

Synthesis and characterization of thermotropic liquid crystalline polyarylate with ether ether ketone segments in the main chain

Luxian Zeng, Ruosong Li, Peng Chen, Jianjun Xu, Pengqing Liu

State Key Laboratory of Polymer Materials Engineering, (Sichuan University), College of Polymer Science & Engineering of Sichuan University, Chengdu 610065, China

Correspondence to: P. Liu (E-mail: liupq@scu.edu.cn)

ABSTRACT: A series of thermotropic liquid crystalline poly(ether ether ketone) arylates (PEEKARs) were synthesized by combining the synthetic oligomeric poly(ether ether ketone) with terminal acetoxylys (PEEK-A) and oligomeric Polyester with terminal carboxyl (PES-C). The structures of the synthesized monomers and oligomerics were characterized by Fourier transform infrared spectroscopy and ^1H Nuclear magnetic resonance spectroscopy, which indicated that the products were successfully synthesized as designed, and three kinds of PEEKARs with different legend of polyester segments were synthesized. The morphologies and properties of PEEKARs were measured by differential scanning calorimetry, wide-angle X-ray diffraction, thermal gravimetric analysis and polarized optional microscopy. The results show that PEEKAR with the minimum polyester segments has the best crystallization properties, but the flowability of which is rather poor and the liquid crystal character is unobvious; meanwhile, PEEKAR with more polyester segments can form a thermotropic liquid crystal intermediate state, and PEEKAR with maximum polyester segments has a somewhat humble crystallization property; as the content of polyester segments increases, the crystal form of PEEKARs changes and the char yields at 600 °C is reduced. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43800.

KEYWORDS: crystallization; liquid crystals; synthesis and processing

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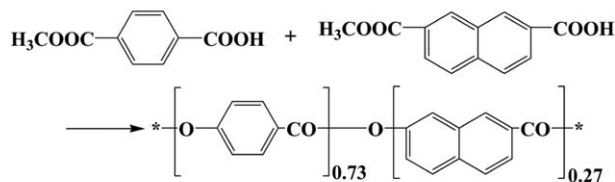
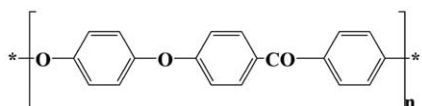
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INTRODUCTION

Thermotropic liquid crystalline polymers (TLCP) have been attracting an increasing amount of research activities because of their excellent mechanical properties, desired thermal stability, and outstanding chemical resistance, etc.¹ Nowadays, the only industrial product of TLCP is Vectra, which has been co-developed by Kuraray and Celanese,² and synthesized from hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) with the molar ratio of 73/27 through melt transesterification process (named Vectra A900, and shown in Scheme 1). Vectra A900 can be spun into high strength and high modulus fibers with excellent humidity resistance, chemical resistance, and abrasive resistance. Meanwhile, it can be used as addition agent blending with thermoplastics, leading to the so-called *in situ* composites to improve some properties of the matrix.^{3–7} Liang *et al.*⁸ have studied Vectra A900/Poly(ethylene terephthalate) (PET) composite fiber, and found that Vectra A900 could act as nucleating agent to promote the crystallization ability of the fiber. The modulus of the as-spun fibers can monotonically increase with increasing the content of Vectra A900. Han and Kim⁹ have found that the Vectra resin could work as processing agent to effectively decrease the viscosity of Poly(phenylene sul-

fide) (PPS) because of the formation of fibrous structure of Vectra A900 in PPS matrix at high shear rates. To expand the application area of Vectra, a series of modified Vectra have emerged, such as Vectra A950 (75/25 HBA/HNA copolyester) and Vectra B950 (60/20/20 HNA/AP/TA copolyester).^{10,11} Vectra A950 and B950 can also be used as addition agent to reinforce thermoplastic, such as poly(ester amide),^{12,13} poly(phenylene sulfide),¹⁴ poly(propylene).^{15,16} Rath and co-workers¹⁷ have studied the properties of Vectra A950/PPS blends with a compatibilizer. Their results showed that, contributing to the fine fibril induced by Vectra, mechanical properties were increased by the addition of Vectra with a bit compatibilizer. Wong and Mai¹⁸ have demonstrated that the tensile strength as well as modulus of PC/PBT blend with a 60/40 weight ratio can be increased two-fold and four-fold by adding Vectra B950, respectively.

However, Vectra is not a universal processing agent for all thermoplastics. For instance, Poly(ether ether ketone) (PEEK, the chemical structure is shown in Scheme 1) is known as the most outstanding thermoplastic but restricted for applications because of its poor processability even after blending with Vectra. This is because Vectra has poor compatibility with PEEK. Our previous works have reported two modification strategies

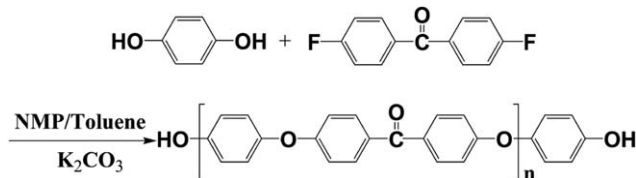
Vectra A900:**PEEK:**

Scheme 1. Synthetic route for Vectra A900 and chemical structure of PEEK.

