Preparation of Polysiloxane Oligomers Bearing Benzoxazine Side Groups and Tunable Properties of Their Thermosets

Chunli Zhu, Yanze Wei, Jing Zhang, Pengfei Geng, Zaijun Lu

Key Laboratory for Special Functional Aggregated Materials of Ministry of Education, National Engineering
Research Center for colloidal materials, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100,
People's Republic of China
Correspondence to: Z. Lu (E-mail: z.lu@sdu.edu.cn)

ABSTRACT: A new pathway for the preparation of polysiloxane oligomers bearing benzoxazine side groups were reported via the hydrolysis and co-polycondensation of benzoxazinyl siloxane (SBZ) with dimethyldiethoxysilane (DEDMS). The structures of SBZ and oligomers were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. The average molecular weights of the obtained oligomers were estimated from size exclusion chromatography and ^{1}H-NMR to be in the range of 2000–4000. The oligomers gave transparent films by casting in THF solution. The films were further thermally treated to produce crosslinked films via the ring opening polymerization of benzoxazine side group. The effects of siloxane content on polymerization behavior, glass transition temperature, and mechanical properties of the polybenzoxazine thermosets were investigated. Tensile test of the films revealed that the elongation at break increased with increasing siloxane content. The elongation at break of poly(I-50) was up to 12.1%. Dynamic mechanical analysis of the thermosets showed that the T_gs were in the range of 119–165°C. Thermogravimetic analysis also revealed a better thermal stability as evidenced by the 5% weight loss temperatures in the range of 363–390°C. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40960.

INTRODUCTION

As a new class of thermosetting resin, polybenzoxazines have some unique properties, such as excellent heat resistance,[1,2] flame retardancy,[3] processability,[4] and low cost, etc.[5] They have been used in the field of halogen-free flame retardant laminates, brake pads, and insulating materials.[6,7] However, the inherent disadvantage of brittleness limits their further application. Many attempts have been done to improve the toughness of polybenzoxazines including rubber toughening,[8–10] flexible heat-resistant linear polymer toughening,[11–20] and inorganic nanoparticle toughening,[21–24] etc. Among them, rubber toughening had a significant effect to improve the flexibility of polybenzoxazines, but led to dramatically decrease of the heat resistance. Organosiloxane can overcome these shortcomings. However, it shows low compatibility with polybenzoxazine because of its low surface energy. So far, three approaches have been done to improve the compatibility of organosiloxane with polybenzoxazine and further improve the toughness of polybenzoxazines.

First approach is the introduction of the silicon element to benzoxazine monomer.[25–28] For instance, Ishida and coworkers synthe-sized 3-(triethoxysilyl-)n-propyl-3,4-dihydro-2H-1,3-benzoxazine monomer. The second approach is the in situ formation of oli-gosiloxanes in polybenzoxazine matrix.[29–31] For instance, Takei-chi and coworkers prepared the hybrids of polybenzoxazine and polydimethyl-siloxane (PDMS) by synchronizing two types of reactions: the ring-opening polymerization of 6,6'-(1-methyle-thylidene)bis-(3,4-dihydro-3-phenyl)-2H-1,3-benzoxazine and the sol–gel process of DEDMS. The homogeneous hybrid films were obtained up to 13 wt % PDMS content and showed better tensile strength and elongation at break than pristine polyben-zoxazine. At 25 wt % PDMS content, macroscopic phase separa-tion occurred.[30] The third approach is the incorporation of oligosiloxanes to main chain benzoxazenes.[32–36] For instance, Takeichi et al. prepared main-chain benzoxazine prepolymers containing polydimethylsiloxane unit from α,ω-bis(amino-propyl) polydimethylsiloxane and bisphenol-A with formalde-hyde by Mannich reaction. Tensile test of the films revealed that the elongation at break increased with increasing the molecular weight of polydimethylsiloxane unit. The elongation at break was up to 6%. Herein, we report a new pathway for the prepa-ration of polysiloxane oligomers bearing functional benzoxazine

