**Effect of Plasticizer and Shearing Field on the Properties of Poly(arylene ether nitrile) Composites**

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**ABSTRACT:** A novel composite film of hydroquinone/resorcinol-based poly(arylene ether nitrile) (HQ/RS-PEN) improved by bisphenol A based poly(arylene ether nitrile) (BPA-PEN) was prepared, in which BPA-PEN acts as a plasticizer, leading to improved fluidity of the material, thereby favoring the crystallinity of HQ/RS-PEN. Differential scanning calorirometry (DSC), thermogravimetric analysis (TGA), and mechanical and rheological tests have shown that the composites exhibited outstanding thermal and mechanical properties as well as improved fluidity and processing applicability compared with HQ/RS-PEN. At the same time, the crystallization of the poly(arylene ether nitrile) blends with 5 wt % BPA-PEN could be promoted under both static and shear flow fields. Polarizing microscope (POM) and scanning electron microscopy (SEM) showed that the crystalline morphology of HQ/RS-PEN was converted from spherulites to fibrous crystals under shearing. DSC, X-ray diffraction (XRD), and dynamic storage modulus results proved that the crystallization rate and crystallinity of HQ/RS-PEN increased significantly under the shear field. The crystallinity enhanced to a maximum of 20.1% and the melting enthalpy increased to 33.4 J/g at 310 °C under the frequency of 0.01–100 Hz for 20 min.

### 1. INTRODUCTION

Plasticizer, as a kind of polymer material additive, is of great importance in the molding process of polymer materials. For the thermoplastic polymer, especially polar molecules, there is an interaction between the linear macromolecules, which are derived from van der Waals forces (electrostatic forces, induction forces, and dispersion forces) and hydrogen bonds.1 Although the interaction between the molecules gives the polymer good mechanical strength, it also affects the molding processability of the materials. The essence of thermoplastic resin processing is to increase the mobility of polymer by heating and weaken the interaction between them. However, for some polymers with strong polarities and high intermolecular forces, there is great difficulty in their forming process. Adding plasticizer can increase the softness, elongation, and plasticity of plastics, leading to a reduction in flow temperature and hardness of plastics, and facilitate the molding of plastic products.2–5 Therefore, adding a plasticizer to plastic products is an effective way to improve the molding processability of materials.

Poly(arylene ether nitrile) (PEN) has aroused tremendous attention owing to its superb chemical and physical properties, such as good mechanical performance, excellent radiation resistance, and high thermal stability, which make it possible to apply in communication, military, and aerospace fields.6–11 PENs could be divided into semicrystalline PEN and amorphous PEN according to their condensed structure.10,11 Semicrystalline PEN possesses better solvent corrosion resistance and thermal and mechanical properties than amorphous PEN.12 However, semicrystalline PEN has a weaker crystallization ability. Researchers have tried various methods to increase the crystallinity of PEN.13,14 You et al. studied the effect of hot stretching on the crystallinity of the PEN based on biphenol and drew a conclusion that the crystallinity of PEN/PANI-f-BT-b calculated from wide-angle X-ray diffraction (XRD) and dynamic storage modulus results proved that the crystallization rate and crystallinity of HQ/RS-PEN increased significantly under the shear field. For crystalline polymers, the increase of crystallinity will increase the tensile strength of the material as well as their softening temperature and heat distortion temperature. In the extrusion or injection molding process, polymer crystallization is significantly affected by the shear field and the tensile flow field.15–18 Polymer crystallization has thus been intensively investigated, and the research proved that the existence of a
flow field will accelerate the crystallization of polymer melt significantly and determine the final phase morphology and mechanical properties of polymer materials.\textsuperscript{19,20} The change of crystallization behavior of polymers induced by the presence of flow field is called flow-induced crystallization (FIC).\textsuperscript{21–23} As a typical nonequilibrium phase transition, FIC has become a fundamental and significant research concern in polymer science and engineering.\textsuperscript{24,25} Up to now, a large number of experimental and theoretical studies in FIC have been conducted on polyolefin.\textsuperscript{26,27} However, FIC studies in semicrystalline engineering thermoplastics such as PEN are still lacking.