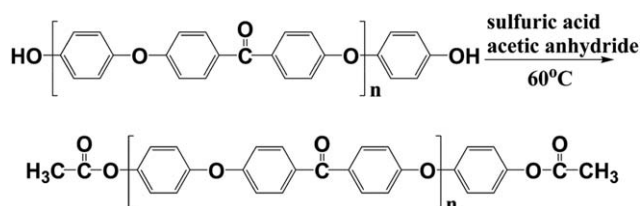
to modify TLCPs for improving the compatibility between PEEK and TLCP.^{1,19–21} However, the synthesized TLCPs and PEEK are just partially compatible, so they are not highly effective processing agent for PEEK. Herein, we developed and synthesized a novel TLCP, Poly(ether ether ketone) arylates (PEEKARs), which combine a novel oligomeric PEEK with terminal acetoxyls (synthesized from 4,4'-difluorobenzophenone and hydroquinone quinol, named as PEEK-A) and a series of oligomeric Polyesters with terminal carboxyl (synthesized from acetylated 6-hydroxy-2-naphthalene formic acid and 4-hydroxybenzoic acid, named as PES-C). The characterization demonstrates that the PEEKARs can maintain the thermotropic liquid crystalline characteristic by controlling the fraction of polyester segments. Since this type of TLCPs possesses the ether ether ketone segments, they are anticipated to have preferable compatibility with the PEEK matrix with the respect to Vectra. The structures and properties of the monomer and polymer were characterized by Fourier transform infrared spectroscopy (FTIR) and ¹H Nuclear magnetic resonance spectroscopy (¹H NMR), differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), thermal gravimetric analysis (TGA), and polarized optional microscopy (POM) between crossed polarizers.

EXPERIMENTAL**Material**

Hydroquinone quinol (HQ), potassium carbonate, toluene, N-methyl-2-pyrrolidone (NMP), 4-hydroxybenzoic acid (HNA), sulfuric acid, acetic anhydride, isophthalic acid (IPA), zinc acetate, diantimony trioxide, dimethyl sulfoxide (DMSO), acetone (all above from Chengdu Ke Long), 4,4'-difluorobenzophenone (DFBP, from Wuhan XinHuayuan Chemical), and 6-hydroxy-2-naphthalene formic acid (from Jinghui Synthesis Material) were analytically pure and used as received.



Scheme 2. Synthetic route of PEEK-.



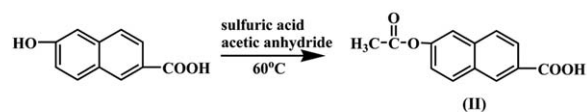
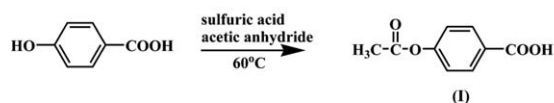
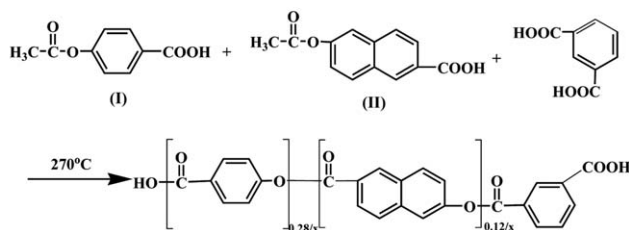
Scheme 3. Synthetic route of PEEK-A.

Synthesis of Poly(ether ether ketone) with Terminal Hydroxyls

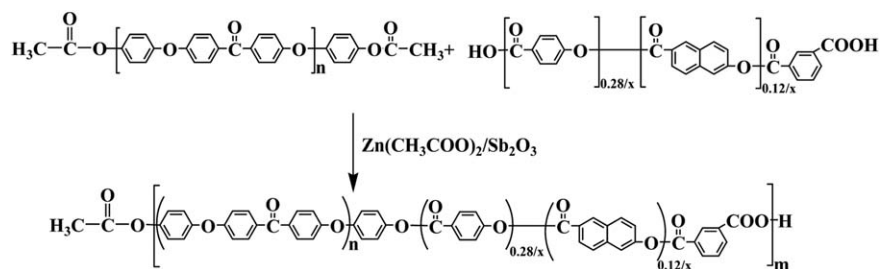
Oligomeric poly(ether ether ketone) with terminal hydroxyls (PEEK-H) were synthesized from HQ and DFBP by nucleophilic substitution (shown in Scheme 2). The detailed procedure of synthesis is shown as follows: 0.2 mol of DFBP, 0.3 mol of HQ, 0.3 mol of potassium carbonate were dissolved in 200 mL NMP and 40 mL toluene (used as an azeotropic solvent to remove the produced water) in a three-neck round-bottom flask equipped with a stirring bar, a nitrogen inlet and a condenser tube, and then vigorously stirred under nitrogen atmosphere. The reaction mixtures were heated to 140 °C for 7 h, and then the temperature was increased to 190 °C for 1 h to remove toluene. At last, the product was cooled to the room temperature and poured slowly into hot distilled water under continuous stirring to precipitate the polymer. The pH value of the product was adjusted to 3–4 through adding hydrochloric acid, and then filtered out and washed repeatedly with distilled water. A pale polymer was obtained after drying under vacuum at 80 °C, and the yield was above 70%.