Table I. Formation, Molecular Weight, and Ring-Opening Ratio of Polysiloxane Oligomers

Code	Formation[a]			Molecular weight		Ring-opening ratio%[d]
	SBZ g (mmol)	DEDMS g (mmol)	H_2O g (mmol)	M_n[b]	M_n (M_w)[c]	
I-0	10.0 (35.6)	0	2.6 (142)	2060	2310 (5600)	8.2
I-10	9.00 (32.0)	1.00 (6.76)	2.8 (155)	2400	3020 (6320)	8.8
I-20	8.00 (28.5)	2.00 (13.5)	3.1 (168)	2700	3200 (7520)	8.6
I-30	7.00 (24.8)	3.00 (20.3)	3.2 (180)	2510	3010 (6410)	8.5
I-40	6.00 (21.3)	4.00 (27.0)	3.4 (193)	2240	2690 (5940)	8.9
I-50	5.00 (17.8)	5.00 (33.8)	3.7 (206)	1920	2580 (5160)	9.1

[a] The weight of PTS: 5% total weight.
[b,d] Determined by ^{1}H-NMR.
[c] Determined by GPC (polystyrene standards).

side groups by copolymerization of DEDMS and 3-(dimethoxymethylsilyl-)-n-propyl-3,4-dihydro-2H-1,3-benzoxazine(SBZ). Compared with other methods, the polymers produced by this copolymerization approach exhibited better flexibility. The elongation at break of the polymer was up to 12.1%, which was the highest value in all reported similar polymers. Specifically, SBZ was synthesized by Mannich reaction of γ-aminopropyldimethoxy-methylsilane (kh660), phenol, and formaldehyde firstly. Subsequently, the copolycondensation of SBZ with DEDMS in the presence of catalyst yielded polysiloxane oligomers bearing benzoxazine side groups. The crosslinked poly(benzoxazine-co-siloxane)s were obtained via the ring opening polymerization of benzoxazine side groups. In this way, we can easily control the chain length and crosslinking density of polysiloxane, and then more easily tune the flexibility of polybenzoxazines at the molecular level.

EXPERIMENTAL

Materials
Phenol, paraformaldehyde, and p-toluenesulfonic acid were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. Chloroform was dried over CaH_2. DEDMS and kh660 were purchased from Nanjing Yudeheng Fine Chemical Co. Ltd. All other reagents and solvents were used as received.

Synthesis of 3-(dimethoxymethylsilyl-)-n-propyl-3,4-dihydro-2H-1,3-benzoxazine
In a typical experiment, a suspension of paraformaldehyde (1.26 g, 40 mmol) in 100 mL chloroform was charged to a 250-mL three-neck flask in an ice bath. About 3.26 g (20 mmol) of kh660 was added drop-wise to the system with vigorous stirring for 30 min. After adding 1.88 g (20 mmol) of phenol, the temperature was gradually increased to 62°C, and stirring was continued for another 3 h. The solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100–200) with a mixture of dichloromethane and ethyl acetate (2 : 1) as the mobile phase to give pure SBZ (4.55 g, 81%) as a yellowish liquid.

Synthesis of Polysiloxane Oligomers
A series of polysiloxane oligomers bearing benzoxazine side groups were prepared by the reaction of SBZ and different mass ratio of DEDMS. The compositions of the synthesized oligomers are illustrated in Table I. The uncrosslinked oligomers were abbreviated as I# and the crosslinked forms were poly (I#). The number (#) was used to indicate the mass percent of DEDMS/(SBZ+DEDMS). The following was an example of the synthesis of polysiloxane oligomer with a 1 : 1 mass ratio of SBZ : DEDMS. Water and DEDMS (5.0 g, 33.8 mmol) in THF (50 mL) were added to a 250-mL three-neck flask equipped with a magnetic stirrer, a reflux condenser, and a Dean-Stark trap. After stirred for 1 h, SBZ (5.0 g, 17.8 mmol) and p-toluene sulfonic acid (PTS, 0.59 g) were added to the solution. The solution was refluxed for 8 h and then removed THF with a rotary evaporator to afford a slightly yellowish viscous liquid. The viscous liquid dissolved in toluene was poured into a separating funnel. The organic phase was washed with distilled water until pH = 7, and dried with anhydrous $MgSO_4$. Toluene was removed through vacuum distillation and a slightly yellowish viscous liquid was obtained (9.24 g, yield: 79%).

