

Synthesis, polymerization kinetics, and high-frequency dielectric properties of novel main-chain benzoxazine copolymers

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ABSTRACT

Novel aromatic main-chain benzoxazine copolymer oligomers are synthesized by the Mannich reaction. Cured main-chain benzoxazine copolymers possess improved processing and high-frequency dielectric properties in comparison with corresponding main-chain benzoxazines, owing to the decreased molecular polarity and molecular weight. It should be noted that the polar/nonpolar heterogeneous solvent indeed plays a key role in the preparation of main-chain copolymer oligomers. The copolymers prepared in the optimized heterogeneous solvent condition has the least activation energy, the minimum high-frequency dielectric constants (2.81, 5 GHz; 2.75, 10 GHz), and a relatively high glass transition temperature (260 °C). Therefore, this work not only provides a simple path for improving processing and high-frequency dielectric properties of main-chain benzoxazine but also gives some insight into the effects of solvent on the formation of copolymers.

1. Introduction

In recent years, polybenzoxazines have received considerable attention in the field of the new-generation high-frequency and high-speed integrated circuits. Polybenzoxazines have a number of unique properties such as excellent mechanical properties, high char yield, near-zero volumetric shrinkage/expansion upon polymerization, low water absorption, excellent resistance to chemicals and UV light, and high glass transition temperature (T_g) even with rather low cross-linking density [1–11]. In particular, the excellent dielectric properties with a relatively low and stable dielectric constant (k) under the high frequency makes benzoxazine a good candidate for the next-generation microelectronic industry.

Main-chain benzoxazines contain benzoxazine groups as a repeating unit in the main chain, thus leading to the enhancement of thermal and mechanical properties of the cured main-chain benzoxazines [12–20]. They can be prepared by the traditional Mannich-type polycondensation of diamine, bisphenol, and formaldehyde [21,22]. However, the high-molecular-weight polybenzoxazine precursor can form the cross-linking network, thus resulting in a weak solubility and poor processing

performance. Because of the considerable molecular-design flexibility, the main-chain benzoxazine approach provides a new and simple route for designing benzoxazine copolymers. The research of benzoxazine copolymers is a challenging fundamental field because they frequently exhibit unexpected properties synergistically derived from the components [23–26]. Ishida synthesized short-chain oligomers using the isomer mixture of bisphenol-F, formaldehyde, aromatic diamine, and aniline (AN) as a reactive diluent [27]. Lin also reported the polybenzoxazine precursor from the Mannich condensation of 2,2-bis [4-(4-aminophenoxy)phenyl] propane, paraformaldehyde, bisphenol F, and phenol, in which phenol was used as a chain terminator [28]. Very recently, Zhang synthesized a new main-chain benzoxazine oligomer from bisphenol-A, 4,4'-diaminodiphenylmethane (DAM), paraformaldehyde, and o-norbornene functional phenol [29]. It should be noted that the synthesized main-chain benzoxazine oligomers have low viscosity, while maintaining the major advantages of main-chain benzoxazines [27–29]. Therefore, the design and development of novel copolymers based on main-chain benzoxazine combined with good high-frequency dielectric, thermal, and processing properties would be considered a very interesting and desirable study for their use in

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practical applications.

In theory, the reaction solvent has a profound effect on the yield of benzoxazine rings. A nonpolar solvent is found to be a favorable choice for benzoxazine formation because a polar solvent allows side reactions and initiates the ring opening of benzoxazine structure, thus leading to the poor yield of benzoxazine monomers [13]. The effects of solvent on the preparation of main-chain benzoxazine have been scarcely reported. Recently, Lin found that aromatic diamine-based main-chain polybenzoxazine precursors prepared in toluene/ethanol heterogeneous solvent exhibit higher purity and molecular weight and lead to better thermal properties than those prepared in chloroform [30]. A basic understanding of the reaction behavior and reaction mechanism for main-chain benzoxazines and their corresponding copolymers prepared with different solvents is essential for a successful research and development of new materials. Thus, the synthetic conditions such as the proper solvent in relation to reaction temperature and reaction time of main-chain benzoxazine and their copolymers should be further optimized.

In this investigation, the novel DAM-based main-chain benzoxazine copolymer oligomers are first synthesized from difunctional diamine, AN, and bisphenol-A with paraformaldehyde by the Mannich reaction. Main-chain benzoxazine copolymer films can then be obtained by the ring-opening polymerization of oxazine rings of the prepared copolymer oligomers. During the preparation process of oligomers, the hydroxyl groups at the end of main-chain benzoxazine can be further reacted with AN to form a structure terminated with oxazine rings, accompanied with the decrease in chain length and molecular polarity (Scheme 1). Therefore, it is expected that AN not only takes part in the formation of the copolymer oligomer but also lowers the viscosity and molecular weight of the precursors. In view of the backbone chemical structure, the consumed hydroxyl groups would be beneficial to reduce the molecular polarity of the aromatic diamine-based copolymers, thereby improving the dielectric properties. Furthermore, toluene and toluene/ethanol are employed as the nonpolar solvent and polar/nonpolar heterogeneous solvent, respectively, to clarify their effects on the chemical structure and high-frequency dielectric properties of main-chain benzoxazine copolymers. Only very few reports are available on the influence of solvent on the preparation and properties of main-chain benzoxazine. Therefore, this work not only provides a simple path for improving processing and high-frequency dielectric properties of main-chain benzoxazine but also gives some insight into the effects of solvent on the formation of main-chain benzoxazines.