Synthesis of PEEK-A

Because of hydroxyl can be oxidized easily at high temperature, it is necessary to acetylation before polymerization. The reaction is shown in scheme 3, and the detailed procedure is shown as follows: in a three-neck round-bottom flask equipped with a stirring bar and a condenser tube, 30 g synthesized PEEK-H with excess of 300 mL of acetic anhydride and three drops of 98% sulfuric acid reacted at 60 °C for 3 h. Then the mixtures

Acetylation of momomers:**Polymerization:**

Scheme 4. Synthetic route of PES-C.



Scheme 5. Synthetic route of PEEKARs.

were poured into 2000 mL distilled water for precipitation. After standing for 12 h to ensure the acetic anhydride was completely hydrolyzed, the products were filtered and washed repeatedly until the filtrate was nearly neutral, and then dried at 90 °C under vacuum. The pale powder was obtained with the yield above 90%.

Synthesis of PES-C

Oligomeric liquid crystal polyester PES-C was synthesized by melt transesterification process (shown in Scheme 4). 6-hydroxy-2-naphthalene formic acid and 4-hydroxybenzoic acid were acetylated before the polymerization reaction, and the procedures were similar to the acetylation of PEEK-H described above. IPA can control the ratio of the reactive groups to terminate the reaction, thereby determining the polymerization degree in this reaction. 0.28 mol of 4-acetoxybenzoic acid (ABA) and 0.12 mol of 6-acetoxy-2-naphthalene (ANA) and the right amount of IPA were placed in a 2 L high temperature and high pressure polymerization reactor equipped with a gas inlet and a gas outlet, a stirring bar, a reflux condenser and a vacuum inlet. The detailed procedure of synthesis is shown as follows: Firstly, bubbling nitrogen for half an hour to remove oxygen; secondly, under a pressure of 1 MPa and a stirring rate of 50 rpm, the temperature was increased to 200 °C for 1 h; thirdly, the temperature was increased to 250 °C for 1 h and to 280 °C for 1 h, respectively; simultaneously, nitrogen was circulating to remove the produced small molecules; finally, the tempera-

ture was increased to 320 °C for 15 min under vacuum. Once the reaction was over, the products were cooled to room temperature. The obtained products were crushed into powder and reflux extracted with acetone by Soxhlet extractor for 12 h, and then dried at 90 °C under vacuum. The degree of polymerization was controlled by the addition amount of IPA, as shown in Scheme 4, the theoretical construction unit number (N) can be calculated according to equation $N = 0.28/x + 0.12/x + 1$, where x is the mole number of IPA. To gain PES-C with theoretical construction unit number of 3, 6, 11 (named as PES-C-3, PES-C-6, PES-C-11), the addition of IPA is 0.2, 0.08, 0.04 mol, respectively.

Synthesis of PEEKARs

The thermotropic liquid crystalline polyarylate PEEKARs with ether ether ketone segments were synthesized by melt condensation polymerization (shown in Scheme 5). Equimolar ratio of PEEK-A and PES-C, and millimolar of zinc acetate/diantimony trioxide (used as catalyst) were placed in the high pressure polymerization reactor. Before polymerization, the reactor was filled with nitrogen and was purged for 0.5 h to remove oxygen, and then the polymerization was carried out in five stages with a constant stirring rate of 50 rpm: firstly, at 180 °C and under a pressure of 1 MPa for 1 h; secondly, at 200 °C and under a pressure of 1 MPa for 1 h; thirdly, at 240 °C and under a pressure of 1 MPa for 1 h; fourthly, at 280 °C and under flowing nitrogen atmosphere for 1 h to remove produced small molecules;

