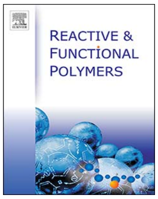
ARTICLE IN PRESS

Reactive and Functional Polymers xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react



Synthesis of benzophenone-center bisphenol-A containing phthalonitrile monomer (BBaph) and its copolymerization with P-a benzoxazine

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ARTICLE INFO

Keywords:
Phthalonitrile
Benzoxazine
Copolymerization
Synthesis and curing
Radiation resistance

ABSTRACT

The benzophenone-center bisphenol-A containing phthalonitrile monomer (BBaph) was successfully produced by a nucleophilic substitution reaction of 4,4′-difluorobenzophenone with 4-nitrophthalonitrile and bisphenol-A in the presence of potassium carbonate. The chemical structure of the synthesized monomer was confirmed by ^{1}H nuclear magnetic resonance (^{1}H NMR), ^{13}C NMR, and Fourier transform infrared spectroscopy (FTIR). The curing study of monomer was evaluated by the FTIR and DSC curves. The poly(BBaph) was subjected to gamma-ray irradiation with 100 kGy dose of ^{60}Co gamma radiation. The variation in chemical structure, mechanical, thermomechanical and thermal properties of poly(BBaph) was evaluated by FTIR, flexural, dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA), respectively. All results confirmed very minute deviation in the estimated properties before and after radiation. The BBaph monomer was blended with typical monofunctional benzoxazine (*P-a*) in different weight ratios. The DSC, DMA, and TGA tests were performed to study the properties of copolymers. The high glass transition temperature (164–227 °C), and stiffness values (2.72–3.03 GPa) was observed for the copolymers. The thermal stability was also improved after the loading of *BBaph* in *P-a*, recorded values were in the range of 367–408 °C, and 46.1–58.7% for 5% weight loss temperature and char yield at 800 °C, respectively.

1. Introduction

Phthalonitrile resins (PN) have been known for their superior thermal and oxidative stabilities, good mechanical properties, high glass transition temperatures (T_g), no thermal degradation prior to T_g and low water absorption [1–4]. These outstanding properties provide a wide range of application for PN such as in the marine, aerospace, and microelectronic industries [5–8]. However, the PN have some shortcoming such as higher melting temperature (T_m), high rigidity, higher curing temperatures and long curing time, which reduce their applications [9,10]. The blending of the PN with the curing additives such as strong organic acids, metallic salts, and strong organic acids/amine salts is one of the solutions for the curing of PN [11–14]. However, the curing additive brings a number of disadvantages on the final product, like they release volatile substances on elevated curing temperature, resulting voids in the cured materials. Many researchers worked on the molecular design of PN to overcome the shortcomings of PN. The benzoxazine-functional [15], phosphorus or silicon [16,17], sulfone and sulfone-ketone [18], and aliphatic-aromatic ether containing phthalonitrile [19] are reported as low-melting and wide processing window PN. Generally, it has been observed that incorporation of ether linkages into the backbone of an aromatic polymer reduces T_m and gives higher processability.

Polybenzoxazines have attracted attention from academia and industry, in the fields of electronics, composites, coatings, and adhesives, due to their synergetic effects of traditional phenolic and advanced epoxy resins [20]. The benzoxazine precursors (phenols, primary amines, and formaldehyde) are characterized as inexpensive which can be obtained from renewable sources [21,22]. Polybenzoxazine resins showed excellent thermal and mechanical properties as high T_g and char yield, good thermal stability, low water absorption and dielectric constant, and near zero shrinkage upon curing [23,24]. However, attempts have been made for further improvement in these properties by introducing different functional groups, such as phthalonitrile [25–28], into the main chain of benzoxazine and copolymerization of benzoxazine with other advanced materials like phthalonitrile [29], epoxies [30], ε-caprolactone [31], and tetra-functional fluorene-based oxazines [32]. The traditional phenol aniline-based benzoxazine (P-a) is well

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http://dx.doi.org/10.1016/j.reactfunctpolym.2017.10.016
Received 17 June 2017; Received in revised form 20 October 2017; Accepted 24 October 2017
1381-5148/

Please cite this article as: Dayo, A.Q., Reactive and Functional Polymers (2017), http://dx.doi.org/10.1016/j.reactfunctpolym.2017.10.016

known for their cheap price, low viscosity and high purity. However, this monomer is frequently not used due to the lower mechanical properties and T_g of poly(P-a). The properties poly(P-a) can be modified by means of the outstanding thermal and thermomechanical properties PN polymers.

