Polymer 50 (2009) 2688–2695

Contents lists available at ScienceDirect

Polymer

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

Synthesis and properties of new crosslinkable telechelics with benzoxazine moiety at the chain end

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ARTICLE INFO

Article history:
Received 10 February 2009
Received in revised form
18 March 2009
Accepted 20 March 2009
Available online 15 April 2009

Keywords:
Benzoxazine
Telechelic
Oligomer

ABSTRACT

New crosslinkable telechelics containing benzoxazine moiety at the chain end have been synthesized using oligomeric bisphenols with aromatic ether structure. The chain length of the oligomer is estimated from the size exclusion chromatography and proton nuclear magnetic resonance spectroscopy (^{1}H NMR). The degree of end-capping by benzoxazine moieties, that is estimated from ^{1}H NMR spectrum, increases during 24 h of the reaction. The telechelic is used to cast polybenzoxazine films with excellent thermal stability. Mechanical and chemical properties of these films are studied as a function of the degree of end-capping.

1. Introduction

High-temperature resistant polymers have been in demand in the past several decades for micro-electronic insulators or high-speed aircraft structures. The desired properties of polymeric material for use as a laminating resin for structural components include: retention of mechanical property over a wide range of temperature and environmental conditions, ease of fabrication, long shelf life, and no evolution of volatiles during processing. Commercially available polymer systems for high-temperature applications include epoxies, bismaleimides and polyimides. Phenolics are another major family of high-temperature polymers, which have played an important role in a variety of areas. Those areas include the construction, automotive, electrical and appliance, and advanced electronics and aerospace technology. The major advantages of phenolics are low flammability, low smoke generation and good electrical properties. On the other hand, phenolics are limited by their brittleness and release of water during condensation polymerization.

Polybenzoxazine is an alternative to many thermosets, such as phenolics, epoxies, bismaleimides and polyimides. They are synthesized by a ring-opening polymerization of aromatic oxazines [1–3]. They can provide increased flexibility in molecular design. Furthermore, they produce no polymerization byproducts. Recently, various types of oligomeric and higher molecular weight polybenzoxazines that have oxazine rings in the main chain have been synthesized. Polybenzoxazines obtained from such precursors exhibit ease of film formation and good mechanical properties [4–20]. The films made from such material represent one of rare crosslinked, self-supporting polymer films.

The aim of this work is to develop a convenient method for preparation of an oligomer that consists of aromatic ether structure as backbone with unimodal molecular weight distribution. This oligomer is then endcapped by well-defined structure, benzoxazine [21,22]. Telechelics with relatively large molecular weight oligomers allow thermoplastic-like properties when film is produced, while allowing later cross-linking for dimensional stability, chemical resistance, and high-temperature stability. It is also the aim of this work to evaluate the role of cross-linking oxazine end-capping group on the mechanical strength and chemical resistance of polybenzoxazine films.

2. Experimental

2.1. Reagent

Chemicals that were purchased from Aldrich Chemical Company (USA) include formaldehyde (37% in water), bisphenol-A (99+%), 4,4′-difluorobenzophenone (99+%), potassium carbonate (99+%), methylamine (40wt% in water), chloroform (99.9+%), dimethyl sulfoxide (99.9+%), toluene (99.9+%) and methanol (99.9%).

All the chemicals were used without further purification.

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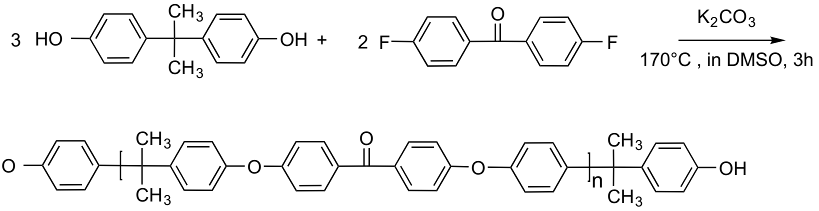
doi:10.1016/j.polymer.2009.03.053



Scheme 1. Synthesis of phenol-terminated oligomer.

2.2. Synthesis of phenol-terminated oligomers

A typical synthesis of phenol-terminated oligomers was conducted in a 100 ml round bottom flask equipped with a Dean-Stark collector, condenser and magnetic stirrer. A synthetic method designed to prepare phenol-terminated oligomers was carried out using the following general procedure as shown in Scheme 1.

To a 100-ml round bottom flask were added 4.36 g (0.02 mol) of 4,4′-difluorobenzophenone, 6.84 g (0.03 mol) of bisphenol-A, 50 g of dimethyl sulfoxide and 5 g of toluene. The mixture was stirred until all the solids dissolved and, after that, 5.56 g (0.04 mol) of potassium carbonate was added. The mixture was heated to 160 °C and stirred at this temperature for 3 h. The mixture was allowed to cool to room temperature and filtered to remove the solid portion. The filtered liquid was poured into rapidly stirred deionized water containing 1wt% acetic acid to precipitate the oligomer. The oligomer was isolated by filtration, washed twice with deionized water, and dried in a vacuum oven to yield white powder.

This oligomer was dissolved again in 50 g of dimethyl sulfoxide. The solution was poured into rapidly stirred 100 g of methanol to precipitate the oligomer. The oligomer was isolated by filtration, washed twice with methanol and dried in a vacuum oven at 100 °C to yield the oligomer as purified white powder (yield 60%).

White powder. ^{1}H NMR (600 MHz, $CHCl_3$ 298 K, ppm): 1.70 (Ar–C–CH_3), 6.30–8.0 (Ar–H).