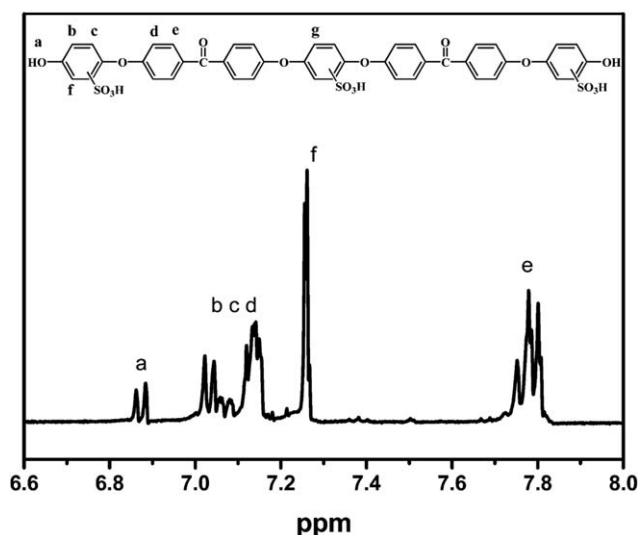
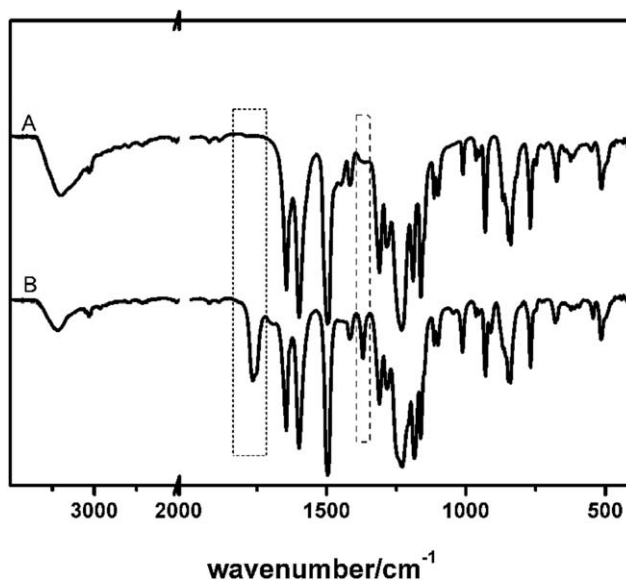
Figure 1. ^1H NMR spectrum of PEEK-H.

Figure 2. FTIR spectra of PEEK-H and PEEK-A (A) PEEK-H; (B) PEEK-A.

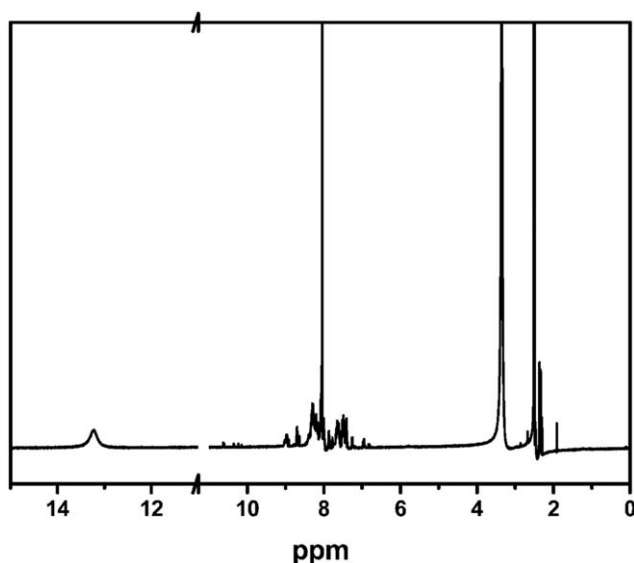


Figure 3. ^1H NMR spectra of PES-C-3.

finally, under vacuum for 0.5 h, and cooling the reactor to room temperature. The obtained gray polymer was crushed into powder and wash repeatedly with DMSO/ H_2O ($v/v = 5:5$), and then dried at 80°C under vacuum.

Measurements

The FTIR spectra were recorded on a Nicolet 560 spectrometer with a KBr pellet. ^1H NMR spectra were measured with a Bruker 600 MHz Ultra Shield NMR spectrometer, and the chemical shift were calibrated using tetramethylsilane (TMS) as an internal standard. DSC data were obtained on a Netzsch DSC 204F1 under a nitrogen flow ($20\text{ cm}^3/\text{min}$) with both heating and cooling rates of $10^\circ\text{C}/\text{min}$, and the scanning range was $50\text{--}400^\circ\text{C}$, and the temperature and heat enthalpy were calibrated with indium standards before running the experiments. WAXD was carried out with an X'Pert Pro X-ray diffractometer, and the scanning rate was $2/\text{min}$ over a scattering angle range

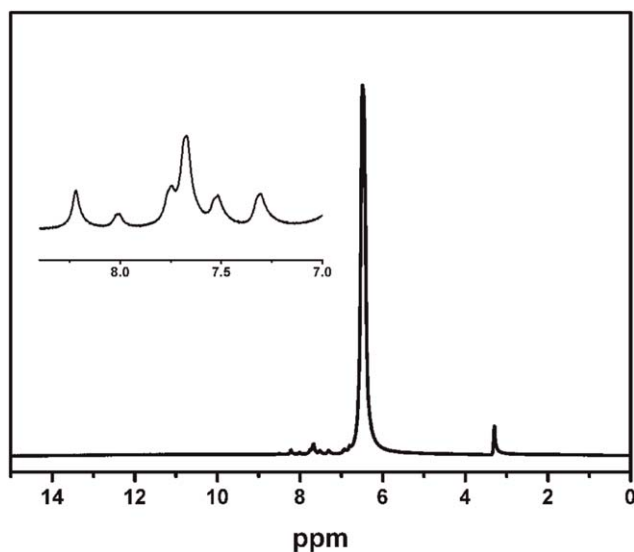


Figure 4. ^1H NMR spectra of PES-C-11.