Crosslinking of Polysiloxane Oligomers
The oligomers were dissolved in THF to prepare 40 wt % solutions, and the solution was cast on a glass plate. The solvent was removed by drying in an air-circulating oven at 80°C for 6 h to give transparent prepolymer films. The films were thermally treated at 100, 140, 180 and 200°C for 2 h each. The color of the film changed from yellowish to dark yellow during the crosslinking process.

Characterizations
^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 300 instrument (Bruker). CDCl$_3$ was used as the solvent. FTIR spectra were recorded on a Bruker Tensor27 FTIR spectrometer (Bruker, GM) in a range of 4000–400 cm^{-1}. Samples were prepared as KBr pellets. Differential scanning calorimetry (DSC) thermogram was recorded with a Mettler-Toledo DSC822^e instrument (Mettler-Toledo, CH) at a heating rate of 10°C/min under a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed on a Mettler-Toledo DMA/SDTA861^e instrument (Mettler-Toledo, CH), a specimen with dimensions of approximately 5.0 × 3.0 × 0.6 mm^3 was tested by a shear mode with a frequency of 1 Hz, and the sample was heated at a rate of 3°C/min from 0°C to 250°C. Thermogravimetric analysis (TGA) was performed on a TGA/DSC STAR^e instrument (Mettler-Toledo, CH) at a heating rate of 10°C/min
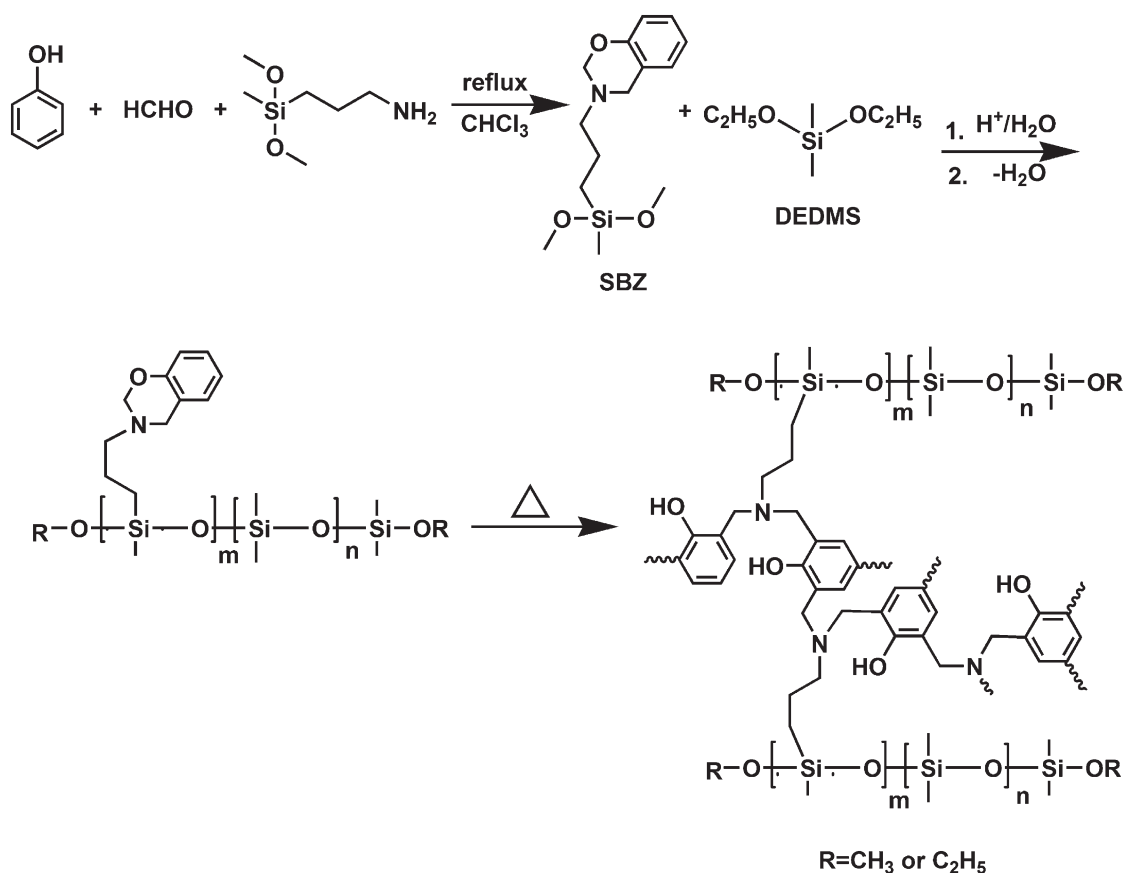
Scheme 1. Synthetic routes to poly(benzoxazine-*co*-siloxane)s.

