Synthesis, characterization and rheological property of biphenyl-based polyarylene ether nitrile copolymers

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Abstract. The high molecular weight biphenyl-based polyarylene ether nitrile copolymers were synthesized by nucleophilic substitution reaction of 2,6-dichlorobenzonitrile (DCBN) with varying molar ratios of 4,4'-dihydroxybiphenyl (BP) and hydroquinone (HQ). The BP content of the copolymers has influence on glass transition temperature (T_g), initial decomposition temperature (T_{id}), mechanical properties and the crystallinity. All the copolymers could be dissolved in NMP, DMF and DMAc on heating, and were stable up to 450°C with a high char yield above 50% at 800°C in nitrogen atmosphere. The glass transition temperature, the melting temperature and tensile strength of copolymers were found to increase with increase in concentration of the BP units in the polymer. The dynamical viscosity and the storage modulus have been influenced by the BP concentration, frequency, temperature and time. This rheological results show that these copolymers have best thermoplastic processability and stability at 300–400°C.

Keywords: polymer synthesis, molecular engineering, thermal properties, rheology, mechanical properties, polyarylene ether nitrile copolymer

1. Introduction

In recent decades, polyarylene ether nitrile (PEN) as special engineering plastics has gained wide applications for its excellent properties in aerospace, electric and automotive industry. Various bisphenols have been studied for synthesis of PEN via nucleophilic aromatic substitution polymerization, these PEN materials exhibit excellent thermal stabilities over a wide-range of temperature [1–6]. The cyano group serves as a potential site for cross-linking reaction and can make polymer transform from thermoplastic to thermosetting [7–11]. Matsuo *et al.* [3] systematically studied the synthesis of 2,6-dihalobenzonitrile with different kinds of bisphenol including the 4,4'-dihydroxybiphenyl and found that mechanical properties of biphenyl-based PEN were better than that of the correspon-

ding ketone or sulfone containing polymers. However the above-mentioned PEN is a homopolymer and insolubility has limited their applications in many areas. Many attempts have been made to improve the solubility of the PEN by copolymerization or incorporation of pendant group [4, 5, 10, 11, 12]. Mechanical property such as elongation is low for PEN homopolymer have limited its applications [3, 6, 12]. In this paper, we report the synthesis of polyarylene ether nitrile copolymers derived from 2,6-dichlorobenzonitrile (DCBN) with hydroquinone (HQ) and 4,4'-dihydroxybiphenyl (BP), and the characterizations of copolymers by thermal properties, mechanical properties and rheological properties.

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2. Experimental

2.1. Materials

2,6-dichlorobenzonitrile, hydroquinone and 4,4'-dihydroxybiphenyl were available commercially and purified by sublimation before use. Anhydrous K_2CO_3 was dried under vacuum at 100°C before use. N-methyl pyrrolidone (NMP) was distilled under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2.2. Polymer synthesis

The procedure of the synthesis of the PEN copolymer has been described in earlier reports [6], and the structure of the polymer synthesized is shown in Figure 1.

Figure 1. Polymerization of PEN (BP/HQ) copolymer

2.3. Preparation of polymer films

The polymer was dissolved in DMF again to get a solution with 7–10% polymer content. After vigorous stirring, the solution was cast onto a clean glass plate to obtain the film. The film then was heated at elevated temperature to 160°C to remove the solvent completely. The films with a thickness of 20–30 μm were obtained.

3. Characterization

Inherent viscosities of the samples were determined at 20°C for 0.5% polymer solution in DMF using Ubbelohde viscometer. The FT-IR spectra of the films were recorded using Nicolet 20 SXB-IR spec-

trophotometer. The ^1H -NMR and ^{13}C -NMR spectroscopy were recorded using BRUKER AV400 NMR instrument using DMF-d_7 as the solvent. Glass transition temperature (T_g) and melting point (T_m) were measured on TA Instrument Q-100 DSC, at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The thermogravimetric analysis of the copolymers was carried out under nitrogen atmosphere using TA Instrument Q-50 series thermogravimetric analyzer at a heating rate of $10^\circ\text{C}/\text{min}$. The wide angle X-ray scattering (WAXD) data were preformed at room temperature using a Rigaku DMAX1400 diffractometer (DMAX1400, Rigaku, Japan; $\lambda = 0.15406 \text{ nm}$) operated at 40 kV and 100 mA with $\text{CuK}\alpha$ radiation. The specimens were fixed on the equipment and data were collected with a step interval of 0.02°C at a rate of $4^\circ\text{C}/\text{min}$.

Tensile strength and elongation at break of the films were measured on an SANS mechanical testing instrument (Shenzhen New SANS material testing machine factory, Shenzhen, China), and gained as average value for every five samples. The rheological behaviors of copolymers were carried out using TA instrument AR-G2 oscillatory rheometer with a heating rate of $10^\circ\text{C}/\text{min}$ under air condition.