Table I. Composition of Three Kinds of PEEKARs

Polymer code	Theoretical n of PEEK-A	Actual n of PEEK-A	Theoretical n of PES-C	Actual n of PES-C
P-1	5	5	3	2.74
P-2	5	5	6	11.56
P-3	5	5	11	28.10

n is construction unit number.

of $2\theta = 5\text{--}45$, and dried polymer powder was used for WAXD measurements. TGA was conducted with a TA SDT Q600 thermal analyzer using a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen at a flow rate of $100\text{ cm}^3/\text{min}$. Texture images were captured by a Leica DMLP POM with a Linkam heating stage between crossed polarizers.

RESULTS AND DISCUSSION

The Characterization of PEEK-H and PEEK-A

Because the dissolving capacity of PEEK-H in common solvent was very poor, the relative molecular weights could not be characterized by gel permeation chromatography (GPC). Another way was developed to calculate the actual degree of PEEK-H, the degree could be calculated using the integration area of hydrogen peaks in different chemical environments in NMR spectrum. To improve the solubility of PEEK-H in $\text{DMSO-}d_6$, the oligomeric monomer should be sulfonated before measuring. The procedure is given as follows: 5 g of PEEK-H dissolved in 20 mL 98% sulfuric acid in a 150 mL flask, and the reaction mixture was kept at 10°C for 1 h, and then poured into ice water. The products were filtered and washed repeatedly with ice water until the filtrate was nearly neutral, and then dried at 70°C under vacuum. As shown in Figure 1, there are eight kinds of H (a–g) with different chemical shifts in PEEK-H which were marked in the molecular formula, the chemical shifts of H_e is easy to distinguish with other H, moreover, the ratio of

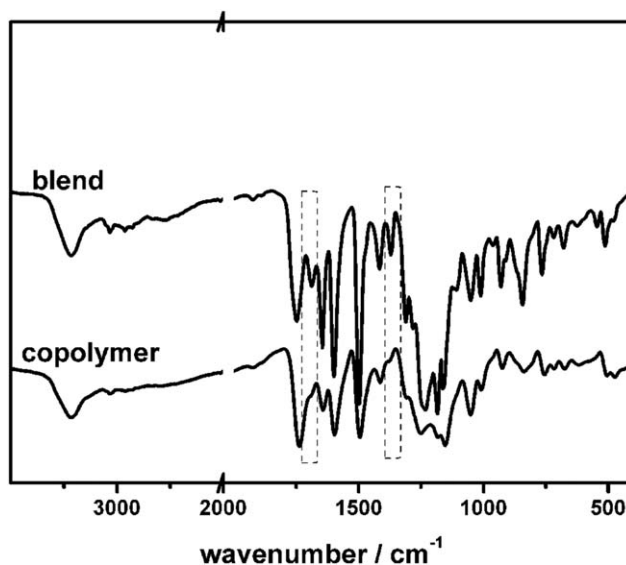


Figure 5. FTIR spectra of PEEKARs (copolymer) and equimolar blend of PEEK-A and PES-C (blend).

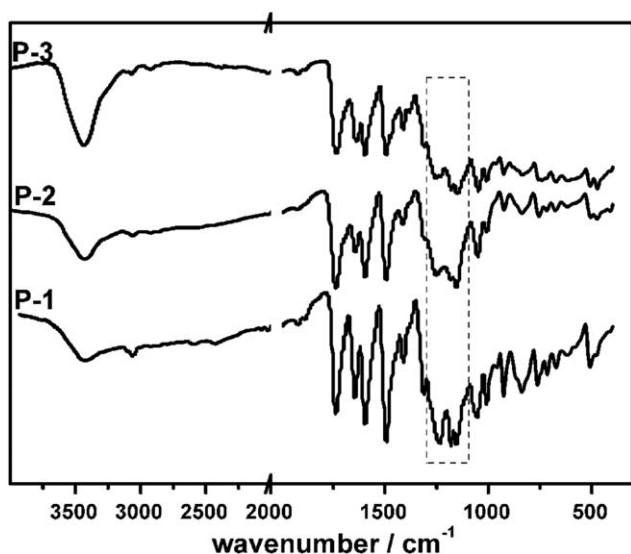


Figure 6. FTIR spectra of PEEKARs.

the intensity of H_e with that of other positions' H will be changed with the degree of polymerization changes, so the degree of polymerization can be represented by the ratio. The number of H_f is equivalent to that of H in sulfonic group which cannot be detected, so H in sulfonic group can be replaced by H_f when calculating. Theoretically, when the construction unit number is 5 (experimental designed) the ratio can be calculated as follows:

$$\frac{\sum A_{H_{a,b,c,d,f,g}}}{A_{H_e}} = \frac{2+2+3+8+2 \cdot 3+1}{8} = \frac{22}{8} = 2.75 \quad (1)$$

According to the NMR spectral data (shown in Figure 1), the ratio is 2.75 which is consistent with experimental design. This implies that the construction unit number of the synthetic PEEK-H is 5.

