

Research Article

Improving the Thermal Properties of Polycarbonate via the Copolymerization of a Small Amount of Bisphenol Fluorene with Bisphenol A

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Polycarbonate is an attractive transparent plastic with high mechanical/thermal properties. A family of copolycarbonates of bisphenol-A (BPA), 9, 9-bis (4-hydroxyphenyl) fluorene (BHPF), and diphenyl carbonate (DPC) were prepared by a transesterification polymerization. The weight-average molecular weight of the polycarbonates ranges from 65,000 to 107,000 g/mol; the copolycarbonates showed T_g and $T_{d-5\%}$ from 63–70°C and 100–105°C higher than the control, respectively. Meanwhile, the processing properties of polycarbonate remain unchanged. These properties endow the polymers with potential for use as high-temperature resistance materials.

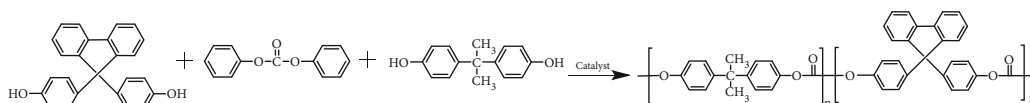
1. Introduction

Polycarbonate is an attractive transparent plastic with good optical transparency, excellent impact resistance, and high tensile strength [1–5]; thus, typical polycarbonate such as bisphenol A polycarbonate (APC) is widely used in food industry and building, automotive, aircraft, data storage, electrical, and communications hardware [6–10].

At present, the total capacity of APC in the world has reached 5.465 million tons, but most APCs are produced in the process of phosgene formed by CO and chlorine, which is a toxic and not friendly to environment. Based on the concept of sustainable chemistry, CO₂ is used to partially replace the traditional toxic compounds such as CO and phosgene for the synthesis of cyclic carbonates [11–13] and polycarbonate [14, 15]. Fukuoka et al. [16] used CO₂ and ethylene oxide to synthesize DPC and then produced PC with BPA, so as to avoid using phosgene. Therefore, using DPC and BPA to synthesize polycarbonate gains more attention recently.

In addition, considering the application of APC in aerospace and other special fields, the heat resistance of APC has

to be enhanced to meet the requirement of severe applied environments. The introduction of aromatic macromolecules to improve the chain segment rigidity and glass transition temperature is an important way to regulate and improve the heat resistance of APC. Fluorene ring was frequently used to improve the heat resistance of polycarbonates. Compared with BPA, the two phenol groups in 9, 9-double (4-hydroxyphenyl) fluorene molecular are connected to a unique structure of fluorene ring, namely, Cardo ring, instead of straight chain propane groups, and the rigidity of the ring structure is significantly higher than that of the nonring structure [17, 18]. At the same time, as four benzene rings attach to a carbon, BHPF has good thermal stability and chemical stability. In addition, the molecules of these two compounds contain two active hydroxyl groups distributed symmetrically, which is able to polycondense with corresponding compounds to form polymer chains. The introduction of this monomer structure can effectively improve the heat resistance of the polymer and obtain better optical and molding properties [19]. Such improvements of polymers in transparency, heat resistance, and insulation



SCHEME 1: Reaction equation of PC from BPA, BHPF, and DPC.

