Thermally Curable Polystyrene via Click Chemistry

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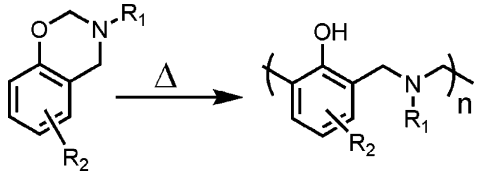
Synthesis of high-performance polymers and their high-tech applications have attracted significant attention in recent years. Conventional polymers do not offer the properties associated with thermoset polymers, and hence their applications as high-performance polymers are limited. Thermoset polymers are normally synthesized using step-growth methods where chain growth and cross-linking processes arise from the same type of chemical reaction.[1] However, thermoset polymers are not easily processable, their manufacturing is not cost-effective, and thus they remain prohibitively expensive for these applications. Cross-linking of linear polymers is one approach to improve the properties and consequently to access the demanding regimes of high-tech applications. Cross-linking of conventional polymers is readily achieved by the incorporation of a multifunctional monomer during the polymerization process.[2−6] High-energy radiation or photochemical irradiation has been used, but in addition to the cross-linking, both methods may also involve chain scission that can result in polymer degradation or the introduction of unwanted impurities.[7] Therefore, particularly in photochemical cross-linking, the incorporation of chromophoric groups into polymers absorbing selectively at irradiation wavelengths, where the polymer is transparent, is a crucial prerequisite.[8] Alternative thermal methods for the formulation of thermosetting materials usually involve Diels−Alder reactions which may suffer from the reversibility.[9,10] Thermally induced irreversible dimerization reaction of benzocyclobutene was proposed as a versatile route to form cross-linked high-performance polymers.[11]

Polybenzoxazines are class of phenolic polymers formed by thermal ring-opening of the corresponding benzoxazines without any catalyst[12−14] (Scheme 1).

They can also be polymerized at room temperature by certain conventional[15,16] and photocationic initiators.[17] In these cases, the mechanism of the polymerization is rather complex, and the resulting polymers have different structures than those obtained by thermal means. Thus, thermally produced polymers have attracted more attention due to their typical characteristics which traditional phenolic resins also exhibit, such as heat resistance, low flammability, and stable dielectric constants. In addition, polybenzoxazines provide unique characteristics like low water absorption and high dimensional stability owing to near-zero shrinkage upon curing which overcome the shortcomings of the traditional phenolic resins.[18−22] Moreover, benzoxazine monomers can easily be prepared from any phenolic compound and a primary amine with formaldehyde, and they therefore exhibit molecular design flexibility.[14,23−26] We have previously reported on several synthetic strategies to combine benzoxazine structures with conventional polymers, namely polystyrene,[27] poly(ϵ-caprolactone),[28] poly(methyl methacrylate),[29] and poly(propylene oxide).[30] The polymers contained one or two benzoxazine functionalities per chain, and thermal ring-opening copolymerization of these macromonomers with

Scheme 1. Thermal Ring-Opening Polymerization of Benzoxazines



low molar mass benzoxazines yielded cross-linked polybenzoxazines. In these cases, the polymers are linked to the network structure as dangling chains. However, the incorporation of benzoxazines as a thermally reactive group into the backbone of conventional polymers has scarcely been investigated.[31]

Recently, 1,3-dipolar cycloadditions from the reactions between azides and alkynes or nitriles, known as "click reaction",[32−34] have been recognized as a useful synthetic methodology and have been applied to macromolecular chemistry offering materials ranging from the block copolymers to the complexed macromolecular structures.[35−37] These cycloaddition reactions enabled the C−C bond formation in a quantitative yield without side reactions and requirement for additional purification steps. The click reactions are particularly important in preparative methods, in which high conversion of functional groups is desirable. Numerous applications of click chemistry in polymer science as well as molecular biology and nanoelectronics have recently been reviewed.[38,39]

We describe herein the functionalization of polystyrene with benzoxazine groups using click reaction of propargyl benzoxazine with azido-containing polystyrene. As will also be shown, these polymers undergo thermal cross-linking by ring-opening polymerization of benzoxazine groups without any catalysts.

In our study, we selected propargyl groups as thermally reactive click component since ethynyl-containing benzoxazines require multistep preparation procedures in low yield and high price.[40,41] Propargylbenzoxazine was synthesized according to the modified procedure described by Agag and Takeichi[42] (Scheme 2).