The number average molecular weight of this oligomer obtained by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as an eluent is around 2200 Da based on the monodisperse polystyrene standards. Additionally, several samples with different molecular weight were synthesized following the same procedure but by changing the ratio of 4,4′-difluorobenzophenone and bisphenol-A.

2.3. Synthesis of the oligomer endcapped with benzoxazine

The benzoxazine-endcapped oligomer was synthesized from the above-mentioned phenol-terminated oligomers, methylamine and formaldehyde by the following procedure as shown in Scheme 2. In order to expedite the reaction, excess methylamine and formaldehyde were used.

A benzoxazine telechelic was obtained by stirring a 1:10:20 molar ratio of phenol-terminated oligomer (10 g, 0.005 mol) (Mn = 2200 Da), methylamine (40wt% in water) (3.88 g, 0.05 mol), and formaldehyde (37% in water) (8.1 g, 0.1 mol) in 70 ml of chloroform at room temperature for 30 min, then followed by refluxing in a flask equipped with a condenser. The amount of the amine and formaldehyde was in far excess possibly due to the poor reactivities of the oligomer. Stoichiometric amount of reactants failed to produce the desired compound in a reasonable period of time. Completion of the reaction was determined by sampling a small portion of the reactants and analyzing by ^{1}H NMR. After 24 h, heating was stopped and the mixture was allowed to cool to room temperature.

In order to remove the initial reactants and fractionate the higher molecular weight oligomers, the chloroform solution was poured into 300 ml of cold methanol. The precipitates were dried for 2 days under vacuum at room temperature.

White powder. ^{1}H NMR (600 MHz $CHCl_3$ 298 K, ppm): 1.60 (Ar–C–CH_3), 3.92 (Ar–CH_2–N), 4.81 (O–CH_2–N), 6.30–8.0 (Ar–H).

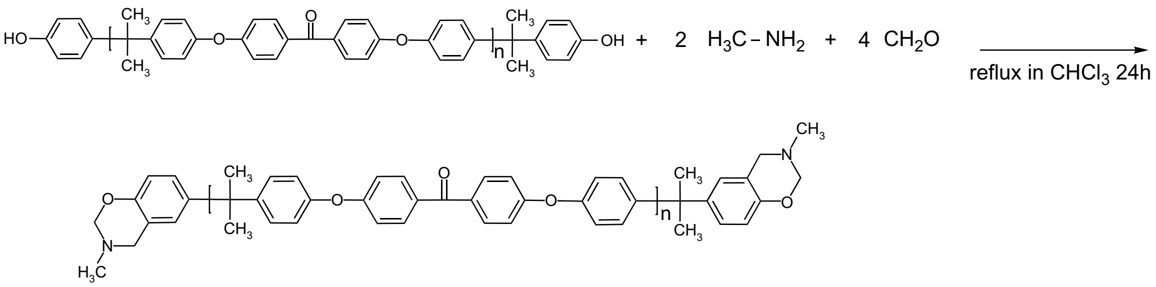
The number average molecular weight of this benzoxazine-endcapped oligomer obtained by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as an eluent was around 2600 Da based on the polystyrene standards. Additionally, several samples with different degrees of benzoxazine end-capping were synthesized following the same procedure but by changing the reaction time.

2.4. Preparation of polybenzoxazine films

The benzoxazine-endcapped oligomer powder (3 g) was dissolved in dimethylformamide (6 g), and the solution was cast on a glass plate using a doctor blade. The solvent was removed by drying at 120 °C for 1 h. Heat treatment of this film at 260 °C for 1 h gave a brown, transparent polybenzoxazine film.

2.5. Measurements

The structure of the purified compound was verified by proton (^{1}H) nuclear magnetic resonance (NMR) spectroscopy using a Varian Inova NMR spectrometer at a proton frequency of 600 MHz. Deuterated chloroform was used as a solvent for obtaining NMR



Scheme 2. Synthesis of benzoxazine-endcapped oligomer.

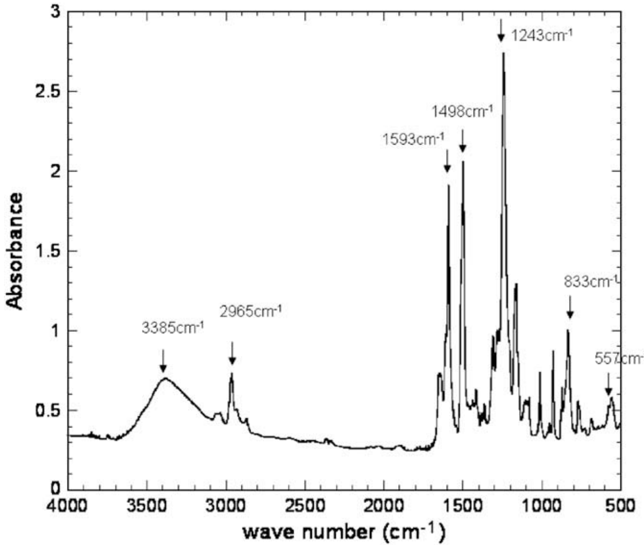


Fig. 1. FT-IR spectrum of the phenol-terminated oligomer.

spectra. Averaging 256 transients yielded ^{1}H NMR spectra with sufficient signal-to-noise ratio. A relaxation time of 10 s was used for the integrated intensity determination of ^{1}H NMR spectra.