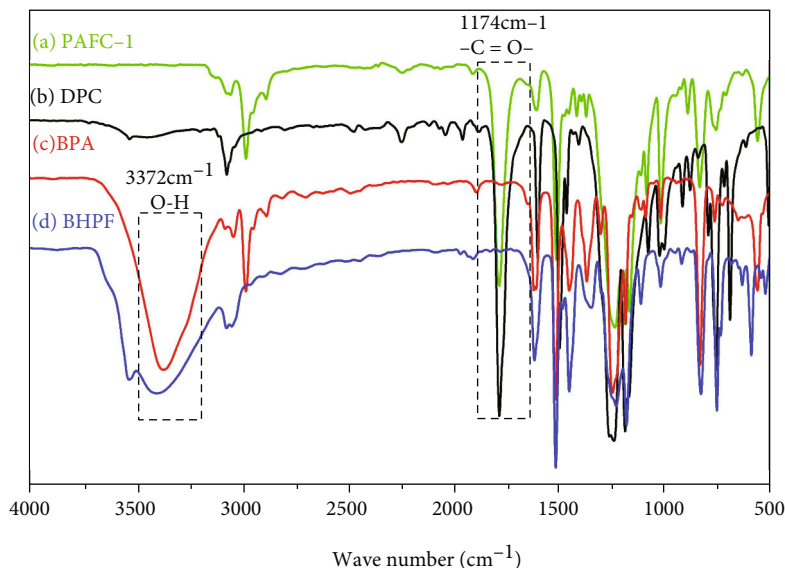


FIGURE 1: FTIR spectra of BPA, BHPF, DPC, and PAFC-1.

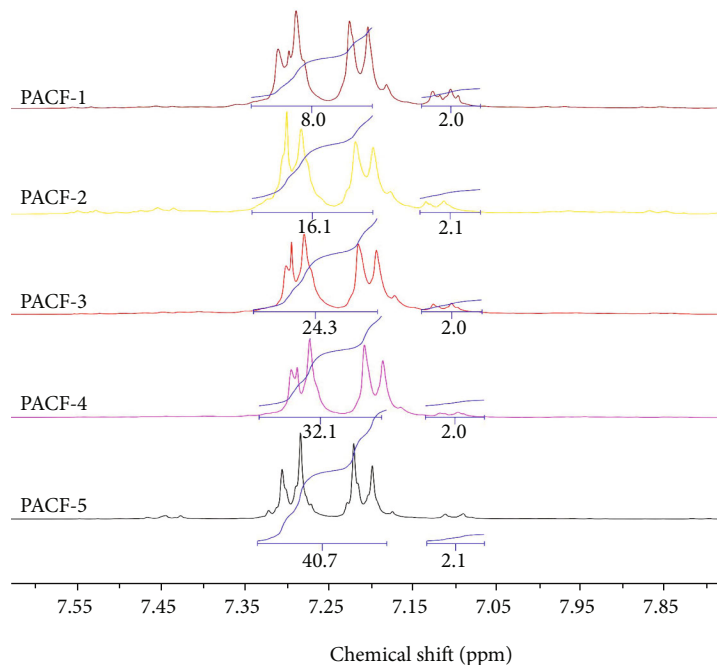
are important to expand their applications [20, 21]. Bales [22] using BHPF with 50% of the mole ratio to prepare APC improved the impact properties of polycarbonate, solvent resistance, and optical clarity, but also increase its T_g up to 270°C. Toshimasa Tokudu [23] prepared polycarbonate with different molar ratios of BPA and BHPF mixed monomers in order to obtain the vitrification temperature for different applications. Their results showed that when the molar ratio of BPA: BHPF was 30: 70, the product T_g was 216°C, while when the molar ratio of monomer was 15: 85, the product T_g raised to 232°C. However, considering the high cost of BHPF, it is of significance to develop a method that effectively improves the thermal performance of PC, but with little increase in cost. We prepared a series of polymers with different feed ratios of BPA and BHPF, named PAFC. The BPA/BHPF (mol/mol) ratios of PAFC-1, PAFC-2, PAFC-3, PAFC-4, and PAFC-5 were 99/1, 98/2, 97/3, 96/4, and 95/5, respectively. As expected, the thermal performance (T_g , $T_g = 203^\circ\text{C}$) of PC could be considerably improved by adding only 1% BHPF, which was about 60°C higher than the glass transition temperature of commercial BPA-based PC, thus, potential application value.

2. Experimental Section

2.1. Materials. Bisphenol-A (BPA, 99.0%), fluorene-9-bisphenol (BHPF, 99.0%), and diphenyl carbonate (DPC, 99.0%) were provided by Aladdin. Sodium bicarbonate (NaHCO_3 , 99.5%), zinc acetate ($\text{Zn}(\text{OAc})_2$, 99.0%), and sodium hydroxide (NaOH , 99.0%) were bought from Tian-

jin Tianli. Dichloromethane (CHCl_2 , 99.5%), chloroform (CHCl_3 , 99.0%), methanol (CH_3OH , 99.50%), and acetone (CH_3COCH_3 , 99.50%) were purchased from Liaoning Quanrui.