In this work, a low-molecular-weight poly(arylene ether nitrile) (PEN) based on bisphenol A structure (BPA-PEN) was added in PEN based on the biphenol/hydroquinone (HQ/RS-PEN) structure to improve the molding processability of the material. In this system, low-molecular-weight polymers can act as "plasticizers" in HQ/RS-PEN with a higher molecular weight, leading to increase the fluidity of the materials. Meanwhile, increased fluidity of polymer can improve its crystallinity.\textsuperscript{28} Therefore, the presence of BPA-PEN could improve not only the molding processability but also the crystallinity of HQ/RS-PEN. Then, the effect of different contents of added BPA-PEN on the crystallization and thermal and mechanical properties of the composite films was studied. Moreover, the effects of crystallization temperature (290, 300, 310, 320, and 330 °C) and shear frequency (1, 10, 50, and 100 Hz) on the crystallization behavior of PEN blends are also investigated in detail.

2. RESULTS AND DISCUSSION

2.1. Structural Characterization of HQ/RS-PEN and BPA-PEN. The chemical structures of HQ/RS-PEN and BPA-PEN were characterized by Fourier transform infrared (FT-IR). As shown in Figure 1, the absorption peaks at 1601, 1508, and 1462 cm\(^{-1}\) belong to absorption bands of benzene rings. Besides, the characteristic band located at 1243 cm\(^{-1}\) is attributed to Ar–O–Ar.\textsuperscript{29} The absorption peak located at 2231 cm\(^{-1}\) is assigned to the CN symmetrical stretch vibration.\textsuperscript{30} These peaks can be discovered in both samples, indicating the fabrication of the PENs. In addition, compared with those of HQ/RS-PEN, the characteristic absorption bands of BPA-PEN at 2923 and 2852 cm\(^{-1}\) are attributed to the nonsymmetrical and symmetric stretching vibrations of −CH\(_3\).\textsuperscript{31} These results mentioned above indicate that HQ/RS-PEN and BPA-PEN were synthesized successfully.

2.2. Thermal, Mechanical, and Rheological Properties of Poly(arylene ether nitrile) Composites. Figure 2 displays the thermal properties of composites with different BPA-PEN mass fractions, the detail data are also summarized in Table 1. It is found that PEN blends show only one glass transition temperature (\(T_g\)) with the BPA-PEN contents changing from 0 to 9 wt %, indicating the good compatibility of BPA-PEN in the HQ/RS-PEN matrix. At the same time, \(T_m\) of the composites decreases from 170.3 to 159.4 °C. This would be the result of the strong molecular mobility of BPA-PEN, which improves the movement of polymer molecular chains effectively. In addition, the melting enthalpy (\(\Delta H\)) exhibits a maximum value with 5 wt % BPA-PEN (17.2 J/g) and then decreases with the further addition of BPA-PEN. When a small amount of BPA-PEN is added, the low-molecular-weight BPA-PEN improves the activity and rearrangement of HQ/RS-PEN. However, further addition of BPA-PEN decreases the content of HQ/RS-PEN and hinders the orderly arrangement of HQ/RS-PEN molecules, resulting in decreased \(\Delta H\).

The thermal stability is an indispensable factor to evaluate the performance of composite films. The thermal decomposition temperature of 5% weight loss (\(T_d\)) was evaluated from their TGA curves (Figure 2b and Table 1). As shown in Table 1, \(T_d\) decreases slightly with the BPA-PEN content rising from 0 to 9 wt %. Nevertheless, the \(T_d\) of the polymer blends is still higher than 480 °C, indicating excellent thermal stability of the PEN composites.

Furthermore, the mechanical properties of the PEN blends were also investigated and are shown in Figure 3a. It can be seen that both the tensile strength (\(T_s\)) and tensile modulus (\(T_m\)) exhibit the same tendency, i.e., they increase greatly with the addition of a small amount of BPA-PEN and then deteriorate as BPA-PEN increases continuously. The \(T_s\) and \(T_m\) of the PEN blend with 5 wt % BPA-PEN increase to 112.3 and 3177.7 MPa, respectively, which can be attributed to the enhanced crystallization of the PEN blends. Because the BPA-PEN with low molecular weight shows poorer mechanical properties, the mechanical properties of the composites decrease when the BPA-PEN adding contents further increase. In addition, it can be seen from Figure 3b that the elongation at the breaking of PEN blends increases from 3.6 to 8.1% with increasing of BPA-PEN, indicating that the plasticity of the system is enhanced. These results mentioned above suggest that BPA-PEN can enhance the mechanical property of HQ/RS-PEN to some extent.