Fourier transform infrared spectra (FT-IR) were obtained using a Bomem Michelson MB100 FT-IR spectrometer which was equipped with a deuterated triglycine sulfate (DTGS) detector. Co-addition of 32 scans was recorded at a resolution of 4 cm^{-1} after purging with dry air. The samples were prepared as KBr pellets.

Size exclusion chromatography (SEC) was performed on a Waters workstation equipped with a Waters 440 ultraviolet (UV) detector fixed at 254 nm and a Waters 440 refractive index (RI) detector. Three styragel columns with pore sizes of 1000 nm, 100 nm and 50 nm were connected in series. Tetrahydrofuran (THF) was used as the carrier solvent.

Polymerization behavior and thermal stability were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. A TA Instruments DSC Model 2920 was used with heating rate of 10 °C/min and a nitrogen flow rate of 65 ml/min for all DSC tests. All samples were crimped in hermetic aluminum pans with lids. A TA Instruments High Resolution 2950 Thermogravimetric Analyzer was used with nitrogen as a purge gas. A heating rate of 20 °C/min with a nitrogen flow rate of 90 ml/min was used for all tests.

Tensile properties were recorded with Instron Universal Testing Machine (Model 5565) at a crosshead speed of 0.1 mm/min using specimen dimensions of Type V (width 3.18 mm, length 9.53 mm, based on ASTM D638-03). Tensile properties of each sample were determined from an average of at least 5 tests.

Chemical resistance was evaluated by solvent-swelling test. A polymerized dumbbell sample with a length of 64 mm was initially immersed in 150 °C solvent (DMSO was used) for 30 min, then taken out of the solvent and kept in air at room temperature for 10 min. Then the length of the immersed sample, Lx (mm), was obtained. The degree of swelling was calculated by the following equation [23].

$$\text{The degree of swelling}(\%) = [(\mathrm{Lx} - 64)/64] \times 100$$

Chemical resistance was also evaluated by gel-fraction test [24]. A certain amount of the dry sample was extracted in a 50 ml flask with DMF at 110 °C for 24 h. The residue (gel) was immersed in MeOH at room temperature for 24 h then dried under vacuum to a constant weight. The gel fraction of polymer is the ratio of the weight of the dry residue to that of the original sample.

3. Results and discussion

Fig. 1 represents the FT-IR spectrum of the phenol-terminated oligomer. The existence of phenolic OH groups is visible in the 3500–3300 cm^{-1} region. The sharp band at 2965 cm^{-1} represents the antisymmetric CH$_3$ stretching of bisphenol-A. The strong band

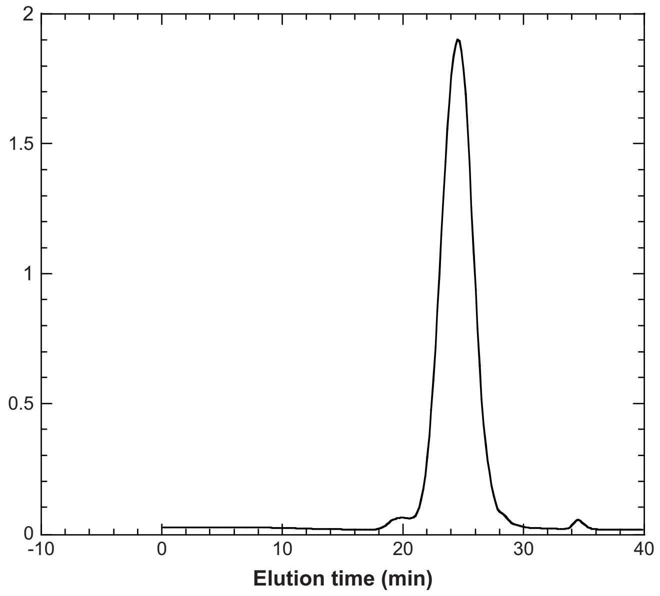


Fig. 2. SEC spectrum of the phenol-terminated oligomer (Mw = 2750, Mn = 2200, PDI = 1.25).

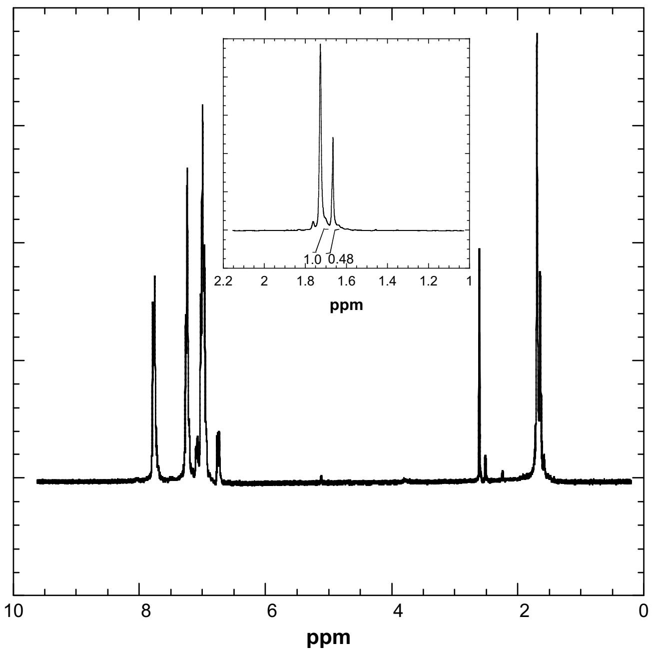
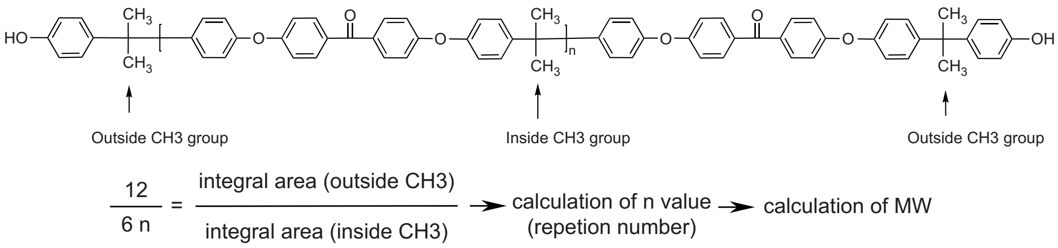