For the synthesis of parent azide functionalized polymer, we first prepared poly(styrene-*co*-chloromethylstyrene), P(S-*co*-CMS), via nitroxide-mediated radical polymerization (NMP) of styrene (S) and chloromethylstyrene (CMS) at 125 °C. The composition of copolymer was determined using ^{1}H NMR spectroscopy. The mole fractions of CMS and S were calculated from the ratio of the peak areas around 4.5 ppm, corresponding to two methylene protons of in the side chain of CMS to the total area between 6.3 and 7.4 ppm, which was attributed to the total aromatic protons. P(S-*co*-CMS) with $M_{n(GPC)} = 11.290$ and 39.8 mol % chloromethyl groups was then quantitatively converted into polystyrene−azide (PS−N_3) in the presence of NaN_3/DMF at room temperature. From the ^{1}H NMR spectrum of PS−N_3 shown in Figure 1a, it was observed that while the signal at 4.5 ppm corresponding to CH_2−Cl protons of the precursor P(S-*co*-CMS) completely disappeared, and a new signal appeared at 4.25 ppm due to CH_2 linked to azide groups. The structure of PS−N_3 was further supported by the observation from IR spectrum of the azide stretching band at 2094 cm^{-1} (Figure 2a).

The PS−N_3 was dissolved in THF and reacted with propargylbenzoxazine in the presence of CuBr/bipyridine ligand at room temperature (Scheme 3).

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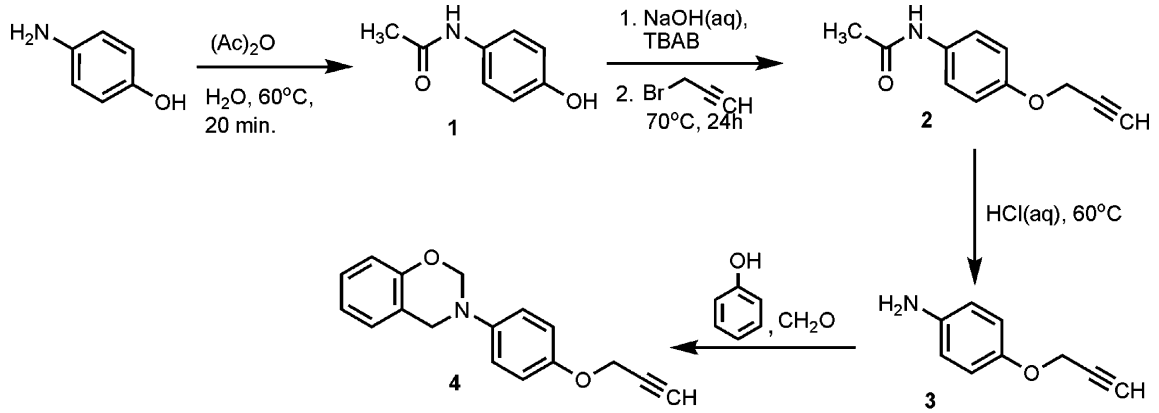
Scheme 2. Synthesis of Propargyl Ether Functional Benzoxazine



TBAB: Tetrabutylammonium bromide.

After removing the catalyst, the polymer was precipitated and dried under vacuum. As far as the ultimate use of the resulting polymer (P(S-*co*-BS)) in thermal curing is concerned, two points were important: the extent of conversion of the side azido moieties and the effect of click reaction on the stability of benzoxazine ring. The former issue was monitored by ^{1}H NMR spectroscopy by observing the disappearance of the methylene protons adjacent to the azido group (N_3-CH_2Ph) at 4.2 ppm and the appearance of the new methylene protons adjacent to the triazole ring at 5.3 ppm (triazole-CH_2Ph) (Figure 1). Moreover, the band corresponding to the $-N_3$ group at 2094 cm^{-1} completely disappeared (Figure 2a). Thus, the side group click reaction was efficient, as evidenced by near-quantitative functionalization. Moreover, general agreement between the molecular weight of the clicked polymer (M_n = 13 500) and that of the precursor azido-polymer (M_n = 7480) obtained by GPC also confirms efficient coupling. The observed increase in the molecular weight is due to the additional benzoxazine moiety incorporated. It was also of interest that whether benzoxazine ring would be preserved during the click reaction. The presence of signals in ^{1}H NMR spectra corresponding to $N-CH_2-O$ and $N-CH_2-Ar$ clearly indicates the retention of the benzoxazine ring during the click reaction (see Figure 1).

