

Interplay between rheological and structural evolution of benzoxazine resins during polymerization

Rongzhi Huang, Sidney O. Carson, Jorge Silva, Tarek Agag, Hatsuo Ishida, Joao M. Maia*

Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

ARTICLE INFO

Article history:

Received 22 October 2012

Received in revised form

22 January 2013

Accepted 27 January 2013

Available online 31 January 2013

Keywords:

Benzoxazine

Rheology

Ring-opening

ABSTRACT

The main aim of this work is to study the influence of different polymerization temperatures on the polymerization processes of phenol/diaminodiphenylmethane (P-ddm)-based benzoxazines. Small amplitude oscillatory shear (SAOS), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR) are used, and the results reveal the evolution of the rheological behavior of benzoxazine resins during polymerization. $\tan \delta$ clearly shows two peaks at lower temperatures and one of them at elevated temperatures. The first low-temperature peak is the ring-opening and the temporary structure of intermolecular hydrogen-bonding, while the second peak, which is much less outstanding in magnitude at higher temperatures, is the actual buildup of a molecular network.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Polybenzoxazines are a class of phenolic resins that possess various unusual and advantageous properties [1]. While traditional phenolics offer many useful properties and still hold the majority of the share of the thermoset market today, their use also has various problems when considering synthesis, processing, and end use. Examples of these include the use of harsh chemicals during synthesis and polymerization, large volumetric shrinkage during processing, production of water during polymerization which leads to void formation, and an inherent brittleness of the material in the polymerized and crosslinked form [2]. Polybenzoxazines offer the same advantages of traditional phenolics such as excellent mechanical strength [3], thermal and thermo-oxidative stabilities [4,5], good chemical resistance [6], abrasion resistance [7] and flame resistance [8] but eliminate most of the problems associated with them. Properties such as near-zero volumetric change upon polymerization [9,10], very high char yield [11], low water absorption [3], and a byproduct free polymerization [12] are unique to benzoxazine-based resins. Polybenzoxazines also show various forms of hydrogen-bonding within the final chemical structure, which contribute greatly to its unique properties [13,14]. Relatively high polymerization temperature can be inconvenient for some applications and, as is for all thermosetting resins, the

improvement in toughness may sometimes be needed, although polymeric benzoxazine precursors, such as main-chain and side-chain type polybenzoxazines that can be later crosslinked, offer much better toughness characteristics [15–26]. When compared with traditional thermoset phenolics and epoxies, polybenzoxazines offer a number of useful advantages that make them an attractive alternative, in addition to offering new application opportunities using those unique properties mentioned earlier.

The potential for rich molecular design flexibility is one of the most important properties of a benzoxazine-based resin, since it makes it possible for the resin properties to be tailored specifically to an application and still offer all of the same chemical and processing advantages. It is mostly for this reason that polybenzoxazines are very viable materials that find increasing number of applications, from replacements of traditional phenolics and epoxies to specifically tailored high performance materials [1].

Chemically, benzoxazine resins are synthesized through a Mannich condensation of a phenolic derivative, an amine, and formaldehyde. Water is the sole byproduct of this monomer synthesis. The potential for molecular versatility comes from the wide availability of phenolic derivatives and primary amine compounds that can be used in the production of the material. To form a crosslinked thermoset structure, multifunctional phenolics and amines are used. Perhaps the most common form of benzoxazine resin that exemplifies all of the resin family's typical properties is produced from bisphenol-A and aniline, commonly designated as BA-a [12,27–29]. Another common variation of bifunctional benzoxazines, which is more advanced in heat resistance and electrical

* Corresponding author.

E-mail address: joao.maia@case.edu (J.M. Maia).

insulation than BA-a, is based on methylene dianiline, and is designated as P-ddm [30] and its cationic ring-opening mechanism (the same as for BA-a) is shown in Fig. 1.

The aim of this study is to understand the rheological evolution of phenol and methylene dianiline (P-ddm) benzoxazines, which is essential to its successful processing. The polymerization kinetics of benzoxazines by using differential scanning calorimetry (DSC) has been reported elsewhere [27,31–34]. However, by combining this with rheological means we expect to establish a complete and fundamental understanding of the kinetics, and monitor how benzoxazine acts over different polymerization temperatures. This has not been done before. In particular, the polymerization kinetics was extensively studied using Rheometer, DSC, and Fourier transform infrared spectroscopy (FT-IR).

2. Experimental

2.1. Preparation of benzoxazine monomer, bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-yl)methane (abbreviated as P-ddm)

110 g P-ddm was synthesized according to the modified method of the procedure for the difficult aromatic amines [35]. Some of the possible structures in these as-synthesized benzoxazines are shown in Fig. 1. Diaminodiphenylmethane (DDM) (>99%), para-formaldehyde (96%), aniline, 1,4-dioxane, and a mixture of xylene isomers were purchased from Aldrich Chemical Company. All chemicals were used without further purification.