To overcome the shortcomings of PN, the benzophenone-center bisphenol-A containing PN monomer (BBaph) was synthesized by the introduction of benzophenone in the main chain of PN resin. The chemical structure of monomer was confirmed by the FTIR, ^{1}H and ^{13}C NMR. The curing of the synthesized monomer was evaluated by FTIR and DSC. The TGA and DMA of the cured polymers were performed to understand the thermal and thermomechanical properties. Furthermore, the *BBaph* was copolymerized with the phenol aniline-based benzoxazine monomer (P-a). The lower T_m of *BBaph* monomer reduces the processability hurdles. The FTIR and DSC were used to study the curing behavior of copolymers. The thermal stability and thermomechanical properties of copolymers were discussed by TGA and DMA.

2. Experimental

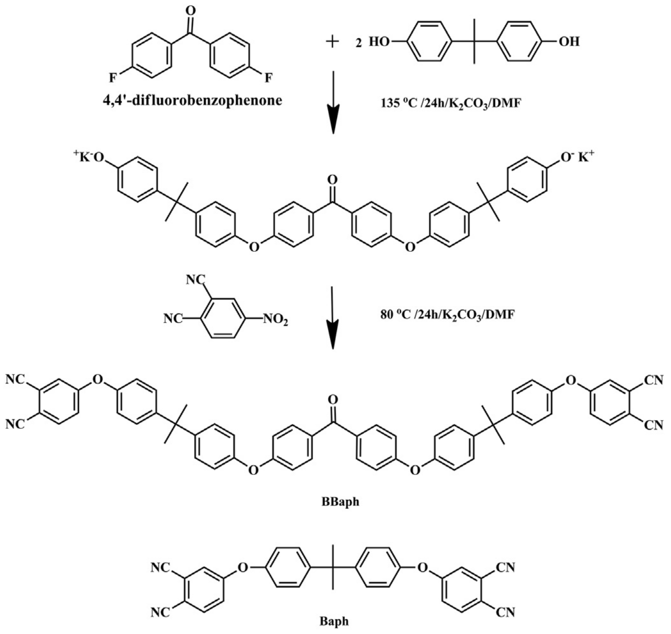
2.1. Materials

Bisphenol-A (BA) (> 99%), aniline (≥ 99%), phenol (99.5%), and *p*-formaldehyde (99.5%) were supplied by Chengdu Chemical Technology Co., Ltd. (China). The 4,4′-difluorobenzophenone (> 99%) and potassium carbonate (≥ 99%) were procured from Tianjin Bodi Reagent Co., Ltd. (China). The 4-nitrophthalonitrile (> 99%) was received from Aladdin Reagent Shanghai Co., Ltd. (China). The N-N-dimethylformamide (DMF, ≥ 99.5%), 4-(4-aminophenoxy)-phthalonitrile (4-APN, > 99%), and NaOH (≥ 99.5%) were kindly donated by Chengdu Kelon Chemical Reagent Co., Ltd. (China).

2.2. Synthesis of benzophenone-center bisphenol-A containing PN monomer (BBaph)

The *BBaph* monomer was synthesized from the reaction of bisphenol-A and 4,4′-difluorobenzophenone with 4-nitrophthalonitrile. Scheme 1 shows the synthetic route of prepared monomer.