Fig. 3. ^{1}H NMR spectrum of the phenol-terminated oligomer (detailed spectrum in the 1–2 ppm region is shown in the insert).



Scheme 3. Calculation of MW from the ratio of integral area of ^{1}H NMR.

at 1243 cm^{-1} is the aromatic ether stretching. The sharp bands at 1593 cm^{-1}, 1498 cm^{-1}, 833 cm^{-1}, 557 cm^{-1} are all assigned to the para-substituted benzene ring.

The number average molecular weight of the synthesized phenol-terminated oligomers obtained by SEC with THF as eluent is 2200 Da based on the polystyrene standards as shown in Fig. 2. The oligomers have a narrow molecular weight distribution with polydispersity index of 1.25.

^{1}H NMR spectrum of the synthesized phenol-terminated oligomer is shown in Fig. 3. It features well-distinguished resonances of methyl groups of bisphenol-A at 1.70 ppm and aromatic structure at the 6–8 ppm region. Detailed analysis of the spectrum in the vicinity of 1.70 ppm allows the identification of the end groups as shown in the insert in Fig. 3. Under the assumption that chemical shift of 1.66 ppm is assigned to the methyl group resonance of bisphenol-A at the chain end and the chemical shift of 1.77 ppm is assigned to the methyl group resonance of bisphenol-A in the main chain, one can determine the degree of polymerization of the phenol-terminated oligomers as shown in Scheme 3. The calculated molecular weight is 2327. This value is in good agreement with the estimated number average chain length from SEC which is described above suggesting that the assumption of the chemical shift described above is correct. Results of estimated molecular weight of different samples are listed in Table 1. The SEC and NMR results are in good agreement.

Fig. 4 shows the ^{1}H NMR spectrum of the synthesized benzoxazine-endcapped oligomer. It features a well-distinguished resonance of the methyl groups of bisphenol-A at 1.70 ppm and the aromatic structure resonances at the 6–8 ppm region. The characteristic benzoxazine resonance at 3.92 ppm is assigned to the methylene group of the benzoxazine ring (benzene–CH_2–N) and also the resonance at 4.81 ppm is assigned to another methylene group of the benzoxazine ring (O–CH_2–N) [1].

Using the ratio of peak area between the peak at 1.66 ppm and the peak at 4.81 ppm, one can determine the degree of end-capping by the benzoxazine group as shown in Scheme 4. Using this equation, the degree of end-capping of the oligomer is calculated to be 96%. The degree of end-capping as a function of reaction time is shown in Fig. 5, suggesting that it takes 24 h to complete this reaction under the conditions employed.

One of the important characteristics of the telechelics with relatively large oligomer core is their ability to cast film. Preparing a self-supported film using a monomeric benzoxazine resin has been difficult. Thus, determining the film strength of the thermosetting telechelics is of great interest. The stress–strain curves of the benzoxazine-endcapped oligomer with different degrees of end-capping are shown in Fig. 6 and the tensile strength, Young's modulus and strain at break are summarized in Table 2.

In general, thermosetting resins are very brittle. For many applications with advantageous properties of thermosetting resins, such as dimensional stability, good chemical and thermal resistance, and ease of processing, addition of ductility is of great interest. Well-known approach of adding elastomeric materials to brittle resins has been reported to improve the ductility of polybenzoxazines derived from monomeric precursors. While improvement in ductility may be achieved using this approach, it sacrifices the intrinsic advantages of thermosetting resins. Therefore, this paper adopted a different molecular design to achieve the ductility without resorting to the thermally weak elastomeric materials. Brittleness might arise from the rigidity of the chain itself or from the existence of molecular or macroscopic defects. In this paper, influence of macroscopic defects on the mechanical properties was not evaluated. It has been reported that the chain propagation of polybenzoxazine is in competition with the intramolecular hydrogen bond formation of the propagating species [25]. This interaction is suspected to lead the polybenzoxazines that

Table 1
Comparison of the number average molecular weight of the phenol-terminated oligomer estimated from SEC and ^{1}H NMR.