2. Experimental

2.1. Materials

DAM (99%) and AN (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Bisphenol A was purchased from Chengdu Chemical Reagent Co., Ltd. Paraformaldehyde (96%) was obtained from Tianjin Fuchen Chemical Reagent Factory. Toluene, ethanol, and methanol were purchased from Tianjin Tianli Chemical Reagent Co.,

Table 1
Solvent effect on the synthesis of benzoxazine copolymer precursors.

Sample	Solvent	Reaction condition	Mn/Da	Mw/Da	Polydispersity index (PDI)
BAM-1	Toluene	90 °C/6 h	878	1775	2.02
BAM-2	Toluene	90 °C/7 h	872	1852	2.12
BAM-3	Toluene	90 °C/8 h	946	1903	2.01
BAM-4	Toluene	100 °C/8 h	795	1517	1.91
BAM-5	Toluene	110 °C/6 h	905	1744	1.93
BAM-6	Toluene	110 °C/8 h	913	1684	1.84
BAM-7	Toluene/ ethanol (2:1 v/v)	80 °C/6 h	750	1421	1.89
BAM-8	Toluene/ ethanol (2:1 v/v)	80 °C/8 h	771	1434	1.86
BAM-9	toluene/ ethanol (2:1 v/v)	80 °C/10 h	759	1414	1.86

Ltd. All other chemicals were used as received.

2.2. Preparation of BAM

Main-chain-type benzoxazine copolymer prepolymers were typically synthesized using bisphenol A, paraformaldehyde, DAM, and AN as starting materials by employing solution methods. The molar ratio of phenolic hydroxyl groups, amine groups, and aldehyde groups was theoretically predetermined as 1:1:2. In addition, the molar ratio of diamine to AN was 1: 2. A mixture of bisphenol A, AN, DAM, and paraformaldehyde was dissolved in the solvent and then refluxed in a flask equipped with a condenser. The detailed experimental conditions are summarized in Table 1. To remove the initial reactants and soluble part, the resulting yellow transparent liquid was precipitated by methanol and then dried in a vacuum oven at 55 °C overnight. A light yellow powder was obtained. Because the copolymer precursors were prepared from AN and DAM, we refer to them as BAM precursors. The BAM precursor samples were named as shown in Table 1.

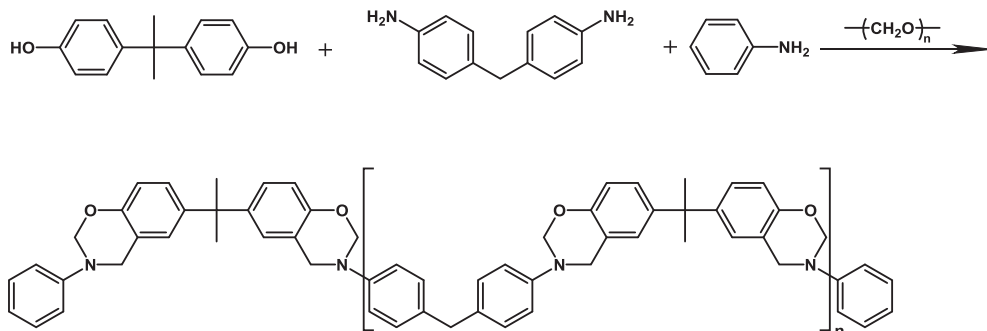
2.3. Preparation of cured copolymer films

The solvent of copolymer precursors was removed from the vacuum oven at 60–80 °C for 2 h and then cured in an ordinary oven at 100 °C for 2 h, 120 °C for 2 h, 160 °C for 2 h, 180 °C for 2 h, 200 °C for 1 h, and 220 °C for 1 h, separately. Finally, the cured BAM films were obtained after cooling down the samples naturally.

2.4. Characterizations

2.4.1. Proton nuclear magnetic resonance (¹H NMR)

¹H NMR spectra were obtained on a Bruker NMR spectrometer (AVANCE III HD, 400 MHz). All the samples were dissolved in deuterated chloroform, and tetramethylsilane (TMS) was used as an internal



Scheme 1. Preparation of main chain benzoxazine copolymer oligomers.

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