from 30°C to 800°C under a nitrogen atmosphere. The gas flow rate was 100 mL/min. Tensile properties were recorded with Material Testing Machine Model UTM5105 at a crosshead speed of 1 mm/min using dumbbell-shaped films with dimensions of approximately $20.0 \times 5.0 \times 1.0$ mm^3. The tensile properties of each sample were determined from an average of at least five tests. Size exclusion chromatography measurements were carried out in tetrahydrofuran (1 mL/min) at 40°C with a Waters 515 liquid chromatograph (Milford, MA) equipped with three Styragel columns (HR-3, HR-4, and HR-6) and a refractive-index detector.

RESULTS AND DISCUSSION

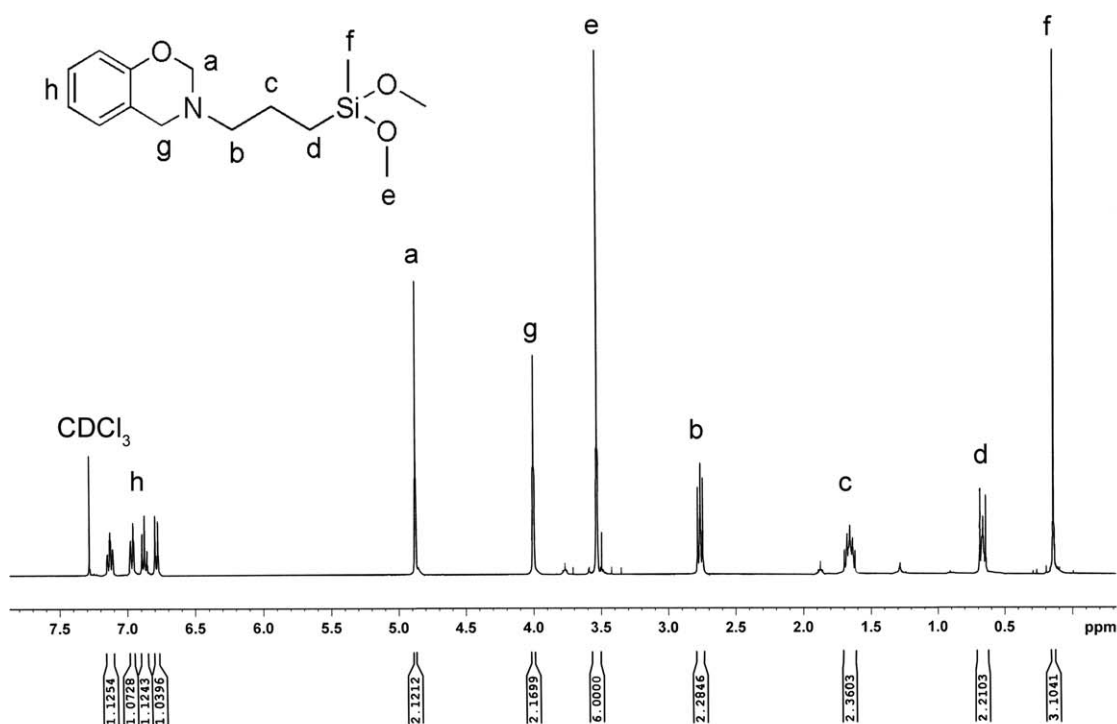### Characterization of Benzoxazine-Containing Siloxane