Figure 2 presents the FTIR spectra of PEEK before (PEEK-H) and after acetylation (PEEK-A). PEEK-A shows an absorption peak of methyl around 1371 cm^{-1} , and a characteristic absorption band of C=O stretching vibration for ester carboxyl in acetoxy group around 1756 cm^{-1} . Meanwhile the absorption peak of the hydroxyl is significantly reduced after acetylation. So it is confirmed that the acetylation has been realized successfully.

The Characterization of PES-C

The construction unit number of PES-C-3 can be calculated from the ratio (A) of the peak intensity of H of terminal car-

boxyl at 13.2 ppm with that of aromatic rings around 8 ppm in ^1H NMR spectra (Figure 3), where DMSO- d_6 is used as solvent. Because the molar ratio of ANA to ABA is 3:7, there are 4.6 H atoms in one construction unit on average. The construction unit number (n) can be calculated according to eq. (2), and from Figure 3 the ratio (A) is 0.167, after calculating the construction unit number of PES-C-3 is given by 2.74.

$$A = \frac{2}{4.6 \cdot (n-1) + 4} \quad (2)$$

PES-C-6 and PES-C-11 cannot be dissolved in DMSO- d_6 , so they have to be broken down to IPA, ANA and ABA through alcoholysis by $\text{D}_2\text{O}/\text{NaOD}/\text{CD}_3\text{OD}$ mixtures. The chemical shift of H in aromatic rings of ANA and ABA is around 6.5 ppm in ^1H NMR spectra (shown in Figure 4, the insert is the amplification of peaks between 7.0 and 8.5 ppm), and the two carboxyls in IPA has strong electron receptor effect leading to the reduction of electron density of H atoms in aromatic rings, as a result the chemical shift of H atoms in aromatic rings rises to around 8 ppm. Thereby the construction unit number can be calculated from the ratio (B) of the peak intensity of H of aromatic rings in IPA with that of aromatic rings of ANA and ABA in ^1H NMR spectra (shown in Figure 4). Through eq. (3), the actual construction unit numbers of PES-C-6 and PES-C-11 are given by 11.56 and 28.10, respectively:

$$B = \frac{4}{4.6 \cdot (n-1)} \quad (3)$$

The Characterization of PEEKARs

Table I shows the composition and code of the three kinds of PEEKARs. The FTIR spectra of PEEKARs (P-3) and equimolar blend of PEEK-A and PES-C was measured to confirm whether the melt condensation polymerization is finished successfully. As illustrated in Figure 5, an absorption peak of carboxyl carbonyl around 1684 cm^{-1} practically disappears after polymerization; meanwhile, the absorption peak of methyl around 1371 cm^{-1} is significantly reduced. These changes in FTIR spectra indicate that most of the terminal carboxyls and acetoxy groups reacted. Consequently, the polymerization was finished as desired.

The chemical structures of PEEKARs with different length of polyester segment were confirmed from FTIR spectra (Figure 6). From P-1 to P-3, the relative intensity of absorption peak of C—O—C in ester group around 1150 cm^{-1} increases gradually comparing with that of C—O—C in aryl ether bond around 1250 cm^{-1} , illustrating that the content of polyester segment increases from P-1 to P-3 corresponding to experimental design.

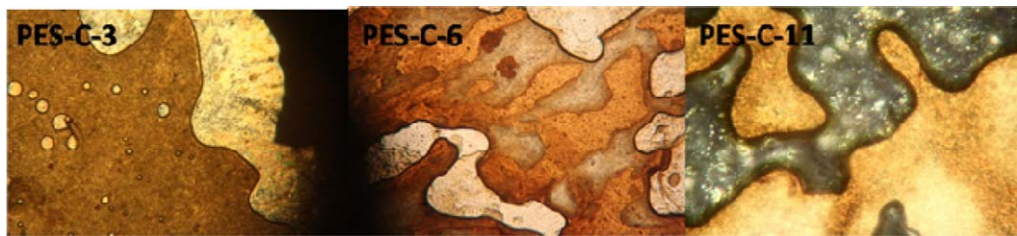


Figure 7. Optical polarized photographs between crossed polarizers of PECs at $380 \text{ }^\circ\text{C}$ (magnification $100\times$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