2.2. Preparation of Fluorene-9-Bisphenol Polycarbonates. The reaction was carried out in a 100 mL reaction still. As shown in Scheme 1, the reaction device diagram is shown in Figure S1. A typical polymerization procedure of PAFC (take PAFC-5 for example) is described below. PAFC-5 was prepared by melting transesterification using BPA (10.83 g, 47.5 mmol), BHPF (0.875 g, 2.5 mmol), and DPC (11.235 g, 52.5 mmol) as reaction monomers. NaOH (1 mg) was used as catalyst. Transesterification is the first stage of the reaction. The reactants and catalyst were slowly heated at 160°C under a nitrogen atmosphere with stirring and remained for 20 min. Then, the temperature was gradually raised to 180°C and remained for another 20 min. Raising the temperature to 200°C, phenol began to appear at a condenser tube. The reaction temperature was then further increased to 220°C for 20 min, to distill phenol off, the byproduct. Condensation polymerization is the second stage of the reaction. After the transesterification process, the temperature of the system was set at 230°C under vacuum pressure (200 torr). After 20 min, the temperature was increased to 250°C under the vacuum pressure of 150 torr. After further reaction for 20 min, the temperature was increased to 280°C under the vacuum pressure of <0.5 torr, and the reaction was completed within 20 min. After the polymerization, to obtain PAFC-5, the product was dissolved in dichloromethane and precipitated in

FIGURE 2: ^1H NMR spectra of PAFCs.

methanol and then dried in a vacuum oven. The purified products were used for the characterization of structure and property.

2.3. *Analysis of ΔC* . The color difference (ΔC) of the synthesized PAFCs was measured by a UV spectrophotometer (Youke Instrument). This parameter represents the yellowness of the synthesized PAFC. A chloroform solution with a PAFC concentration of 0.01 g/mL was used, and ΔC was calculated as follows:

$$\Delta C = \left(\left| \frac{1}{3} - \frac{T_{445}}{T} \right| + \left| \frac{1}{3} - \frac{T_{555}}{T} \right| + \left| \frac{1}{3} - \frac{T_{600}}{T} \right| \right) \times 100, \quad (1)$$

where T_{445} , T_{555} , and T_{600} represent the transmittance of the polycarbonate solution at a wavelength of 445, 555, and 600 nm, which are relative to chloroform and $T = T_{445} + T_{555} + T_{600}$.

3. Instruments

Molecular weight and molecular weight distribution of the polycarbonates were measured on a PL-220 instrument at 40°C, and tetrahydrofuran was employed as the eluent at a flow rate of 1.0 mL/min; data were processed using narrow polystyrene standards. Differential scanning calorimetry (DSC) analysis was conducted with alumina 70 μl at a heating or cooling rate of 10°C/min, and DSC curves were recorded at the second heating scan from 45°C to 600°C. Rheological property test of copolymer: the prepared copolymer was dried at 120°C for 12 h, and its rheological property was tested by hr2 (TA) rheometer. The scanning frequency was 0.05-100 rad/s, and the experimental temperature was 320°C.

TABLE 1: List of the proton NMR signal.