Mole ratio between bisphenol-A and 4,4″-difluorobenzophenone	MW estimated by SEC	MW estimated by ^{1}H NMR
2:1	1520	1608
3:2	2200	2327
4:3	2940	3342

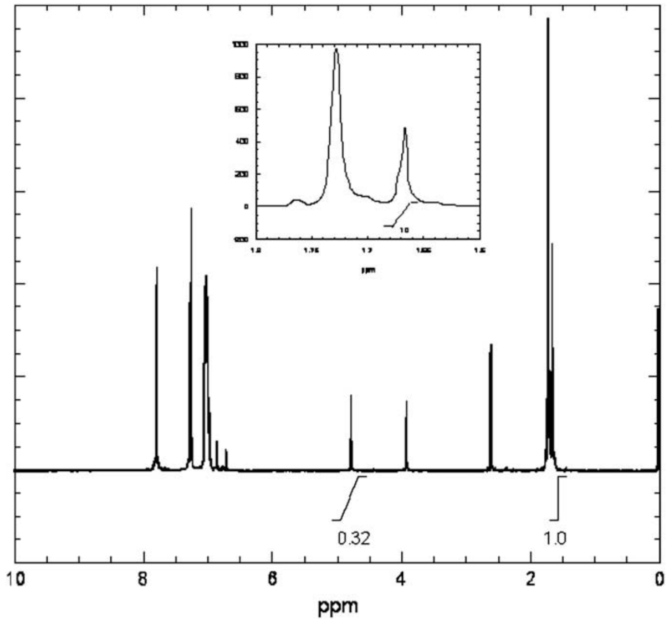
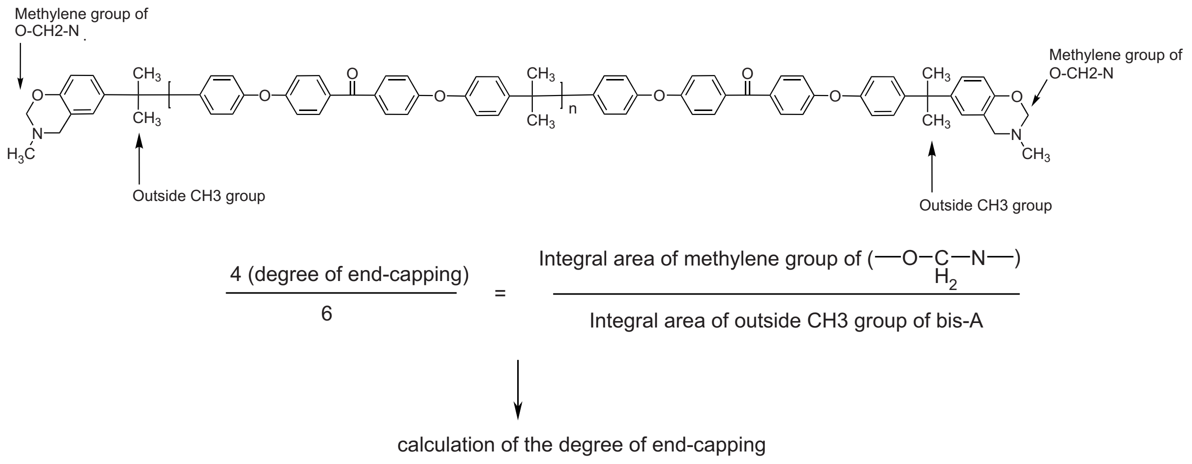


Fig. 4. ^{1}H NMR spectrum of the synthesized benzoxazine-endcapped oligomer with detailed spectrum in the 1.6–1.8 ppm region shown in the insert.



Scheme 4. Calculation of the degree of end-capping from the ratio of integral area of ^{1}H NMR.

is derived from monomeric precursors to highly branched molecules with expected dangling group molecular defects. Having systematically controlled reactive chain-end groups will allow evaluation of the effect of molecular defects on the mechanical properties. The tensile strength is not linear with respect to the degree of end-capping and almost plateaued over 70% of degree of end-capping.

One can explain this trend by the probability of reaction at the chain end. The possibility of reaction between two ends of oligomers is summarized in Table 3. Two ends of oligomers can react and connect each other in the described fashion under the condition that at least one end is capped by benzoxazine (Case A and Case B). Then the probability of reaction between two end groups can be calculated by the equation written in Scheme 5 and plotted against the degree of end-capping in Fig. 7. The plotted line is also not linear and almost plateaued over 70% of degree of end-capping. The appearance of the curve in Fig. 7 is very similar to the trend in Fig. 6. This coincidence is quite logical because the tensile strength and the molecular weight of polymer relate each other strongly and the molecular weight of polymer is related to the probability of chain-end reaction.

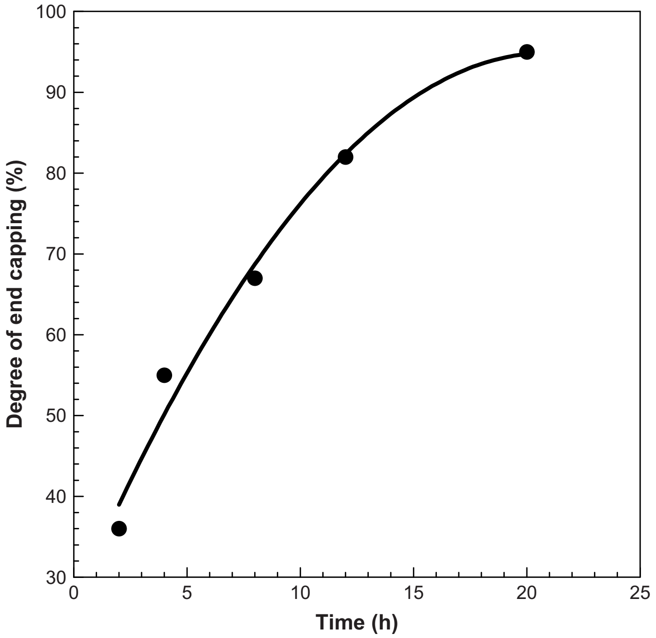


Fig. 5. Change of the degree of end-capping of benzoxazine-endcapped oligomer plotted against reaction time.