The bisphenol-A (6.84 g, 0.03 mol), 4,4′-difluorobenzophenone (3.27 g, 0.015 mol), potassium carbonate (6.21 g, 0.045 mol), and DMF (20 mL) were added into a three neck 250-mL round bottom flask. The flask containing reactants was connected to a refluxing condenser and mechanical stirrer; blend was refluxed at 135 °C for 24 h, then cooled to room temperature. Afterwards, 4-nitrophthlonitrile (5.19 g, 0.03 mol), potassium carbonate (4.08 g, 0.03 mol), and DMF (20 mL) were added to the solution and refluxed for another 24 h at 80 °C, and cooled to room temperature. Then, the cooled solution was thoroughly washed with 5 wt% NaOH solution and distilled water until the precipitates were observed. The precipitates were separated from the solution by the filtration and overnight vacuum dried at 80 °C for the removal of any reactant. The yield of the *BBaph* monomer was 82.3% and the melting point (T_m by DSC) was 84.6 °C. FTIR (KBr, cm^{-1}): 3070 (−CH asymmetric stretching vibration in benzene), 2980 ($-CH_3$), 2235 (−CN stretch), 1651 (−C=O), 1500 and 1590 (benzene ring skeleton vibration stretch), 1280 and 1080 (C−O−C stretch). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): 6.67, 7.06, 7.12, 7.32, 7.75, and 8.04 (m, 30H, Ar−H), 1.67 (s, 12H, $-CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): 193.5 (s,1C, C=O), 161.8, 161.2, 153.3, 153.1, 152.0, 148.1, 146.8, 132.6, 132.0, 129.1, 128.8, 127.8, 123.1, 122.3, 120.2, 120.0, 119.8, 117.5, 108.5 (48C, the carbons of the benzene ring), 115.2, 115.8, 116.4 (m, 4C, − CN), 42.5 (m, 2C, quaternary carbon), and 31.04 (m, 4C, $-CH_3$). Elem. anal. calcd for $C_{59}H_{42}N_4O_5$: C, 79.89%; H 4.77%; N 6.32%; Found: C, 79.65%; H, 4.90%; N, 6.71%. ^{1}H and ^{13}C NMR of the newly developed monomer are shown in Fig. S1.



Scheme 1. Synthesis route of benzophenone-center bisphenol-A based PN monomer (BBaph) and structure of traditional bisphenol-A based PN monomer (Baph).

2.3. Synthesis of bisphenol-A based PN monomer (Baph)

For the comparative study of the PN properties, the traditional bisphenol-A based PN monomer (*Baph*) was synthesized from 4-nitrophthalonitrile and bisphenol-A according to the procedure described in the literature [33]. The chemical structure of *Baph* is already represented in Scheme 1.

2.4. Synthesis of phenol-aniline based benzoxazine monomer (P-a)

The P-a monomer was synthesized via melting method reaction of phenol, aniline, and *p*-formaldehyde according to the literature [34].

2.5. Curing of the PN monomer

The phenol-based PN monomers can't be self-cured [33], so they were blended with 4-APN (weight ratio 9:1) in a beaker and melted on the melting apparatus. The melted blends were poured into a stainless steel mould having the required test sample dimension and degassed in a vacuum oven at 130 °C for the removal of any entrapped gases. The degassed blends were isothermally heated in an air-circulating oven at 200, 225, 250 and 280 °C for 3 h at each heating stage. The ramp heating rate was kept at 10 °C/min.

2.6. Curing of the benzoxazine/phthalonitrile copolymers

The *BBaph* monomer was blended with P-a, without any addition of the catalyst, in the different weight ratios and melted on the melting apparatus and mixed uniformly after melting. The blends were poured into a stainless steel mould and overnight degassed in the vacuum oven at 100 °C for the removal of any entrapped gases. The degassed blends were isothermally heated in an air-circulating oven at 160, 180, 200, and 220 °C for 2 h at each heating stage. The ramp heating rate was kept at 10 °C/min.

2.7. Characterization

Bruker AVANCE-500 nuclear magnetic resonance (NMR) spectrometer was employed to obtain the ^{1}H and ^{13}C NMR spectra, Si $(CH_3)_4$ and DMSO-d_6 were used as standard and solvent for all tests. The Vario