4. Results and discussion

Polyarylene ether nitriles copolymers were synthesized by nucleophilic substitution reaction of 2,6-dichlorobenzonitrile with 4,4'-dihydroxybiphenyl and hydroquinone. The molar ratio, yields and inherent viscosity values of the reactions are shown in Table 1.

4.1. Solubility

All samples are insoluble in common organic solvents including dipolar aprotic solvents like DMSO, DMF, DMAc and NMP at room temperature, but three copolymers can dissolve in NMP, DMF and DMAc solvent on heating.

Table 1. Conditions for the synthesis of PEN (BP/HQ)

Sample	Molar ratio (BP:HQ)	Inherent viscosity [g/dl]	Dehydration time [h] at $140\text{--}160^\circ\text{C}$	Polycondensation time [h] at $180\text{--}200^\circ\text{C}$	Yield ratio [%]
PEN-2	25:75	0.86	2.5	4	98.3
PEN-3	50:50	0.91	2.5	4	98.8
PEN-4	75:25	1.21	2.5	4	99.0
PEN-5	100:0	insoluble	2.5	4	98.5

Figure 2. FT-IR spectra of PEN (BP/HQ) polymer

Figure 3. ^1H -NMR spectrum of copolymer PEN-3

Figure 4. ^{13}C -NMR spectrum of copolymer PEN-3

4.2. FT-IR and NMR characterization

The structure of the copolymers was characterized with a FT-IR spectroscopy as shown in Figure 2. From top to bottom the five samples have a structure of BP: HQ = 100:0, 75:25, 50:50, and 25:75, respectively. For all polymers, the characteristic stretching vibration absorption of $-\text{OH}$ of BP and HQ at 3290 and 3260 cm^{-1} disappeared. The absorption at 2231 cm^{-1} is characteristic symmetrical stretching of CN group. The absorptions at 1247 and 1280 cm^{-1} are assigned to $-\text{C}-\text{O}-\text{C}-$ of BP, and absorption at 1190 cm^{-1} is the characteristic peak of $-\text{C}-\text{O}-\text{C}-$ of HQ, both of them are ortho to CN, respectively. The absorption of CN groups at 2231 decreased with the increase of BP concentration, because of the CN concentration decreased with the increase of BP concentration. Figure 3 and Figure 4 are ^1H -NMR and ^{13}C -NMR spectra of copolymer PEN-3 as a typical copolymer sample. The characteristic assignment of ^1H -NMR and ^{13}C -NMR peaks are displayed in Figure 3 and Figure 4. The chemical shift (δ , ppm) of ^1H -NMR: 6.8, 7.0 (Ar-O, o), 7.4 (Ar-Ar-O, m), 7.6, 8.0 (Ar-CN, p). The chemical shift (δ , ppm) of ^{13}C -NMR: 95 (Ar-CN), 110 (Ar-CN, m), 113 ($-\text{CN}$), 120 ($-\text{O}-\text{Ar}-\text{O}$, o), 122 ($-\text{O}-\text{Ar}-\text{Ar}-\text{O}-$, m), 128 ($-\text{Ar}-$), 136 (Ar-CN, p), 152 (O-Ar), 155

(–O–Ar–Ar–O–, p), 160 (Ar–CN, o), 161 (–O–Ar). From the chemical shift information, the Ar–CN, –Ar– and –Ar–Ar– segments were existed in main chain of PEN. All these information confirmed that BP, DCBN and HQ have reacted as showed in Figure 1.

4.3. Mechanical measurement and analysis

The mechanical measurement such as tensile strength and elongation at break are listed in Table 2. The values of tensile strength increase with the increasing content of BP, which may be attributed to the rigidity brought about by the BP component. The mechanical measurements of the samples also show that tensile strength of PEN (BP/HQ) is higher than that of PEN (RS/HQ) copolymer [6]. The elongation at break of PEN-3 was the highest in all copolymers, which may be attributed to the irregularity in main chain according to the low crystalline behaviors.

4.4. Thermal properties

The glass transition temperatures of the copolymers were calculated from the curves of DSC shown in Figure 5 and Table 2. It can be seen that T_g increases with the increasing BP content in the copolymers, and the T_g of PEN (BP/HQ) copolymers is higher than that of PEN (RS/HQ) [6]. From the Figure 5, PEN-2 and PEN-5 have apparent melting transition, which is 255 and 348°C, respec-

