Reactive & Functional Polymers 75 (2014) 9–15

Contents lists available at ScienceDirect

Reactive & Functional Polymers

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

The polymerization behavior and thermal properties of benzoxazine based on *o*-allylphenol and 4,4′-diaminodiphenyl methane

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ARTICLE INFO

Article history:
Received 27 September 2013
Received in revised form 28 November 2013
Accepted 2 December 2013
Available online 9 December 2013

Keywords:
Benzoxazine
o-Allylphenol
Ring opening polymerization
Dynamic mechanical properties
Thermal stability

ABSTRACT

Three bifunctional benzoxazines (*o*AP-ddm, *o*C-ddm, and P-ddm) were synthesized from 4,4′-diaminodiphenyl methane, formaldehyde, and three phenols, namely *o*-allylphenol, *o*-cresol, and phenol. The polymerization temperatures and activation energies of *o*AP-ddm and *o*C-ddm are very similar and higher than those of P-ddm; however, their reaction enthalpies exhibit inverse behavior. The storage moduli of the corresponding polybenzoxazines, P*o*AP-ddm, P*o*C-ddm, and PP-ddm, are approximately 2.1, 3.2, and 2.9 GPa at 25 °C, respectively, and their glass transition temperatures are 139, 166, and 198 °C, respectively. The thermal stabilities of P*o*AP-ddm and P*o*C-ddm are similar and lower than that of PP-ddm. The results indicate that polybenzoxazines based on *ortho*-substituted phenols provide higher flexibility than their counterparts prepared from unsubstituted phenol.

1. Introduction

Benzoxazines are oxygen- and nitrogen-containing six-membered heterocyclic compounds with one or two oxazine rings in their molecular structures, and they are generally synthesized via the Mannich reaction from phenols, primary amines, and formaldehyde. Monofunctional benzoxazines were initially synthesized from monophenols, monoamines, and formaldehyde; however, polymers with high molecular weights could not be formed [1–7]. After benzoxazines were synthesized from bisphenol-A, aniline/methylamine, and formaldehyde [8,9], it was observed that bifunctional benzoxazines could be polymerized into polybenzoxazines with excellent mechanical strength and high thermal stability. These unique advantages endow benzoxazines with a wide range of potential applications, such as in the electronics and aerospace industries, in which they can be used as resin matrices for high-performance composites. Therefore, the study of benzoxazines attracts increasing attention from academia and industries, and a series of benzoxazines have been synthesized.

Bifunctional benzoxazines can be synthesized from bisphenols (or monophenols), monoamines (or diamines), and formaldehyde. Most studies are focused on benzoxazines based on bisphenols and monoamines [8–16] because these monomers are easily synthesized from bisphenols and primary amines by varying only one component, leading to molecules with different structures. However, studies on the aromatic diamine-based benzoxazines were seldom reported early on due to the poor solubility of many aromatic diamines in the common solvents used for benzoxazine preparation, and an insoluble gel frequently formed in the synthesis reaction of benzoxazines [17–20]. Recently, some high performance benzoxazines were synthesized from aromatic diamines [19–27], including 4,4′-diaminodiphenyl methane (DDM), 4,4′-diaminodiphenyl ether (DDE), and 4,4′-diaminodiphenyl sulfone (DDS), and these compounds could be polymerized into polybenzoxazines with high glass transition temperatures (T_gs) and good thermal stability.

Introducing some special functional groups into benzoxazine molecules can improve the properties of the resultant polybenzoxazines [19,28,29], which is generally achieved via phenol-containing or amine-containing raw materials. In practice, some functional groups such as allyl [28,29], nitrile [30,31], acetylene [11,32,33], propargyl [34], methacryloyl [35], and methylol [36] are incorporated into benzoxazine molecules, which effectively enhances the T_gs and thermal stabilities of the resultant polybenzoxazines.

Allyl is generally thought to be a reactive group. For allyl-containing benzoxazines, the allyl groups can undergo free radical polymerization along with the oxazine ring-opening polymerization [29]. Practically, most allyl-containing benzoxazines are synthesized from allyl-terminated amines [29,37,38], and some *o*-allyl-terminated phenol-based benzoxazines are monofunctional monomers [28,29,39–41], except the benzoxazine based on diallyl bisphenol A [42,43]. Studies on *o*-allylphenol-based monofunctional benzoxazines demonstrate that the chain flexibility of the corresponding polybenzoxazines is high, and their T_gs are relatively low

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http://dx.doi.org/10.1016/j.reactfunctpolym.2013.12.001

[29,41], whereas studies on *o*-allylphenol-based bifunctional benzoxazines are rarely reported.

In this study, a bifunctional benzoxazine, bis(4-(8-allyl-2*H*-benzo[e][1,3]oxazin-3(4*H*)-yl)phenyl)methane (*o*AP-ddm), was synthesized from *o*-allylphenol, DDM, and formaldehyde. The chemical structure of *o*AP-ddm was confirmed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and elemental analysis. The thermally activated polymerization behavior of the *o*AP-ddm monomer was investigated by FTIR, solid-state ^{13}C NMR, and differential scanning calorimetry (DSC). Moreover, the dynamic mechanical properties and the thermal stability of the corresponding polybenzoxazine (P*o*AP-ddm) were investigated. In addition, to elucidate the effect of the *o*-allyl group on the polymerization reaction of *o*AP-ddm and the properties of P*o*AP-ddm, the polymerization behaviors of another two benzoxazines (*o*C-ddm and P-ddm) based on *o*-cresol and phenol with DDM were studied, and the properties of the corresponding polybenzoxazines (P*o*C-ddm and PP-ddm) were evaluated.