The thermal curing behavior of resulting polymer was examined by DSC. Figure 3 shows the DSC profile for benzoxazine containing polystyrene.

The thermogram shown in Figure 3 revealed two exotherms with onsets around 150 and 250 °C and a T_g of the polystyrene segment at ca. 111 °C at the first run. In general, depending on the substituents and functional groups present in the structure, the benzoxazine ring opens at the temperature range between 210 and 250 °C. Thus, the exotherm at 250 °C corresponds to the ring-opening polymerization of benzoxazine moiety and consequently cross-linking of the polymer. The unexpected second exotherm at 150 °C may be due to the transformation of 1,2,3-triazole ring. There is no information, to the best of the authors' knowledge, in the literature on the thermal stability of the triazole ring, formed via click chemistry, at elevated temperatures. Interestingly, DSC thermograms of several model compounds possessing triazole ring have also exhibited a similar exotherm. The possibility of the decomposition of the triazole ring by the evolution of nitrogen was disregarded as it would have exhibited an endotherm. Moreover, no weight loss due to the nitrogen evolution was observed in thermal gravimetric analysis (TGA) of the polymer. Additionally, the second DSC run did not show any T_g or exotherm, indicating highly densed

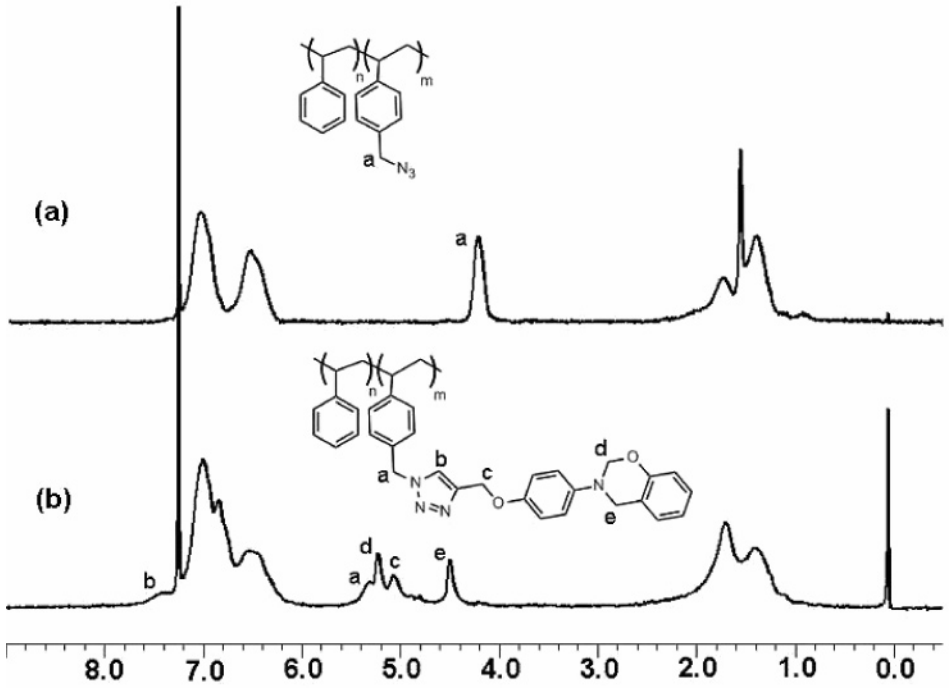


Figure 1. ^{1}H NMR spectra of (a) azide ($PS-N_3$) and (b) benzoxazine containing polystyrenes (P(S-*co*-BS)).