Figure 5. The DSC spectra of PEN(BP/HQ) copolymers

tively. But the melting point of PEN-4 is not observed. PEN-5 has double melting transition peaks, which may be contributed to regular macromolecular structure and thermotropic nematic transition. Figure 6 shows the TGA curves of polymers. From Figure 6a, the initial decomposition temperature (T_{id}) of three copolymers is higher than 450°C. The thermal properties of three samples are listed in the Table 2. The T_{id} of BP homopolymer is higher than 500°C, the introduction of HQ decreases T_{id} of the copolymers, but with the HQ content increase, the T_{id} of the copolymer increase again, which could be attributed to the decrease of distance between CN groups on the main chain, and the increase of the regularity of the macromolecular structure. Figure 6b is TGA derivative curves of copolymers, the decomposition stages were observed. The PEN-2 is one stage decomposition

Figure 6. TGA curves of PEN (BP/HQ) copolymers, a) weight loss percent, b) derivative curves

Table 2. Thermal and mechanical property of PEN (BP/HQ) copolymer

Polymer	T_g [°C]	ΔH_g [J/g]	T_m [°C]	ΔH_m [J/g]	T_{id} [°C]	Tensile strength [MPa]	Elongation at break [%]
PEN-2	189	0.19	255	26.1	471	113	7
PEN-3	167	0.32	–	–	511	118	9
PEN-4	201	0.28	325	27.2	495	123	6
PEN-5	216	0.07	348, 352	28.5	520	–	–

model; the main decomposition temperature is 477°C. But PEN-3 and PEN-4 exhibit two stages decomposition mechanism, the main decomposition temperature is 525–530°C, the decomposition

temperature at the second stage is about 600°C, which may be led by high BP concentration into macromolecular main chains.

Figure 7. The XRD spectra of PEN(BP/HQ) copolymers

Figure 8. The storage modulus and dynamic viscosity of copolymers with temperature at 10 Hz
a) storage modulus; b) dynamic viscosity

4.5. WXR analysis of PEN

Figure 7 is the WXR spectra of copolymers. The regular structure could increase the crystallinity of polymer. Copolymer PEN-2, PEN-4 and PEN-5 have apparent semi-crystalline polymer nature, but the copolymer PEN-3 which further confirms the tendency towards the amorphous nature, has fewer tendency to crystallize the BP-based PEN and HQ-based PEN, and has a lower melting transition temperature. The results are very well corresponding with DSC results and the mechanical measurements.

4.6. The rheological behaviors of copolymers

Figure 8 shows the relationships between the storage modulus (G') (Figure 8a) or the dynamic viscosity (η) (Figure 8b) and the temperature at frequency 10 Hz. The storage modulus and viscosity of all copolymers decreased with the increase of temperature. The viscosity of copolymer decreased gradually with the increase of temperature from 250 to 400°C, and the viscosity of copolymer increase with the increase of BP concentration. But the storage modulus decreased quickly from 350 to 400°C. So, these copolymer have good thermoplastic processing properties at 300–400°C, which improved the processing temperature window of PEN homopolymer.

Figure 9a shows the storage modulus (G') of the copolymers with frequency. The increase of the storage modulus shows more significant in the high frequency range (>1 Hz), also, it is observed that the storage modulus of the copolymer with high concentration of BP increase more significantly at the high frequency. The storage modulus of copolymers reached to plateau at the low frequency (<1 Hz), which were led by tangling with macromolecular chains. The dynamic viscosity (η) decreased with the increase of frequency, and the dynamic viscosity (η) increase with the BP concentration at same frequency.

Figure 10 shows that the effects of storage modulus and dynamic viscosity on time at 320°C. From the results, all copolymers are basically stable at 320°C for 60 min. It means that the copolymer could be

Figure 9. The storage modulus and dynamic viscosity of copolymers with frequency at 320°C
a) storage modulus; b) dynamic viscosity

processed at 320°C by thermoplastic processing methods. But the storage modulus and viscosity of the PEN-3 increase significantly after 30 min, which may be contributed to the curing reaction of CN group, this is confirmed by FTIR spectroscopy (Figure 11), and the triazine character could be observed at 1520 cm^{-1} . The storage modulus (G') and the dynamic viscosity (η) increase with the BP concentration at same time, which may be attributed to the rigidity brought about by the BP component.

5. Conclusions

High molecular weight PEN (BP/HQ) copolymers can be synthesized by nucleophilic substitution reaction of DCBN with BP and HQ in NMP medium using K_2CO_3 as catalyst, and exhibit excellent thermal and mechanical properties, the introduction of BP enhances the T_g and T_{id} of the copolymers. All copolymers have good rheological behaviors, the dynamic viscosity decreased stably

Figure 10. The storage modulus and dynamic viscosity of copolymers with time at 320°C
a) storage modulus; b) dynamic viscosity

Figure 11. The FTIR spectra of PEN-3 cured at different time for at 320°C (the shadow Indicate the characteristic absorption of triazine)

with the increase of the temperature; the dynamic viscosity decreased quickly with the increase of the frequency, and was constant basically with the increase of time at 320°C, which are basement of the future processes and application in special engineering plastics.

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