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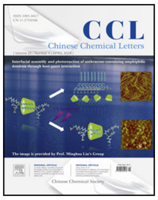

Original article

Allyl phthalazinone synthesis, polymerization and polymer properties

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ABSTRACT

A phthalazinone monomer with an allyl group, *i.e.* 4-(3-allyl-4-hydroxyphenyl)phthalazin-1(2*H*)-one, was synthesized and then copolymerized with 4-(4-hydroxylphenyl)(2*H*)-phthalazin-1-one and 2,6-diflurobenzonitrile by means of aromatic nucleophilic polycondensation to provide a series of crosslinkable poly(aryl ether nitrile)s. The virgin copolymers exhibited good solubility in polar organic solvents with relative high molecular weights (Mw: 45,130–58,403, inherent viscosities: 0.58–0.75 dL/g). After cross-linking, the thermal stability and solvent resistance of the polymer increased.

1. Introduction

Poly(aryl ether nitrile)s (PAENs) are a class of high performance polymers that have attracted much attention as structural materials in aerospace and electronic industries because of their outstanding mechanical properties, high thermal stability, good chemical inertia and excellent radiation resistance [1,2]. In addition, the cyano groups may also function as potential cross-linking sites, provide potential site for further functionalizations, and promote adhesion of the polymers to many substrates *via* interactions with other polar chemical groups [3,4]. On the one hand, a large number of PAENs have extremely high glass transition temperature and poor solubility in organic solvents, thus making them difficult to be used as thin membranes and coatings. In our previous study, we synthesized a series of PAENs containing 4-(4-hydroxylphenyl)(2*H*)-phthalazin-1-one (DHPZ) moiety, which behaves like a biphenol to give good solubility and high rigidity to the polymer backbone [5]. On the other hand, the products based on these soluble polymers suffer from poor solvent-resistance. The introduction of crosslinkable moieties into the polymer chains is often adopted as an efficient approach to improve the solvent-resistance, dimensional stability and enhance the T_g values [6]. Allyl bisphenols, such as 2,2′-bis(4-allyloxy phenyl)propane (APP) [7], 4,4′-allyloxybiphenyl (ABP) [8,9], are important crosslinkable moieties for poly(arylene ether)s and can be synthesized by the aromatic nucleophilic substitution (S_NAr) reactions. In this work, a new phthalazinone monomer containing an allyl group (4-(3-allyl-4-hydroxyphenyl)phthalazin-1(2*H*)-one) (allyl-DHPZ) was synthesized. The PAENs with different cross-linkable group content were synthesized by copolycondensation of bisphenol monomer with 2,6-diflurobenzonitrile (DFBN). Both the synthesis and thermal crosslinking behavior of this crosslinkable polymer were discussed.

2. Experimental

2.1. Allyl-DHPZ synthesis

DHPZ (Dalian Polymer New Materials Co., Ltd.), NaOH and deionized water were constantly stirred and heated to 70 °C until it is nearly dissolved. Then the allylbromide was added to the reaction mixture. After 8 h, cold water was added and the precipitated powders were collected, washed for several times with boiling 95% ethanol, finally filtered, and dried in an oven to give 4-(4-(allyloxy)phenyl)phthalazin-1(2*H*)-one (mp 168–169 °C, yield 91.3%). FTIR (KBr, cm^{-1}): ν 3021 (s, =CH), 2931 (s, –CH$_2$), 2233 (C≡N), 1689 (C=O), 1261 (m, C–O–C); ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.63 (d, 2H), 5.30–5.53 (m, 2H), 6.07–6.17 (m, 1H), 6.99–7.13 (m, 2H), 7.49–7.61 (m, 2H), 7.72–7.88 (d, 3H), 8.56 (d, 1H), 10.73 (d, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 77.14, 114.82 (2C), 117.89, 126.72, 127.16, 127.66, 128.29, 129.31, 130.76, 131.26, 132.51, 132.72, 132.97, 158.84, 159.33.

4-(4-(Allyloxy)phenyl)phthalazin-1(2*H*)-one obtained in the previous step was kept at 200 °C under N$_2$ for 8 h and the mixture was cooled to room temperature. The precipitates were collected and purified by crystallization from boiling DMAc. The product was obtained as a white powder. Yield 81.3%; MS: 278.1066; FTIR (KBr, cm^{-1}): ν 3200–3600 (O–H), 3020 (s, =CH), 2930 (s, –CH$_2$), 2235

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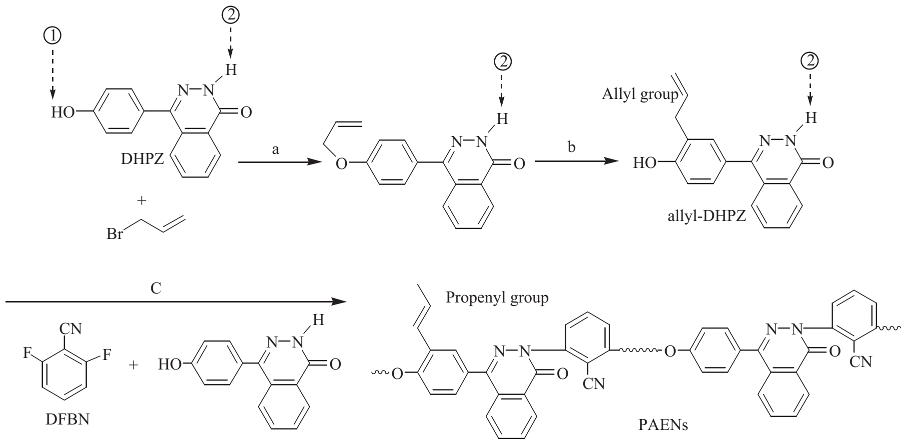

Scheme 1. Synthetic routes of PAENs. Reagents and conditions: (a) NaOH/H_2O, 70 °C, 8 h; (b) N_2, 200 °C, 8 h; (c) K_2CO_3/DMSO, 150 °C.