Figure 4 shows the dependence of frequency on the complex viscosity of PEN blends at 340 °C. It is observed clearly that the complex viscosity of PEN blends decreases as the frequency increases from 0.04 to 100 Hz, indicating that the PEN blends are non-Newtonian fluids.\textsuperscript{32} At the same frequency, the complex viscosity of the PEN blends decreases as the content of BPA-PEN addition increases. Combined with the increase of elongation at break, the decrease of \(T_m\) and dynamic complex viscosity of the composites with increasing BPA-PEN content from 0 to 9 wt % indicates that the addition of BPA-PEN can enhance the fluidity of HQ/RS-PEN and ameliorate the processability of HQ/RS-PEN.

Figure 5 shows the Cole–Cole model curves of the PEN composites, which is intended to study the compatibility between BPA-PEN and HQ/RS-PEN. It is well known that the effect of fillers on the relaxation behavior of polymers could be obtained by the viscoelastic behavior of polymer multi-
component composites. It can be discovered that the shape of all the Cole−Cole curves is close to a semicircle (Figure 6a−e), indicating that the introduction of BPA-PEN did not change the relaxation mechanism of HQ/RS-PEN, and there is good compatibility between BPA-PEN and HQ/RS-PEN. In addition, the height of the Cole−Cole curve also reflects the viscosity and molecular weight of the polymer matrix. The height of the Cole−Cole curve of PEN composites is significantly lower than that of pure HQ/RS-PEN. It indicates that the viscosity of PEN composites melt reduces after the introduction of BPA-PEN, which is also consistent with the conclusion of Figure 4.

The processing of crystalline polymer is a nonisothermal crystallization process. The influence of BPA-PEN contents on the crystallization of PEN blends was investigated by cooling down from 340 °C under a cooling rate of −5 °C/min at 10 Hz shearing. As can be seen from Figure 6a, the dynamic storage modulus of the blends exhibits a tendency to increase first and then decrease with decreasing temperature. The increase of dynamic storage modulus is related to enhanced crystallinity. Moreover, the storage modulus of PEN composites reaches a maximum at a higher crystallization temperature with the introduction of BPA-PEN (BPA-PEN ≤ 5 wt %). Notably, the dynamic storage modulus possesses the most obvious response at the content of BPA-PEN of 5 wt % under decreasing temperature and reaches a maximum of 1940 MPa at 275 °C. More stable crystal nucleus of PEN is formed at a higher temperature due to the fact that the BPA-PEN with a strong locomotor activity can promote the orderly arrangement of HQ/RS-PEN segments under shearing, thus causing the crystallization induction period of PEN composites to shorten and the storage modulus to increase more evidently. At the same time, the dynamic storage modulus curve can be converted into the curve of relative crystallinity described as follows by eq 1:

Table 1. Glass Transition Temperature (Tg), Melting Point (Tm), Melting Enthalpy (∆H), Thermal Degradation Temperatures (Td), Elongation at Break (Eb), Tensile Strength (TS), and Tensile Modulus (TM) of PEN Blends

| sample (wt %) | Tg (°C) | Tm (°C) | ∆H (J/g) | Td (°C) | Eb (%) | TS (MPa) | TM (MPa) |
|--------------|---------|---------|----------|---------|--------|----------|----------|
| 0            | 170.3   | 324.5   | 13.4     | 106.2   | 106.2  | 2782.4   |          |
| 3            | 168.1   | 324.5   | 15.1     | 108.1   | 108.1  | 2984.7   |          |
| 5            | 163.8   | 325.1   | 17.2     | 112.3   | 112.3  | 3177.7   |          |
| 7            | 162.7   | 324.3   | 11.8     | 77.1    | 77.1   | 2605.6   |          |
| 9            | 159.4   | 324.2   | 11.1     | 8.13    | 8.13   | 2428.6   |          |

Figure 2. Thermal properties of PEN blends with different BPA-PEN contents: (a) differential scanning calorimetry (DSC) curves and (b) thermogravimetric analysis (TGA) curves.

Figure 3. Mechanical properties of PEN blends: (a) tensile strength and tensile modulus and (b) elongation at break.