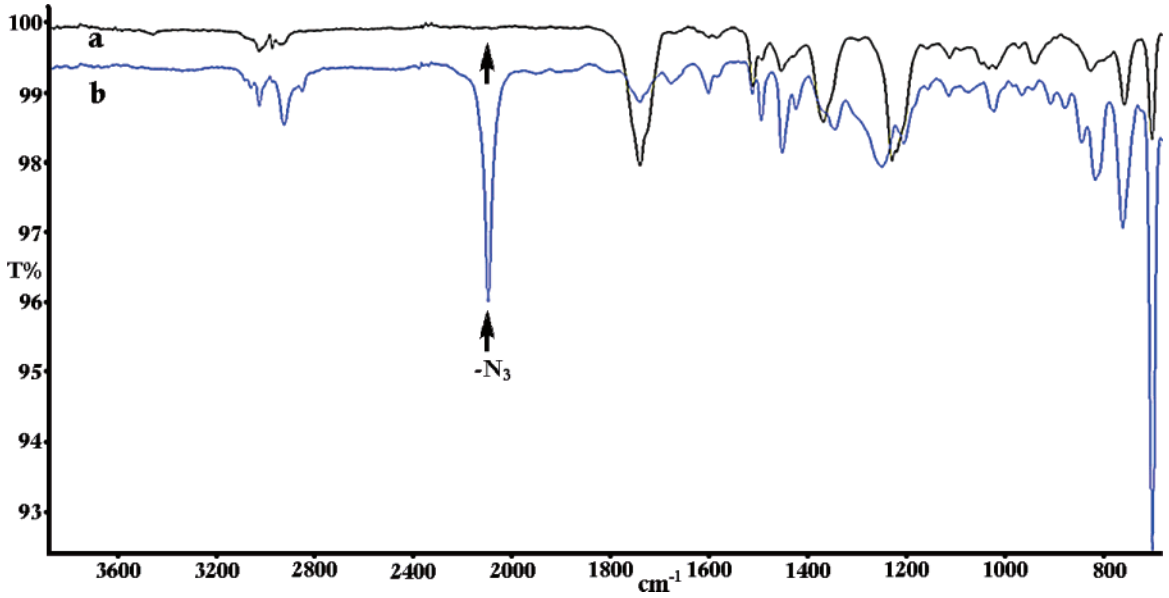
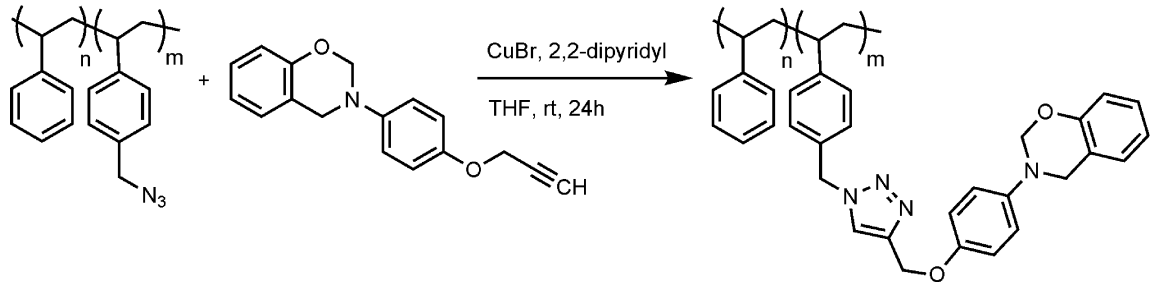


Figure 2. FT-IR spectra of (a) benzoxazine (P(S-*co*-BS)) and (b) azide (PS−N_3) containing polystyrenes.

Scheme 3. Synthesis of Polystyrene Containing Benzoxazine Side Groups (P(S-*co*-BS) by Click Chemistry



network formation and that the transformation of triazole ring did not influence the cross-linked structure. It should also be noted that the polymer was not soluble in all common solvents after the thermal treatment.

Thermal stability of the thermally cured polystyrene was investigated by TGA and compared with those of the precursor P(S-*co*-CMS) and chemically cross-linked polystyrene-*co*-divinylbenzene) (P(S-*co*-DVB). The TGA profiles presented in Figure 4 indicate that the temperatures for 5 and 10% weight loss temperatures (T_5 and T_{10}) for P(S-*co*-CMS) and P(S-*co*-DVB) are 278 and 312 °C and 206 and 322 °C, respectively, whereas for thermally cured polystyrene, T_5 and T_{10} are