Scheme 1 illustrates our strategy for the preparation of poly (benzoxazine-*co*-siloxane)s. First, SBZ was synthesized using phenol, paraformaldehyde, and kh660 at a molar ratio of 1 : 2 : 1 via Mannich reaction. The obtained SBZ was easily soluble in common organic reagents, such as dichloromethane, chloroform, toluene, dioxane, ethyl acetate, and tetrahydrofuran. Subsequently, the copolycondensation of SBZ with DEDMS yielded polysiloxane oligomers bearing benzoxazine side groups. The crosslinked poly(benzoxazine-*co*-siloxane)s were obtained via the ring opening polymerization of benzoxazine side groups.

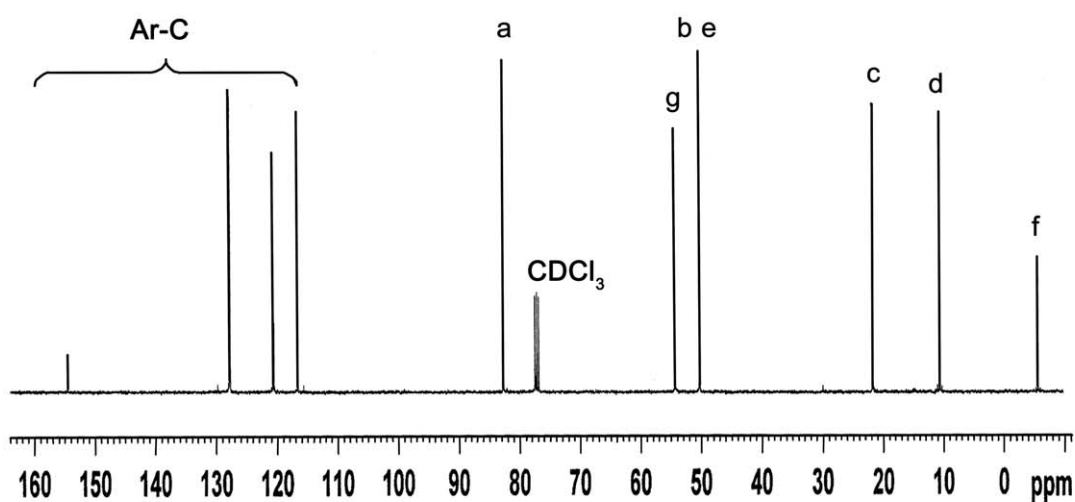Figure 1 shows the ^{1}H-NMR and ^{13}C-NMR spectra of SBZ. The characteristic proton resonances of the oxazine ring appeared as two singlets at 4.00 and 4.87 ppm which were assigned to Ar—CH$_2$—N and O—CH$_2$—N (integral ratio = 2.17 : 2.12), indicating the formation of benzoxazine ring. The methylene proton of propyl linkage was observed at 1.6(c) ppm. The N-bonded and Si-bonded methylene protons of propyl linkage were also observed at 2.7 (b) and 0.5 (d) ppm, respectively. Additionally, the peaks at 3.53 ppm and 0.14 ppm were characteristic absorptions of Si—O—CH$_3$ and Si—CH$_3$ (integral ratio = 3.1 : 6.0). The multiplets at 6.77–7.15 ppm were assigned to the protons of the aromatic ring.