Figure 4. Dynamic complex viscosity of PEN blends with different BPA-PEN contents under the frequency of 0.01−100 Hz at 340 °C.
\[ \alpha(t) = \frac{X}{X_\infty} = \frac{G'_t - G'_0}{G'_{\text{max}} - G'_0} \]  

where \( G'_0 \), \( G'_t \), and \( G'_{\text{max}} \) represent the storage modulus at the beginning of crystallization, in the middle of crystallization, and at the end of crystallization, respectively. The relationship curve between temperature and relative crystallinity of PEN blends is shown in Figure 6b. All of these curves exhibit an "L-like" shape, demonstrating that the crystallization rate is slow in the early stage, while rapid in the middle stage. Similar to the dynamic storage modulus, the blend with 5 wt % BPA-PEN crystallizes first (at the highest temperature). This indicates that PEN blends with a low content of BPA-PEN is beneficial for crystallization under the shear field, especially when the BPA-PEN content is 5 wt %.

2.3. Effect of Shearing on Crystal Morphology. As shown in Figure 7a, the PEN blend with 5 wt % BPA-PEN before shearing exhibits a cross-extinction phenomenon under a polarizing microscope (POM). Meanwhile, the fracture morphology of the PEN blend before shearing exhibits a typical spherulite with a grain size of about 0.15–0.25 \( \mu \text{m} \) (Figure 7c). Figure 7b,d shows the POM and scanning electron microscopy (SEM) images of the PEN blend with 5 wt % BPA-PEN after shearing for 30 min at 10 Hz. It is
observed that the crystalline morphology changes from spherulite to fibrous crystal. The oriented structure of PEN crystals can greatly enhance the mechanical performance of PEN,

2.4. Effect of Shearing Temperature on Isothermal Crystallization. As mentioned above, the addition of BPA-PEN is beneficial for enhancing the fluidity and processing applicability of HQ/RS-PEN. In addition, 5 wt % BPA-PEN can effectively promote the shear-induced crystallization of HQ/RS-PEN. Therefore, the effect of shear temperature on the crystallization behavior of the PEN blend with 5 wt % BPA-PEN was further investigated. Figure 8 shows the storage modulus of the PEN blend with 5 wt % of BPA-PEN sheared at different temperatures under 0.01–100 Hz for 20 min. It can be discovered that the dynamic storage modulus increases first with the shear temperature increasing to 310 °C. Then, it decreases gradually with further increases in shear temperature, indicating that the crystallization rate is the fastest at 310 °C.

The DSC curves of the PEN blend with 5 wt % BPA-PEN at different shear temperatures are shown in Figure 9a. It is observed that the T_s of PEN composite increases gradually with increasing shear temperature, which can be attributed to the two aspects. On one hand, the formation of the orientated polymer segment under the shearing field and the more regular arrangement of the molecular segment lead to the increase of T_s. On the other hand, PEN goes cross-linking reaction, resulting in the formation of a three-dimensional net structure. When shear temperatures are 290 and 300 °C, the PEN blends exhibit two phase transition temperatures, which are a lower melting point (T_m1) and a higher melting point (T_m2). In addition, the T_m1 moves to the high temperature continuously as the shear temperature increases while the T_m2 remains almost unchanged (Table 2). These results could be ascribed to the typical double melting phenomenon. The double melting behavior is formed by four processes: melting of most of the original crystals, their recrystallization, remelting of the recrystallized portion, and melting of the remaining crystal regions. Moreover, the total melting enthalpy (ΔH) reaches its maximum value (33.4 J/g) at the shear temperature of 310 °C with the increase of shear temperature and then decreases with the further increase of shear temperature (Table 2), same as that of dynamic storage modulus. The crystallinity of the PEN blend with 5 wt % BPA-PEN sheared at different temperatures under the frequency of 0.01–100 Hz for 20 min was investigated by wide-angle X-ray diffraction (WAXD) patterns, which is shown in Figure 9b. The significant diffraction peaks around at 2θ = 17.2, 25.3, and 27.0° are observed in the curves of all the samples, respectively. The crystallinity of the PEN blend sheared at different temperatures are calculated and listed in Table 2. The crystallinity is up to 20.1% when sheared at 310 °C, which is also in accordance with the results of the DSC curves.