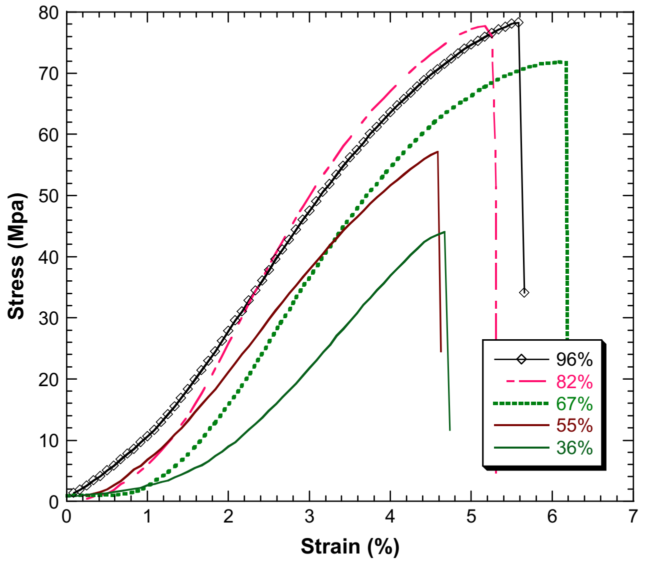


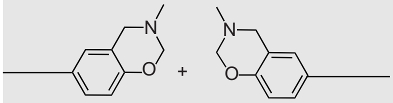
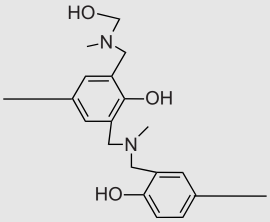
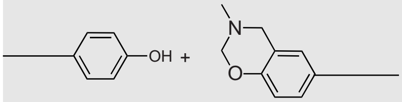
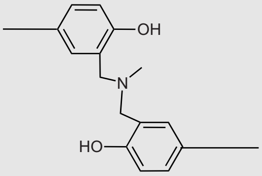
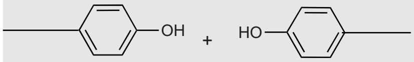
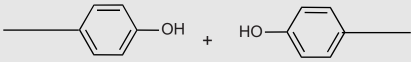
Fig. 6. Tensile stress–strain diagram of the polymerized benzoxazine-endcapped oligomer. The percentage in the insert indicates the degree of end-capping.

The polymerization behavior of the benzoxazine-endcapped oligomer was studied by DSC as shown in Fig. 8, where the DSC thermogram of the benzoxazine-endcapped oligomer juxtaposed with that of phenol-terminated oligomer. The melting transition is observed around 120 °C in both curves. This peak can be

Table 2
Mechanical properties of polymerized benzoxazine-endcapped oligomer with different degrees of end-capping.

The degree of end-capping (%)	Tensile strength (MPa)	Modulus (GPa)	Strain at break (%)
36	44	1.6	4.6
55	60	1.7	4.5
67	73	2.1	6.1
82	77	2.4	5.2
96	78	2.0	5.5

Table 3
Possibility of reaction between various pair of end group.

Two chain ends in the vicinity	Possibility of reaction between two ends
[Case A] 	Reaction is possible in the fashion illustrated below. 
[Case B] 	Reaction is possible in the fashion illustrated below. 
[Case C] 	Reaction is impossible. 

assigned to the melting endotherm of the main chain. The exothermic peak centered at 265 °C is the ring-opening polymerization of the benzoxazine-endcapped oligomer and this peak is observed only in the curve of this oligomer. This temperature is slightly higher than that of the conventional benzoxazine monomers, suggesting the low reactivity due to the lower mobility of the oligomer [26].

Thermal stability of polymerized benzoxazine-endcapped oligomer was studied by TGA as shown in Fig. 9. Main decrease occurred above 450 °C and this is mainly attributed to the degradation of the main chain itself [27]. Temperature of 5% weight reduction is 478 °C and this value is far above that of highly thermostable polybenzoxazine derived from, 6′-bis(2,3-dihydro-3-phenyl-4H-1,3-benzoxazinyl)ketone, abbreviated as 44O-a [28]. This high thermal stability is explained in part due to the high thermal stability of main chain polyetherketone and also due to the low content of benzoxazine moieties. Polybenzoxazines contain C–N–C (Mannich base) bridges that link the phenolic moieties together and this chemical bonds cannot survive the high temperature [29]. The char yield of this polymer is low in comparison to many polybenzoxazines reported. This is due to the low concentration of the benzoxazine moiety as it is used only at the chain ends, while the main structure is polyetherketone that has lower char yield in comparison to polybenzoxazine.

While the benzoxazine-endcapped oligomer has relatively low content of benzoxazine moieties, this reactive oligomer is expected to be crosslinked effectively because the benzoxazine moieties are placed at the chain end. With this effective cross-linking, good chemical resistance is expected. Therefore, solvent-swelling and gel-fraction tests were performed as shown in Figs. 10 and 11. Even at a low degree of end-capping (36%), the sample retained its shape in the solvent (DMF), suggesting a well crosslinked network

$$\text{Probability of 2 non-reactive end groups in the vicinity (\%)} = 100 \times \left(1 - \frac{\text{Degree of end-capping}}{100}\right)^2$$

↓

In other cases, reaction is possible between 2 end groups in the vicinity.

↓

So, probability of reaction is calculated by equation described below.

$$\text{Probability of reaction (\%)} = 100 \times \left(1 - \left(1 - \frac{\text{Degree of end-capping}}{100}\right)^2\right)$$

Scheme 5. Calculation of the probability of reaction between two ends of oligomers.