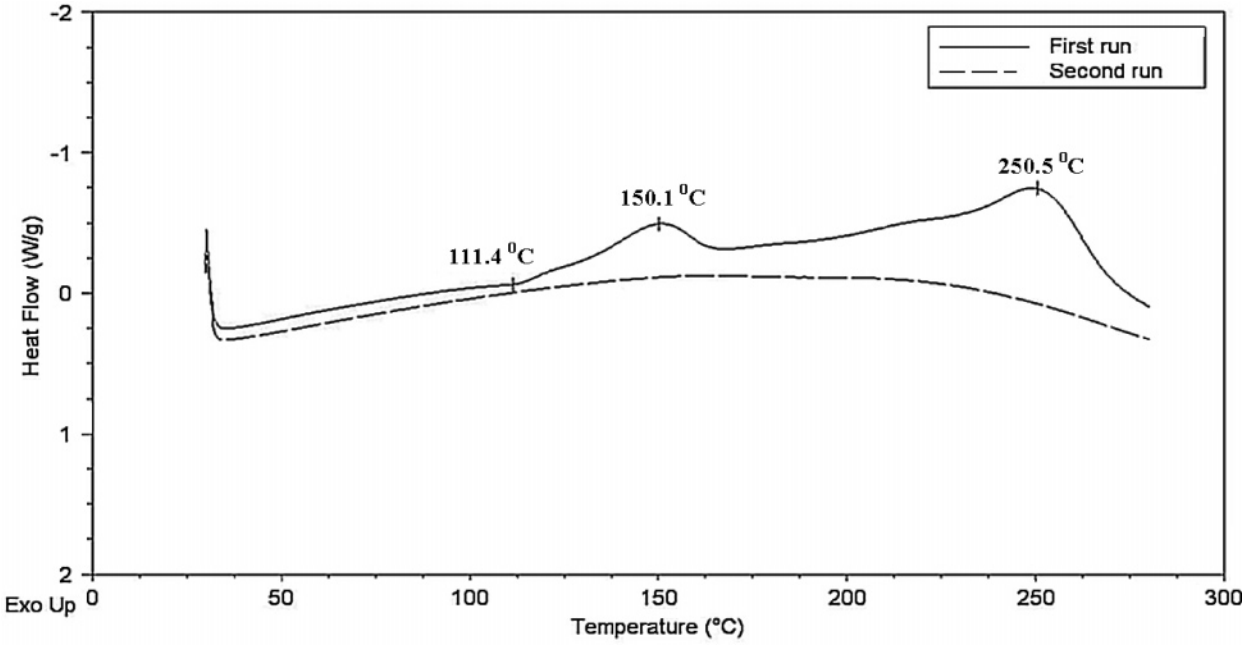


Figure 3. DSC thermogram of benzoxazine containing polystyrene (P(S-*co*-BS)).

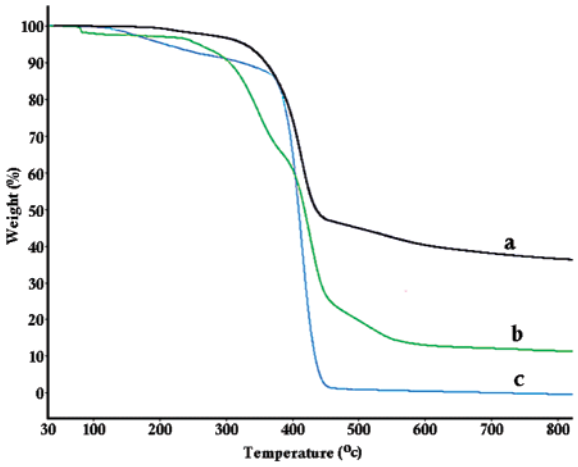


Figure 4. TGA thermogram of (a) benzoxazine containing polystyrene (P(S-*co*-BS)), (b) P(S-*co*-PCMS), and (c) P(S-*co*-DVB).

increased to 327 and 358 °C. Moreover, the char yield of the thermally cured polystyrene was 36.5% and much higher than P(S-*co*-CMS) (11.5%) and P(S-*co*-DVB) (0.0%). Another noticeable feature is that the degradation of the thermally cured polystyrene is similar to the degradation profile of polybenzoxazines.

In summary, a simple click reaction route to side-chain benzoxazine functional polymers is described. This route has the unique feature of being quantitative and at the same time preserving the benzoxazine ring structure. The benzoxazine groups have been shown to readily undergo thermal ring-opening reaction in the absence of added catalyst to form cross-linked polymer networks. The polymers cured in this way exhibited much more thermal stability than those of the structurally similar cross-linked polymers prepared by simple polymerization reactions in the presence of a conventional cross-linking agent. It is anticipated that this new family of thermally curable polymers can be used as intermediates for the design of more complex macromolecular systems such as interpenetrating networks, nanoparticles via intramolecular chain collapse,[11] and high-performance thermoset polymers when used in conjunction with low molar mass benzoxazines. Further studies along this line are now in progress.

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Supporting Information Available: Experimental procedures and ^{1}H NMR and FT-IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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