2.5. Effect of Shearing Frequency on Isothermal Crystallization. An investigation of the effect of shear temperature on crystallization showed that the PEN blend with 5 wt % BPA-PEN has the fastest crystallization rate and the highest crystallinity when the shear temperature is 310 °C. In this section, the effect of shear frequency (1, 10, 50, and 100 Hz) on its crystallization is further investigated by shearing at 310 °C for 30 min. As shown in Figure 10a, two melting peaks appear in all DSC curves. According to the previous result, wide melting is a result of the T_m1 coming from the spherulites when sheared at 310 °C. While another peak (around 336 °C, T_m2) would have resulted from the highly oriented fibrous crystals transformed from these spherulites under shearing, which is also consistent with the results of SEM and POM images. In addition, T_m1 and T_m2 are almost the same even when sheared under different frequencies for 30 min. The detailed physical parameter values of the samples are summarized in Table 3. Figure 10b shows the XRD patterns.
of the PEN blend with 5 wt % BPA-PEN after shearing at 310 °C under different frequencies for 30 min. Three diffraction peaks at 2θ = 17.2, 25.3, and 27.0°, respectively, are observed in the curves of all samples.38 According to Figure 10b, the intensities of diffraction peaks at 2θ = 17.2, 25.3, and 27.0° is sharpest when the shear frequency is 10 Hz. Furthermore, the crystallinity of PEN blends at different shear frequencies is calculated and listed in Table 3. The highest crystallinity is 18.8% when the shear frequency is 10 Hz, which is identical to the DSC result.

2.6. Effect of Shearing Time on Isothermal Crystallization. Moreover, the effect of shear time on the crystallization behavior of the PEN composite with 5 wt % BPA-PEN at 310 °C under 10 Hz was investigated. It can be found from the DSC curve (Figure 11a) that as the shearing time increases, the ΔH_{mh} of the PEN composite continuously decreases; however, ΔH_{ma} of the composite constantly increases. It indicates that the crystals of the PEN composite formed are mainly spherulites in the initial stages of crystallization, but the spherulites gradually transform into fibrous crystals with an increase in the shearing time. The fibrous crystals are most uniform and the total ΔH of PEN composite reaches a maximum value of 26.5 J/g when shearing 30 min. Similarly, it can be seen from WAXD patterns (Figure 11b) that three crystal diffraction peaks at 2θ = 17.2, 25.3, and 27.0° appear in the curves of all samples, respectively. The

| frequency (Hz) | quiescent | 1 | 10 | 50 | 100 |
|---------------|-----------|---|----|----|----|
| ΔH (J/g)      | 17.2      | 12.2 | 26.5 | 26.0 | 23.6 |
| melting point (T_{mh} °C) | 325.1 | 319.5 | 320.2 | 320.4 | 322.4 |
| T_g (°C)      | 163.8     | 163.6 | 164.5 | 164.8 | 165.1 |
| crystallinity (%) | 10.5 | 13.2 | 18.8 | 16.6 | 15.2 |

Figure 11. (a) DSC curves and (b) WAXD patterns of the PEN blend with 5 wt % BPA-PEN after shearing at 310 °C under 10 Hz for different times.
crystallinity of the PEN blend sheared at different times is calculated by Jade software and listed in Table 4. The crystallinity is up to 18.8% when sheared for 30 min. However, as the shear time extends to 60 min, the total $\Delta H$ and the crystallinity of the PEN composite are reduced to 20.6 J/g and 14.4%, respectively. This results from the fact that the unstable crystals are melted with increasing shearing time.

### 3. CONCLUSIONS

In summary, this study found that the fluidity and crystallization ability of HQ/RS-PEN were improved by the addition of BPA-PEN, and the obtained PEN blend films exhibit better thermal and mechanical properties than the HQ/RS-PEN matrix. At the same time, the crystallization of the PEN blend films with 5 wt % BPA-PEN was promoted under both static and shear fields. POM and SEM results indicated that the crystal form of HQ/RS-PEN was converted from a spherulite to an extended fibrous crystal in the shear field. The DSC, XRD, and storage modulus data showed that the crystallization of HQ/RS-PEN was accelerated and the crystallinity of the composites increased under the shear field. When the shear temperature was 310 °C under the frequency of 0.01–100 Hz for 20 min, the crystallization rate of the composites was the fastest, the crystallinity of the composites reached a maximum of 20.1%, and the melting enthalpy reached a maximum of 33.4 J/g. Experiments proved that the crystallization of HQ/RS-PEN can be improved effectively by BPA-PEN in the shear field.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials

N-Methyl-2-pyrrolidone (NMP) was obtained from Tianjin Bodi Chemicals Co. Ltd. (Tianjin, China). 2,6-Dichlorobenzonitrile (DCBN), bisphenol A (BPA), resorcinol (RS), hydroquinone (HQ), potassium carbonate ($K_2CO_3$), and toluene were purchased from Chengdu Kelong Chemicals (Sichuan, China). All of the reagents were commercially available and used as received.