Sample	BPA/BHPF feed ratio (mol/mol)	NMR signal (chemical shift, ppm)	
		Ar-H	BHPF
PAFC-1	99/1	7.07-7.13 (m,2H)	7.18-7.33 (m,8H)
PAFC-2	98/2	7.07-7.13 (m,2H)	7.18-7.33 (m,16H)
PAFC-3	97/3	7.07-7.13 (m,2H)	7.18-7.33 (m,24H)
PAFC-4	96/4	7.07-7.13 (m,2H)	7.18-7.33 (m,32H)
PAFC-5	95/5	7.08-7.13 (m,2H)	7.18-7.33 (m,40H)

4. Results and Discussion

4.1. *FT-IR of PAFC*. Figure 1 shows the IR spectra of BPA, BHPF, DPC, and PAFC-1 as a typical example. The characteristic absorption peak is about 1769 cm^{-1} , which is attributed to C=O. In addition, the broad peak at 3000-3600 cm^{-1} is usually attributed to O-H stretching vibration. This broad peak is presumably due to the influence of hydrogen bond on O-H in monomers [24]. While the O-H stretching peak of BPA and BHPF at 3000-3600 cm^{-1} disappears on the infrared spectrum curve of PAFC-1, indicating the occurrence of melt transesterification reaction. PAFC was synthesized successfully.

4.2. *^1H NMR of PAFCs*. In the experiment, NMR tests were carried out on the copolymers of different proportions. The ^1H NMR spectra were shown in Figure 2, and the results were summarized in Table 1. At the chemical shift $\delta = 7.07$

TABLE 2: Results of copolycondensation of BPA and BHPF with DPC.

Sample	BPA/BHPF feed ratio (mol/mol)	Yield (%)	M_n^a (g/mol)	M_w^a (g/mol)	PDI ^a	T_g^b (°C)	$T_{d-5\%}^c$ (°C)	ΔC^d (%)
PAFC-1	99/1	92	20,900	65,000	3.10	203	420	1.68
PAFC-2	98/2	93	21,000	78,000	3.30	205	425	1.70
PAFC-3	97/3	97	23,100	105,000	3.56	207	425	1.75
PAFC-4	96/4	98	24,800	107,000	3.31	210	425	1.76
PAFC-5	95/5	95	28,900	103,000	3.60	210	425	1.85
APC ^e	100/0	—	—	—	—	140	320	—

^aDetermined by THF-GPC. ^bMeasured by DSC with a heating rate of 10°C min⁻¹. ^cDegradation temperature for 5% weight loss was measured by TGA with a heating rate of 10°C min⁻¹ (with N₂). ^d ΔC is calculated by formula (1). ^eParameters of conventional polycarbonate.

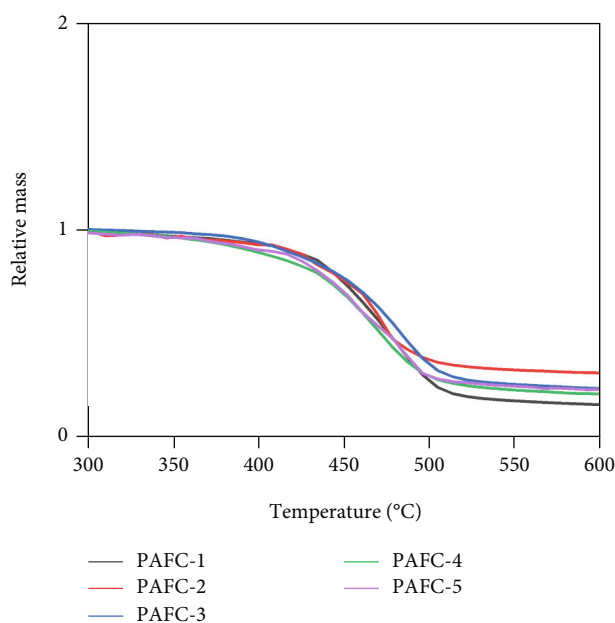


FIGURE 3: TGA curves of PAFCs.