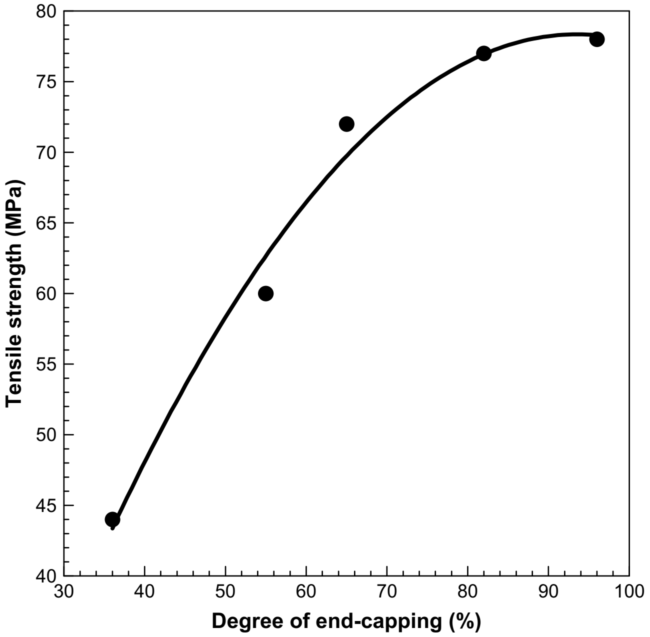


Fig. 7. Tensile strength of polymerized benzoxazine-endcapped oligomer plotted against the degree of end-capping.

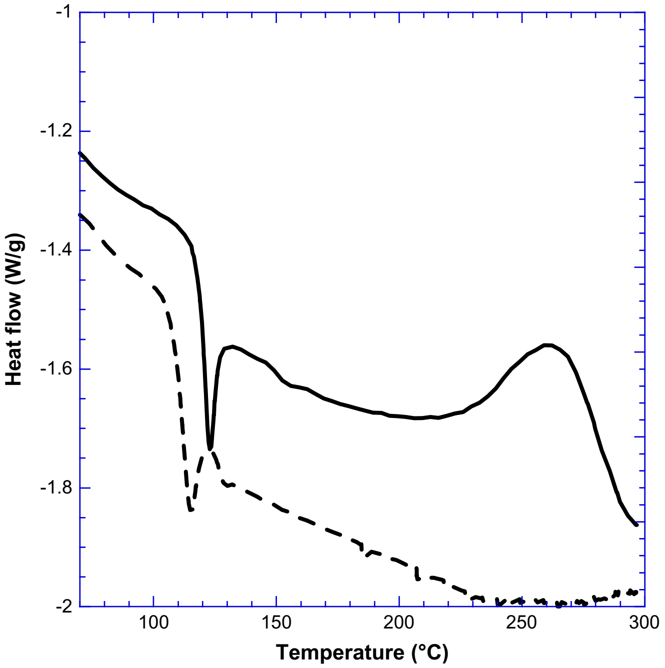


Fig. 9. DSC thermogram of benzoxazine-endcapped oligomer. Solid line: benzoxazine-endcapped oligomer, and broken line: phenol-terminated oligomer.

structure in the polymer. At this point, the degree of swelling is 28% and gel fraction is 84.8%. These values are expected to increase as the degree of end-capping increases but these values plateaued over even at the point of 55% of degree of end-capping (Fig. 12).

This fact suggests that the cross-linking reaction becomes difficult above this value. Our hypothesis on the cause of this phenomenon is as follows: the benzoxazine-endcapped oligomer with relatively low content of benzoxazine moieties reacts with the other chain end and extends its chain length as shown in Table 3 (chain extending reaction). This chain extending reaction undergoes smoothly even at a low degree of end-capping, but to achieve the network structure, another chain end (third chain end) should access to this reaction site and react to the amino-methylol functional group which is described in Table 3, Case A (cross-linking reaction). This cross-linking reaction mainly occurs at the high degree of end-capping and it does not proceed so easily because of the high viscosity of the system. Further detailed molecular characterization is needed to verify above interpretation.

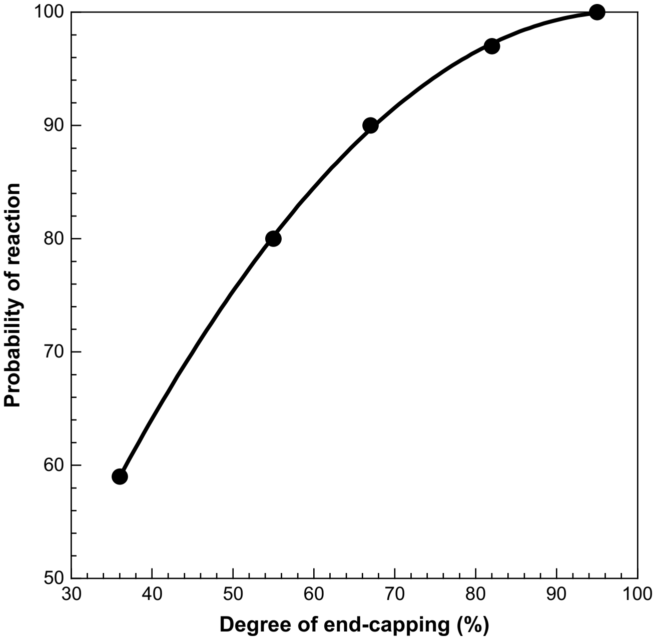


Fig. 8. Probability of reaction of two ends of oligomers (calculation results based on the equation in Scheme 5).