Table 1
Properties of PAEN.

Polymer	Yield (%)	η_{inh}[a] (dL/g)	Mn[b]	Mw[b]	PDI[c]	T_g[d] (°C)	TGA[e] (°C)	Gel content (%)
PAEN-A	96	0.75	25,062	58,403	2.33	297	506	75.7
PAEN-B	90	0.68	21,204	49,392	2.33	294	492	93.2
PAEN-C	92	0.63	19,651	45,130	2.30	283	478	97.5
PAEN-D	87	0.58	17,890	47,911	2.68	279	465	96.4
PAEN-E	83	0.65	20,134	46,774	2.32	272	453	98.6

[a] η_{inh} was measured at a concentration of 0.5 dL/g in chloroform at 25 °C.
[b] Mn, Mw values were determined by GPC in $CHCl_3$ with PS as standard.
[c] PDI values (Mw/Mn) were determined by GPC in $CHCl_3$ with PS as standard.
[d] Glass transition temperature measured by DSC with a heating rate of 10 °C/min in nitrogen before cured.
[e] Thermal decomposition temperature, defined as the temperature of 1% weight loss, at a heating rate of 20 °C/min in nitrogen after curing.

(C≡N), 1688 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.35 (d, 2H), 4.96–5.14 (m, 2H), 5.91–6.06 (m, 1H), 6.99 (m, 1H), 7.23–7.34 (m, 2H), 7. 73 (d, 1H), 7.86–7.94 (m, 2H), 8.33 (d, 1H), 9.76 (d, 1H), 12.71 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.71, 114.62, 115.67, 125.77, 126.02, 126.26, 126.69, 127.94, 128.31, 129.22, 130.64, 131.35, 133.53, 136.83, 158.72, 159.17.

2.2. Polymer synthesis

The PAEN (A–E) with different crosslinkable group content were synthesized by S_NAr polycondensation of DFBN with various content of allyl-DHPZ and DHPZ (Scheme 1). The proportions of the allyl-DHPZ/DHPZ were 0.05/0.95, 0.1/0.9, 0.2/0.8, 0.3/0.7, 0.4/0.6, respectively. PAENs with inherent viscosities ranging from 0.58 dL/g to 0.75 dL/g were readily obtained. GPC analysis of the resulting polymers revealed that they had an averaged molecular weight of over 17,890 and polydispersities in the range of 2.3–2.7 (Table 1).

2.3. Thermal curing of the PAENs

The crosslinkable PAENs were firstly dissolved in chloroform at a concentration of 30 wt%. Then the films were casted from the solution and dried at room temperature under vacuum. The thermal cross-linking processes of the films were then performed by heating the polymer films at 280 °C for 2 h under vacuum.

3. Results and discussion

Traditionally, the *O,O*′-diallyl phenols are formed by the thermal Claisen rearrangement of the corresponding bisallyloxy ethers [10]. The N–H groups (2) in the DHPZ proved to behave like phenolic O–H groups (1) [11]. Similarly, the monomer DHPZ with two allyl groups should react, like bisphenols *via* a novel *N*–allyl coupling reaction, with allylbromide using anhydrous K_2CO_3 as a base in dimethyl sulfoxide (DMSO). Due to the weaker nucleophilicity of the N^- in phthalazinone, we were not able to allylate this nitrogen. In this work, 4-(4-(allyloxy)phenyl)phthalazin-1(2*H*)-one was synthesized using NaOH as a base in water. In the ^{1}H NMR spectrum, the chemical shifts and assignments were consistent with the proposed structure of the monomer (Fig. 1).

The polycondensations used typical S_NAr procedures in the presence of DMSO and K_2CO_3 as the solvent and base, respectively. The allyl group isomerized into a 1-propenyl group under these conditions, which is a known transformation. The crosslinking density could be readily controlled by adjusting the ratio of allyl-DHPZ to DHPZ.

The solubility tests of both powdered virgin and cured PAENs were also conducted to investigate the crosslinking behavior. The virgin PAEN A–E exhibited good solubility in polar organic solvents such as $CHCl_3$, DMAc, DMF, NMP at room temperature. Therefore, it is straightforward to prepare films, coatings or fibers from the solutions of uncross-linked polymers. Both the cured powders and cured films become insoluble in organic solvents. Testing gel content of cured polymers can be done using a direct method to evaluate the content of curing reaction. Thus the gel content of the powdered cured samples was tested by Soxhlet extraction according to the ASTM D2765 method. As shown in Table 1, the gel contents increased with the increase of the crosslinkable propenyl group content. In Fig. 2, The characteristic absorption peaks of the propenyl group near 1309 cm^{-1} and 974 cm^{-1} caused by the out of plane vibrations of the “–CH=CH–” almost disappeared totally after curing, indicating that propenyl pendants are efficient crosslinking groups for the synthesized polymers.

The glass transition temperature (T_g) of virgin PAEN A-E was measured by DSC at a heating rate of 10 °C/min under nitrogen atmosphere, and the DSC scanning curves are shown in Fig. 3. Their