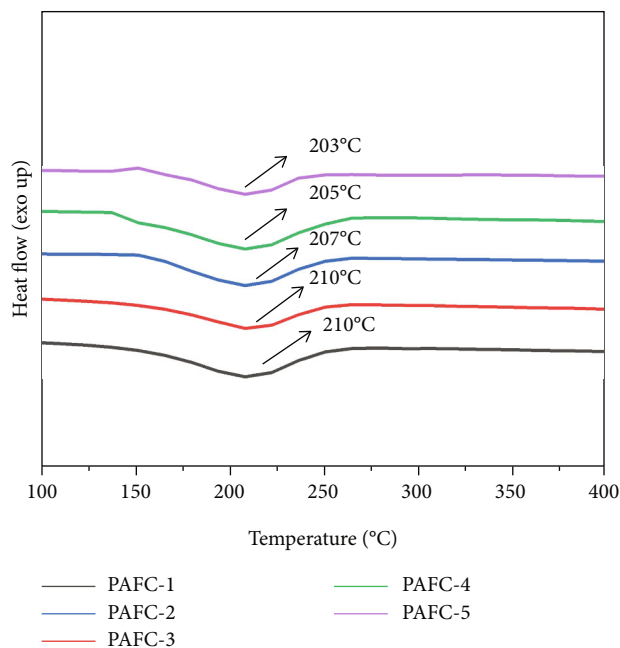


FIGURE 4: DSC curves of PAFCs.

(7.08) – –7.13, the corresponding Ar-H is on cyclohexane. The chemical shift $\delta = 7.18 - 7.33$ corresponds to H at the BHPF position. Therefore, according to the results of NMR determination, the structure of BPA and BHPF can be preliminarily determined. The number of H at the position of BHPF is proportional, so the content of BHPF was almost consistent with the feed ratios.

4.3. Molecular Weights and Solubility of PAFCs. As summarized in Table 2, Figure 3, GPC data of the copolycarbonate were given. The yield of polycarbonate was all above 90%, with high molecular weights. M_n and M_w were in the range of 20,900–28,900 g/mol and 65,000–107,000 g/mol, respectively. The molecular weight distribution of the copolycarbonate was narrow with M_w/M_n of 3.1–4.6, which could be attributed to existence of Cardo ring and its symmetrical structure. Meanwhile, the melting transesterification was improved by removing phenol, which increased the polymerization degree of copolycarbonate, thus, high molecular weight of polymers. The process of reducing the yellowness in polymerization is an important issue for PC applied in the field of optical transparent materials. As listed in

Table 2, the ΔC of PAFCs is between 1 and 2. The change of ΔC should mainly be ascribed to the derivation of monomers. Meanwhile, we obtained the copolymer film (Figure S3), and it showed good transparency. A powder X-ray diffraction pattern of the polycarbonate showed the copolycarbonate is amorphous state (Figure S2). The crystal material has poor transparency due to its anisotropy, while the amorphous material has better transparency.

4.4. TGA Curves of PAFCs. Thermal stability is a key property in the polymer processing. Figure 3 shows TGA curves for PAFC-1, PAFC-2, PAFC-3, PAFC-4, and PAFC-5. The temperature at which 5 wt % is degraded ($T_{d-5\%}$) is given in Table 1. The $T_{d-5\%}$ data of the copolycarbonates showed that all the PAFC samples were thermally stable up to 420–425°C. BHPF has four benzene rings attached to a carbon, and the rigidity of the ring structure is significantly higher than that of a nonring structure. The introduction of monomer in the structure effectively improves the thermal stability of the polymer. The T_d of copolymer polycarbonate is