#### 4.2. Synthesis of PENs

HQ/RS-PEN (hydroquinone/resorcinol = 8:2) as a typical semicrystalline PEN and BPA-PEN were synthesized by nucleophilic aromatic substitution polymerization according to the previous work, and the structure of PEN is shown in Figure 12. The measured inherent viscosities of the HQ/RS-PEN and BPA-PEN polymers were 0.74 and 0.17 dL/g in N-methyl-2-pyrrolidone (NMP) at 75 ± 0.1 °C, respectively.

#### 4.3. Preparation of PEN Composite Films

A series of PEN composite films were prepared by introducing semicrystalline HQ/RS-PEN as a matrix and adding different mass fractions of BPA-PEN (1, 3, 5, 7, and 9 wt %). The detailed steps are as follows. First, the mixture was dissolved in NMP solvent at 120 °C with mechanical agitation. Then, the mixture solution was cast on a clean horizontal glass plate in an oven at 80, 100, and 120 °C each for 1 h, and 160 and 200 °C each for 2 h to evaporate the solvent slowly and prevent the generation of air bubbles or pinholes on the surface of the film. Finally, the obtained films were cooled from 200 °C to room temperature with a rate of 10 °C/min slowly.

#### 4.4. Shear-Induced Crystallization of PEN Composites

The shear-induced crystallization tests of PEN blends were executed on the advanced rotary rheometer with the sample diameter of 25 mm. During the isothermal crystallization, the effect of shear temperature and shear frequency on crystallization behavior, the prepared films were heated rapidly to 340 °C for melting and maintained at 340 °C for 10 min to eliminate the thermal history. The samples were cooled down to the predetermined temperature (290, 300, 310, 320, and 330 °C, respectively) afterward. Finally, the shearing experiments were performed at the corresponding temperature and at the dynamic scanning frequency from 0.01 to 100 Hz for 20 min. While exploring the effect of shear frequency on crystallization, the samples were cooled down to 310 °C after eliminating the thermal history. Different shear frequencies (1, 10, 50, and 100 Hz) were applied to the polymer melts by plate clamps and the shear time was 30 min.

#### 4.5. Characterization

The structures of HQ/RS-PEN and BPA-PEN were characterized by Fourier transform infrared (FT-IR) (8400S, Shimadzu). The thermal behavior of polymers was analyzed by TA Instrument DSC-Q100 (DSC) and TA Instruments TGA-Q50 (TGA) under a nitrogen atmosphere. Mechanical properties of polymers were investigated on a series desktop electromechanical universal testing machine (SANS CMT6104, Beijing, China). The reported values of each sample were calculated as an average of five specimens. Powder X-ray diffraction (XRD) (RINT2400, Rigaku) was used to investigate the crystal structure and crystallinity of composites. The crystal morphologies of the samples were characterized by scanning electron microscopy (SEM) (JSM, 6490LV) at 20 kV and POM observations (MP41, China). The samples for SEM testing were prepared as follows: first, the samples were ruptured in liquid nitrogen; then, the two samples were etched in NMP for 20 min; lastly, the samples were sputtered with gold on the fractured surface.

### Table 4. Values of Physical Parameters of the PEN Blend with 5 wt % BPA-PEN after Shearing at 310 °C under 10 Hz for Different Times

| time (min) | 10 | 30 | 60 |
|-----------|----|----|----|
| $\Delta H$ (J/g) | 16.5 | 26.5 | 20.6 |
| melting point ($T_{m,n}$ °C) | 323.0 | 320.2 | 314.7 |
| melting point ($T_{m,h}$ °C) | 334.8 | 335.5 | 336.2 |
| $T_g$ (°C) | 163.8 | 164.5 | 164.8 |
| crystallinity (%) | 14.1 | 18.8 | 14.4 |

#### Figure 12. Synthetic route for HQ/RS-PEN and BPA-PEN polymers.
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