomposition temperatures (T_{md} maximum rate of weight loss), and the char yields of PEKARs are shown in Table III. As shown in Figure 8, with the content of the AEK units increasing, T_{id} and T_{md} increase slightly, which means that the introduction of AEK units could improve the thermal stability of PEKARs to some extent, the reason is that carbonyl groups have higher bond energy and stronger molecular interaction. Furthermore, char yields at 800°C decrease with the content of AEK increasing because the modified groups have more non-carbon elements.

CONCLUSION

A series of novel polyarylates – PEKARs containing aryl ether ketone groups were successfully synthesized from PABA, PMP(COOH)₂, and *p*-DHPBP through melt transesterification. All proposed polyarylates are semi-crystalline polymers, but the crystallinity decreases with increasing the content of AEK. PEKARs with AEK units less than 30% remain in thermotropic liquid crystalline states; however, there is no clear point when the content of AEK is below 20%, matching the processing window of PEEK and being suit for processing agents. The introduction of AEK units can reduce the symmetry of the main

chains, leading to decreasing the ability of crystallization and changing the crystalline form. With the content of AEK increasing, the change of the melting temperature is not monotonous because of the competition between the asymmetry of main chains and the molecular interaction. The thermal stability of PEKAR increases slightly with increasing the content of AEK units.

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