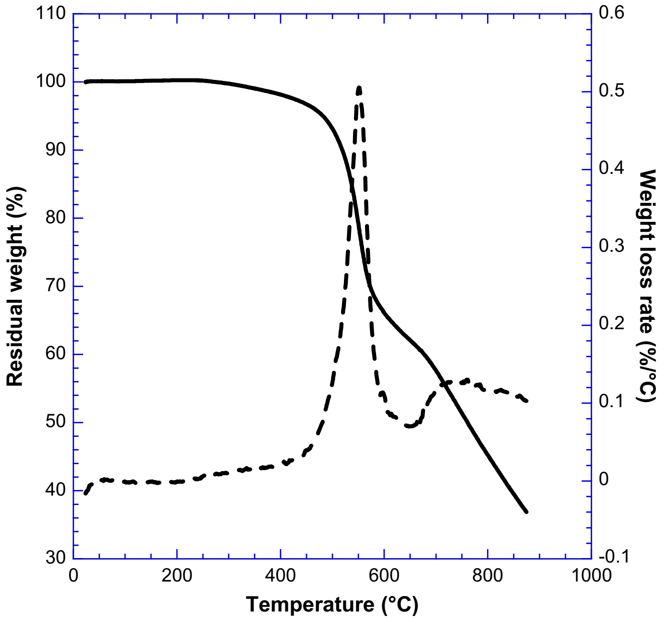


Fig. 10. TGA thermogram of polymerized benzoxazine-endcapped oligomer. Solid line: residual weight (%), and broken line: derivative weight (%/°C).

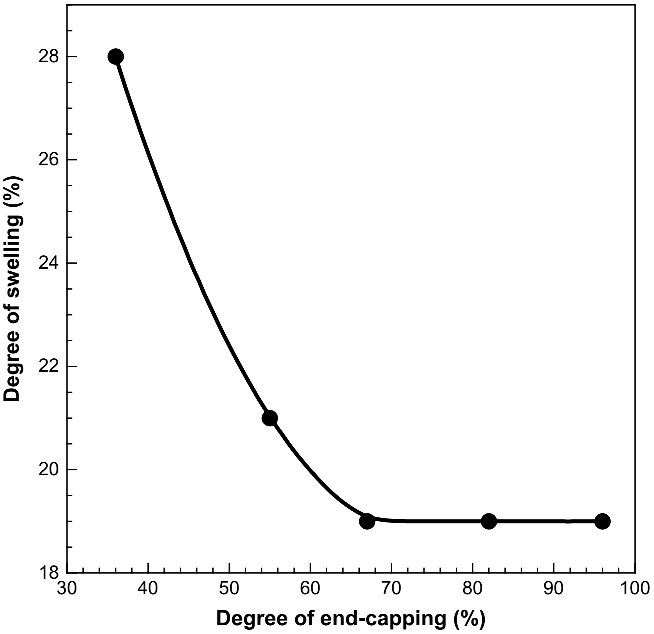


Fig. 11. The degree of swelling of polymerized benzoxazine-endcapped oligomer immersed in solvent (DMF, 80 °C).

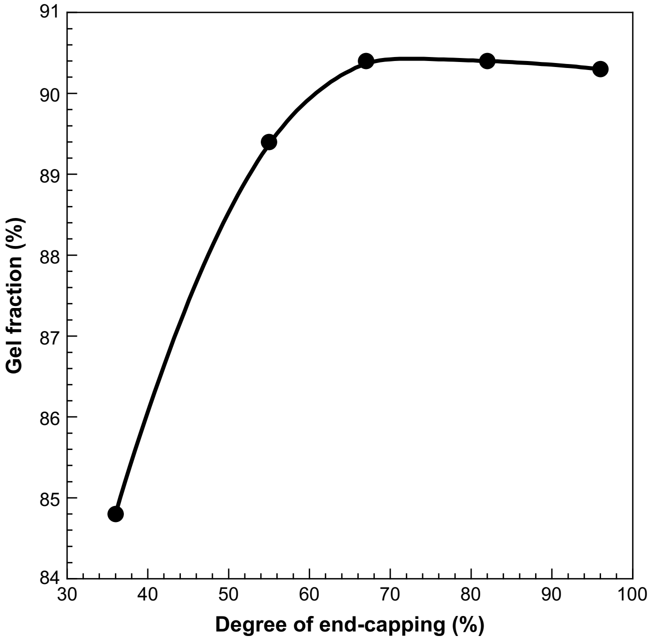


Fig. 12. Gel fraction of polymerized benzoxazine-endcapped oligomer extracted by solvent (DMF, 110 °C, 24 h).

4. Conclusion

In this study, we have successfully synthesized a new class of thermally crosslinkable oligomer consisting of aromatic ether structure as backbone with benzoxazine functional groups attached to both ends. The chemical structure was characterized by NMR, FT-IR and SEC. The quantitative and group analysis was made by proton NMR. The obtained compound is a thermoplastic oligomer with a number average molecular weight of 2200 Da and a polydispersity index of 1.25. This reactive thermoplastic can be further crosslinked using elevated temperature to produce the tough resin with good thermal stability. The mechanical property and chemical resistance of these telechelics are investigated based on the function of degree of end-capping and explained based on the mechanism of chain-end reaction.

Acknowledgment

The authors gratefully acknowledge the financial support of Sekisui Chemicals Corporation, Ltd.

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