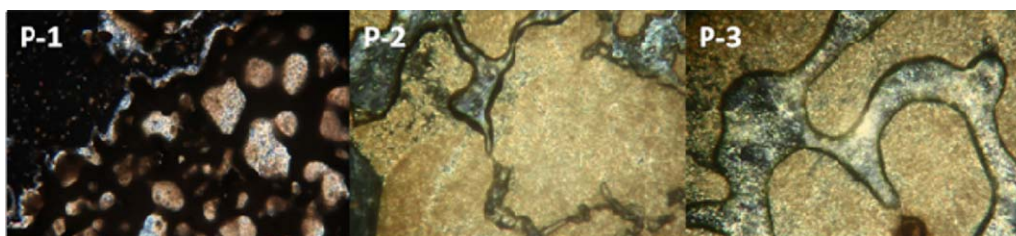


Figure 8. Optical polarized photographs between crossed polarizers of PEEKARs at 380 °C (magnification 100×). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

IR (KBr): 3550–3200 cm^{-1} ($-\text{OH}$, $\nu_{\text{O-H}}$), 1734 cm^{-1} ($-\text{CO}-$, $\nu_{\text{C=O}}$), 1637 cm^{-1} ($-\text{C}-\text{C}=\text{O}-\text{C}-$, $\nu_{\text{C=O}}$), 1597–1469 cm^{-1} ($-\text{Ar}-$, $\nu_{\text{C=C}}$), 1234 cm^{-1} ($\text{C}-\text{O}-\text{C}$, $\nu_{\text{as C-O-C}}$), 1180 and 1150 cm^{-1} ($-\text{C}-\text{COO}-\text{C}-$, $\nu_{\text{C-O-C}}$).

The Performance of PEEKARs

The texture of PEEKARs and PEC was observed by hot stage POM at 380 °C. As it is shown in Figure 7, PES-C-3, 6, 10 exhibit characteristic bright texture in its melted state owing to the birefringence, indicating that these three PES-Cs can form thermotropic liquid crystal intermediate states. Since the thermotropic liquid crystalline characters of PEEKARs are provided by polyester segments, P-2 and P-3 with more polyester segments can form liquid crystalline structure which can be seen in Figure 8. When the length of polyester segment decreases (sample P-1), the liquid crystal characters are not obvious and the flowability is rather poor.

The thermal properties of the three PEEKARs were evaluated by means of DSC and TGA. The DSC results are shown in Figure 9 and summarized in Table II. It is clear that P-1 has the highest melting enthalpy in heating stage and the highest crystal enthalpy in cooling stage, suggesting that P-1 with the least polyester segments has the best crystallization properties. This is because the large number of symmetric ether ether ketone segment in P-1 make the molecular chain with high symmetry and easy to orientate regularly. Moreover, two endothermic peaks locating far away from each other are observed in the heating curves of P-2 and P-3. The former broad peak is melting peak, and the latter

sharp peak cannot be considered as the typical clear point of liquid crystalline polymer, which corresponds to the results of POM, and it may be ascribed to the volatilization of small molecule produced from transesterification in high temperature.²² Meanwhile, P-2 with more polyester segments shows a bad crystallization property, the melting enthalpy is very low and the crystallization peak in cooling stage is almost disappeared. The reason is that ether ether ketone segment and polyester segment restrict the movement of each other, limiting the regular arrangement of its main chains. With the content of polyester segment increasing, P-3 presents a better crystallization property, because polyester segments are long enough to form their own crystalline regions.

The thermal stabilities were measured by TGA (shown in Figure 10). The 5% lose weight temperatures of all the samples are above 400 °C, which can meet the processing window of PEEK. And it can be seen that the char yield at 600 °C is reduced with

Table II. DSC Data of PEEKARs

Sample	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})
P-1	328	62.48	214	30.44
P-2	307	9.08	—	—
P-3	323	60.13	221	21.63

T_m represents the melting temperature; ΔH_m represents the melting enthalpy; T_c represents the crystallization temperature; ΔH_c represent the crystallization enthalpy.

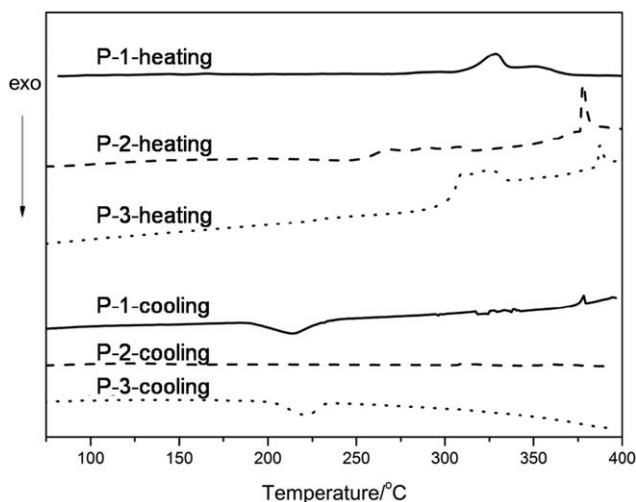


Figure 9. DSC curves of PEEKARs.