2.2. Characterization

2.2.1. Proton nuclear magnetic resonance (^1H NMR) spectroscopy

^1H NMR spectra were acquired in deuterated dimethyl sulfoxide on a Varian Oxford AS600 at a proton frequency of 600 MHz. The average number of transients for ^1H is 64. A relaxation time of 10 s was used for the integrated intensity determination of ^1H NMR spectra.

2.2.2. Rheological analysis

Rheological analysis was performed for P-ddm (~0.7 g) using an Anton Paar Rheometer (Model Physica MCR 501) and 25 mm disposable parallel plates. Small amplitude oscillatory shear (SAOS) time sweep experiments over temperatures ranging from 140 °C to 220 °C in increments of 20 °C and temperature sweep from 140 °C to 220 °C with heating rate of 3 °C/min were performed using a constant frequency of 10 rad/s for all experiments. During the measurements, the stress was continuously increased between 10 Pa and 600 Pa, so as to maintain an acceptable signal strength, *i.e.*, a high enough strain to produce consistent and reproducible results, while keeping the materials' response in the linear viscoelastic regime as polymerization progresses. Stress relaxation

experiments with a shear step strain of 10% were performed on fresh P-ddm samples, as well as on samples corresponding to critical stages during the polymerization process (which will be explained later) at 140 °C. In these cases the experiment was stopped and the temperature lowered to 110 °C so as to prevent further polymerization within the testing time scale.

2.2.3. Differential scanning calorimetry (DSC)

To study the non-isothermal behavior of P-ddm benzoxazines, differential scanning calorimetric (DSC) analysis was carried out on a TA Instruments Q-100 DSC. Non-isothermal experiments on monomer at a ramp rate of 3 °C/min, or products collected at certain polymerization stages at 10 °C/min were carried out from 0 °C to 300 °C. The reaction was considered complete when the curves leveled off to the baseline and no more drastic changes in heat were observed. Experiments were always performed below 300 °C to prevent any possible degradation inside the chamber. After the exothermic peak, when the DSC curve reached the baseline level again, the sample was cooled rapidly to 0 °C. Further heating of the sample was done to determine the residual heat of reaction.

2.2.4. Fourier transform infrared (FT-IR) spectroscopy

Fourier transform infrared (FT-IR) spectra were obtained using a Bomem Michelson MB100 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Co-added spectra of 32 scans were recorded at a resolution of 4 cm^{-1} . Transmission spectra were obtained at room temperature using the KBr pellet technique for partially or completely polymerized samples.

3. Results and discussion

3.1. Synthesis and characterization of P-ddm

^1H NMR spectrum of P-ddm is shown in Fig. 2. ($(\text{CD}_3)_2\text{SO}$, 600 MHz, δ): 6.49–7.39 ppm (Ar–H), 5.33 ppm (O–CH₂–N), 4.54 ppm (O–CH₂–N), 3.67 ppm (Ar–CH₂–Ar), 2.47 ppm ($(\text{CD}_3)_2\text{SO}$), 3.30 ppm (H_2O), 3.54 ppm (dioxane). The oxazine ring content in the whole composition can be calculated by the following equation:

$$\text{Ring content}(\%) = \frac{I}{2I'} \times 100$$

where I is the integrated intensity of the methylene protons of Ar–CH₂–N in the benzoxazine ring, I' is the integrated intensity of the methylene protons of Ar–CH₂–Ar. The oxazine ring content thus determined for P-ddm is 95%. We did not attempt to further purify the monomer since this level of purity determined is similar to that of technical grades of benzoxazine monomers, so it's a production-representative sample.

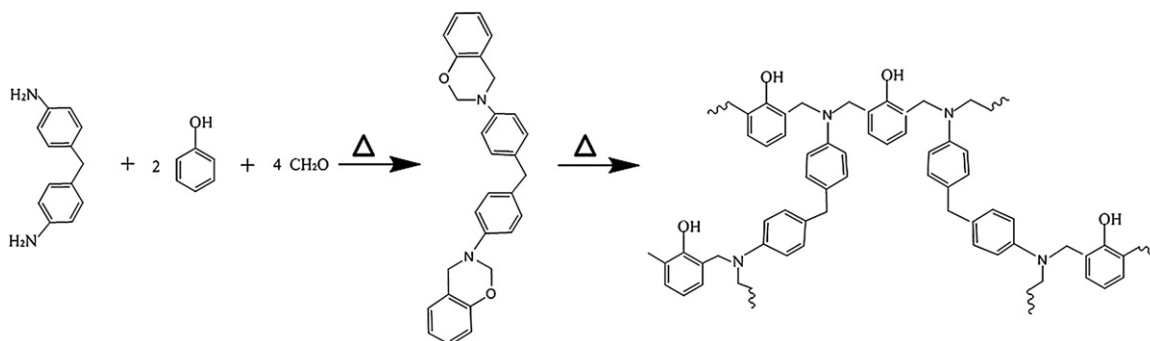


Fig. 1. Ring-opening mechanism of P-ddm.

Download English Version:

<https://daneshyari.com/en/article/5182013>

Download Persian Version:

<https://daneshyari.com/article/5182013>

[Daneshyari.com](https://daneshyari.com)