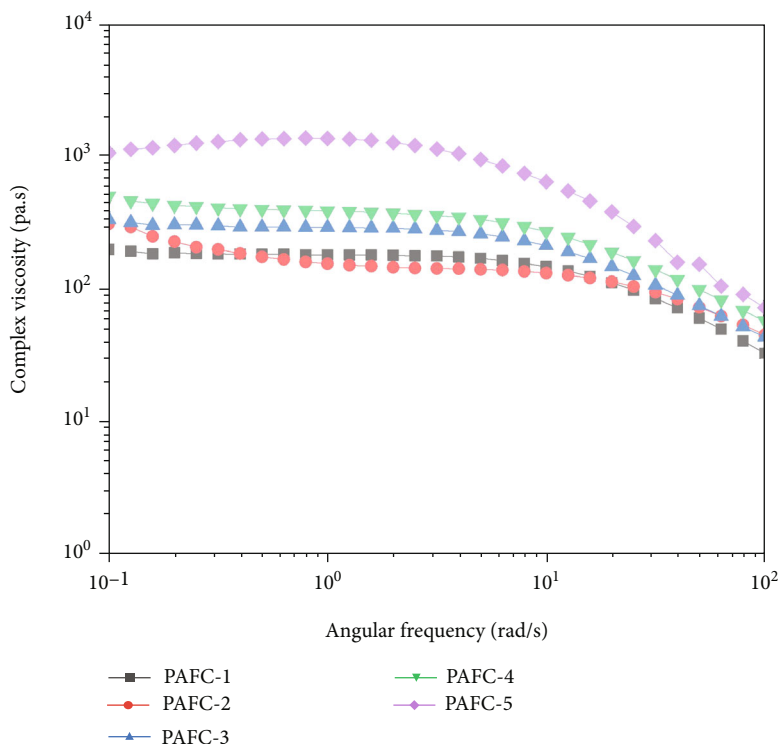


FIGURE 5: Changes of complex viscosity, η as function of angular frequency, ω for BHPF/(BPA + BHPF) molar ratio of PAFC at 320°C.

function of the content of bisphenol fluorene, going up with the increase of bisphenol fluorene content, own to the thermal stability of bisphenol fluorene. The copolycarbonates we prepared showed a $T_{d-5\%}$ at 60-75°C higher than the control.

4.5. DSC Curves of PAFCs. The T_g of the copolycarbonates analyzed using DSC (Figure 4) was 203, 205, 207, 210, and 210°C, as the content of BHPF was increased from 1 to 5 mol%. The most important factor affecting T_g of copolycarbonates is the flexibility of the molecular chain. The higher the flexibility of the main chain, the lower the T_g ; the higher the rigidity of the main chain, the higher the T_g . Thanks to the good thermal stability of Cardo rings in BHPF, the T_g of copolycarbonates containing BHPF we prepared was improved considerably.

4.6. The Rheological Curve of PAFCs. Figure 5 displays the viscosity of PAFC-1, PAFC-2, PAFC-3, PAFC-4, and PAFC-5 along with the change of shear velocity under low shear rate. The viscosity change with shear rate almost remains the same. When the copolymer is applied by force, viscous flow performance, and show that the elastic deformation, this is called the rheology of polymer fluid. In Figure 5, in the low shear region, due to the timely reconstruction of the tangles destroyed by shear, the density of tangles remains unchanged, so the viscosity remains unchanged. It is the first Newton region for PAFCs. In the medium shear zone, the tangles are destroyed faster than the reconstruction speed, and the viscosity decreases. That

is the pseudoplastic zone for our copolymer. Figure 5 indicates that PAFCs have good processing properties.

5. Conclusions

In this study, high-temperature resistant polycarbonates with different BHPF contents were successfully prepared by a melt-polycondensation method with BPA, DPC, and BHPF. The Mw of the prepared PAFC was 107,000 g/mol, and the thermal properties were greatly improved. The T_g of PAFC reached up to 210°C, which was 1.5-fold higher than the commercial BPA-based PC (140°C). $T_{d-5\%}$ was as high as 425°C, which is 1.33-fold higher than that of commercial BPA-based PC (320°C). From the experimental results, it can be found that when 1 mol% of BHPF was added, the thermal properties (T_g) of polycarbonate are greatly improved. With the content of BHPF was increased from 1 to 5 mol%, T_g shows a slow-growth trend. This discovery has tremendous application potential in high-temperature resistant plastic industry.

Data Availability

The data used to support the findings of this study are included within the article and the supplementary information file.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

X.Z. contributed to the conception of the study; Y.L. performed the data analyses and wrote the manuscript; J.W, X.G, X. Li, and X. Liu helped perform the analysis with constructive discussions.

Acknowledgments

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Supplementary Materials

The following are submitted in "Supporting Files," Figure S1: the reaction device. Figure S2: XRD pattern of the polycarbonate. Figure S3: the picture of the polycarbonate film. (*Supplementary Materials*)

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