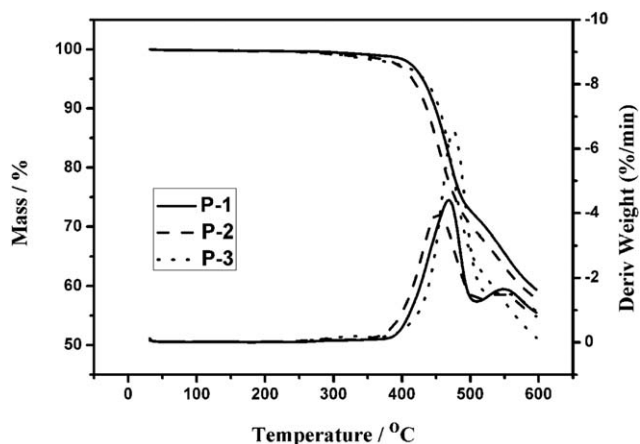


Figure 10. TGA curves of PEEKARs in N_2 .

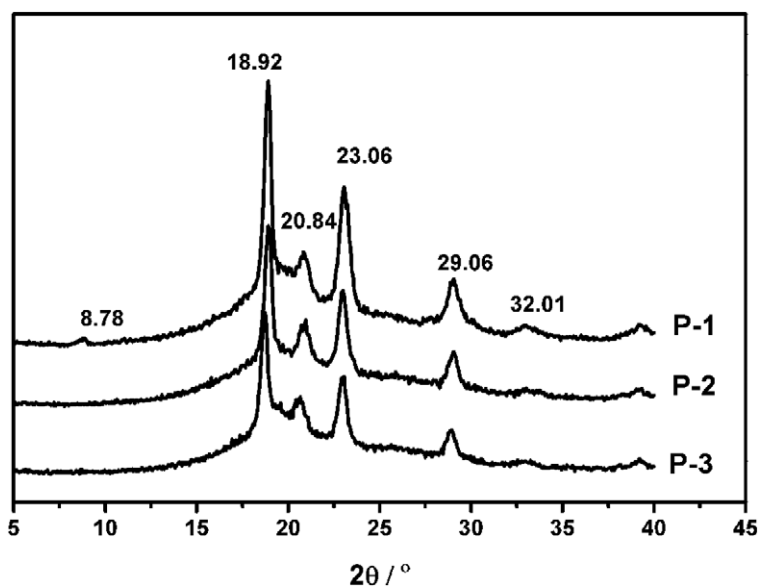


Figure 11. The WAXD patterns of PEEKARs.

the content of polyester segment increasing, which indicates that polyester segments are easier to decompose into volatile small molecules than ether ether ketone segments.

The WAXD patterns (shown in Figure 11) suggest that all prepared PEEKARs are semicrystalline polymers. There are obvious crystalline diffraction peaks at the 2θ of 18.92° , 20.84° , 23.06° , 29.06° , and 32.01° in the WAXD patterns. But the intensity of diffraction peak of 32.01° is declining from P-1 to P-3 with the polyester segment content increasing, meanwhile the diffraction peak at 8.78° disappear in P-2 and P-3, indicating that the crystal form of PEEKARs changes with the increase of polyester segment content.

CONCLUSIONS

A series of thermotropic liquid crystalline polyarylates (PEEKARs) with ether ether ketone segments in main chains were successfully synthesized by the combination of self-synthetic oligomeric PEEK-A (providing ether ether ketone segments) and a series of PES-C (providing polyester segments) through melt condensation polymerization. These PEEKARs were anticipated to have the thermotropic liquid crystalline characteristic provided by PES-C, as well as good compatibility with the PEEK matrix because of ether ether ketone segments, so they are promising to be considered as processing agent of PEEK. The structural characterization confirms that all the synthesized products are consistent with the experimental design. The construction unit number of the synthetic PEEK-A is 5, and that of the synthetic PES-Cs is 2.74, 11.56, and 28.10, respectively. PEEKARs were named as P-1, P-2, and P-3 with polyester segments increase. PES-Cs can form thermotropic liquid crystal intermediate states since the thermotropic liquid crystalline characters of PEEKARs are provided by polyester segments, P-2 and P-3 with more polyester segments can form a thermotropic liquid crystal intermediate state and show superior mobility. P-1 with the maximum symmetrical unit of ether ether ketone seg-

ments has the best crystallization properties, while the flowability is rather poor, and as a result, the liquid crystal character is not obvious. P-3 with the maximum polyester segments has a somewhat humble crystallization property, P-2 has the worst crystallization properties. With the content of polyester segment increases from P-1 to P-3, the char yield at 600°C reduces. All the PEEKARs match the processing window of PEEK and are suitable for being used as processing agent. In addition, the crystal form of PEEKARs changes with the increase of polyester segment content.

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