2. Experimental

2.1. Materials

o-allylphenol was supplied by Shandong Laizhou Hualu Accumulator Co., Ltd., China. DDM was purchased from Aladdin Chemical Reagent Co., Ltd., China. Phenol, *o*-cresol, formaldehyde (37% aqueous), toluene and chloroform were analytical reagents and were obtained from Tianjin Chemical Reagent Co., China. All of the chemicals were used as received.

2.2. Synthesis of oAP-ddm, oC-ddm, and P-ddm

In a 100-mL, three-necked round bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, 4.96 g of DDM, 8 mL of formaldehyde, and 40 mL of toluene were added. The mixture was stirred for 30 min in an ice bath before adding 6.6 mL of *o*-allylphenol. Then, the temperature was gradually increased up to reflux and stirring was maintained for approximately 22 h. Thereafter, the solvent was removed by distillation under reduced pressure, and the residue was dissolved in approximately 20 mL of chloroform. The chloroform solution was washed several times with a 3 mol/L NaOH aqueous solution and deionized water, respectively. Subsequently, the solution was washed several times with a 0.1 mol/L HCl aqueous solution and deionized water, respectively, followed by evaporation of the chloroform under reduced pressure. The product was dried at 70 °C in a vacuum oven for 24 h, and finally, a garnet brown, transparent, high viscous liquid was obtained. The yield of *o*AP-ddm was approximately 66%.

*o*C-ddm and P-ddm were synthesized using the procedure described above.

2.3. Preparation of PoAP-ddm, PoC-ddm, and PP-ddm

First, benzoxazine monomer was placed into a steel mold, and the mold was placed into a vacuum oven. Then, the vacuum oven was step-heated to 100, 120, 140, 160, and 180 °C and held at each temperature for 1 h and then at 200 °C for 6 h.

2.4. Measurements

Both ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance III 600 NMR spectrometer at a proton frequency of 600 MHz and the corresponding carbon frequency. Deuterated chloroform ($CDCl_3$) was used as the solvent, and tetramethylsilane (TMS) was used as an internal reference. Solid-state NMR experiments were performed at room temperature (25 °C) on a Bruker Avance III 400 NMR spectrometer operating at a ^{13}C resonance frequency of 100.568 MHz. The samples were analyzed under cross-polarization/magic-angle spinning (CP/MAS) conditions using 4-mm zirconia rotors at a spinning frequency of 5 kHz. A 90° pulse width of 4 ms was employed, and the CP Hartmann–Hahn contact time was set at 3.0 ms. The chemical shifts of ^{13}C spectra were externally referenced to the carbon signal of solid adamantane (38.48 ppm relative to TMS).

The FTIR spectra were obtained with a Nicolet 380 FTIR spectrometer at a resolution of 4 cm^{-1}. *o*AP-ddm was dissolved in chloroform, and the solution was coated on a KBr disk to form a thin uniform film. When the solvent was completely evaporated at approximately 40–50 °C in a vacuum oven, the disk was scanned by the FTIR spectrometer. Thereafter, the disk was placed in an oven with a fixed temperature under air atmosphere. During the polymerization reaction, the disk was removed periodically for measurements.

The quantitative analyses of C, H, N, and O were performed on an Exeter Analytical CE-440 elemental analyzer.

The non-isothermal polymerization reactions of *o*AP-ddm, *o*C-ddm, and P-ddm were monitored by a PerkinElmer Diamond differential scanning calorimeter operating in nitrogen. The three benzoxazine samples of approximately 6.5 mg were scanned at five heating rates: 5, 7.5, 10, 12.5, and 15 °C/min.

A Perkin–Elmer DMA-8000 dynamic mechanical analyzer was used to determine the dynamic storage modulus (E') and loss factor ($\tan\delta$) of P*o*AP-ddm, P*o*C-ddm, and PP-ddm using the single cantilever bending mode. Measurements were performed on rectangular specimens with dimensions of 10.0 mm × 5.7 mm × 2.3 mm by heating from approximately 25–280 °C, with a heating rate of 2 °C/min and a frequency of 1 Hz.

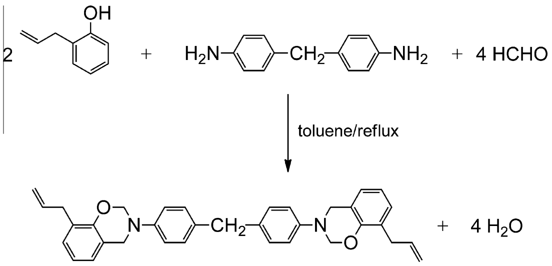
Thermogravimetric analysis was performed on a Shimadzu TGA-40 thermogravimeter, and P*o*AP-ddm, P*o*C-ddm, and PP-ddm fine powder samples of approximately 3.4 mg were heated to 800 °C at a heating rate of 10 °C/min in dynamic nitrogen.

3. Results and discussion

3.1. Synthesis and characterization of oAP-ddm

*o*AP-ddm was synthesized from *o*-allylphenol, DDM, and formaldehyde via a solution method [44]. The synthesis reaction mechanism is illustrated in Scheme 1. The chemical structure of *o*AP-ddm was confirmed by ^{1}H and ^{13}C NMR, FTIR, and elemental analysis.

Fig. 1a presents the ^{1}H NMR spectrum of *o*AP-ddm. The resonances at 5.58 and 4.81 ppm correspond to the methylene protons (H10 and H11) of O—CH_2—N and Ar—CH_2—N of the oxazine ring, respectively. The chemical shifts (ppm) at 3.69 and 3.70 (4H, H3), 5.38–5.41 (4H, H1), and 6.29–6.36 (2H, H2) correspond to the aliphatic protons in the allyl, and 4.09 (2H, H16) is assigned to the



Scheme 1. Chemical reaction of *o*AP-ddm synthesis.