^{13}C-NMR spectra further proved the structure of SBZ. The characteristic carbon resonances of the oxazine ring at 54.3 ppm for Ar—CH$_2$—N and at 82.5 ppm for O—CH$_2$—N were clearly observed, respectively. The characteristic carbon resonances of silicon linkage at 50.5 ppm for O—CH$_3$ were also clearly observed.

The structure of SBZ was also confirmed by FTIR (Figure 2). The peak at 926 cm^{-1} due to the out-of-plane C—H vibration of the benzene ring attached to an oxazine ring was clearly observed. The absorption bands at about 1230 and 1023 cm^{-1} were assigned to the typical asymmetric and symmetric stretching of C—O—C. The bands at 1498 cm^{-1} were assigned to the disubstituted benzene ring. Additionally, the strong peak at 1089 cm^{-1} was characteristic absorption of silicon alkoxy groups. The absorption of Si—CH$_3$ at 816 and 1261 cm^{-1} was also observed. Both NMR and FTIR confirmed the structure of SBZ.

Figure 1. ^{1}H-NMR and ^{13}C-NMR spectra of SBZ.

Characterization of Polysiloxane Oligomers Bearing Benzoxazine Side Groups

We chose acid as catalyst in the polycondensation process for the preparation of polysiloxane oligomers.[37,38] At first, we attempted to use inorganic acid such as HCl, H_2SO_4 to synthesize oligomers. However, the oligomers showed poor film forming properties. Subsequently, we used organic acid PTS to synthesize oligomers. A series of polysiloxane oligomers bearing benzoxazine side groups were synthesized via the hydrolysis and condensation of SBZ with different mass ratio of DEDMS (see Scheme 1). The homogeneous transparent oligomer films were obtained, indicating that no macroscopic phase separation occurred.

Figure 3 shows the SEC chromatograms of I-0, I-20, and I-40. The number average molecular weight (M_n) of polysiloxane oligomers was in the range of 2000–4000 and the polydispersity index (PDI) was 1.3–1.8. M_n data can be calculated from [1]H-
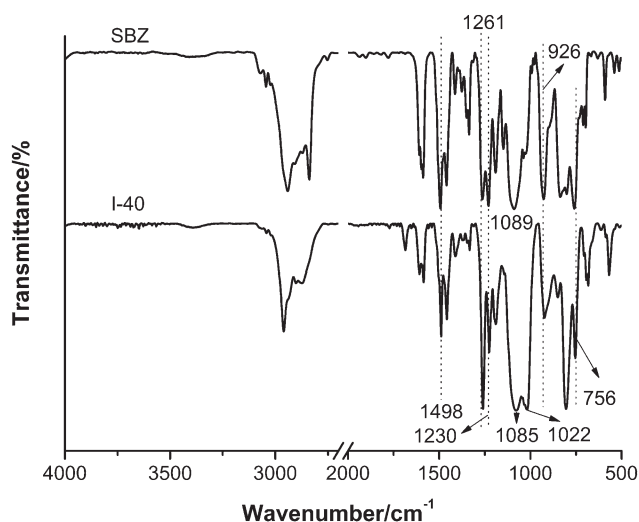
Figure 2. FTIR spectra of SBZ and I-40.

NMR. The calculating formula is $M_n = 235m + 74n = 235 \times A_1/A_2 + 74 \times (A_3 - 0.5 \times A_1)/A_2$, where m and n are the repeating unit numbers of the benzoxazine-containing siloxane and dimethyl siloxane, respectively. A_1, A_2, and A_3 are the integral areas of Si—CH$_2$—CH$_2$—CH$_2$—N, O—CH$_3$, and Si—CH$_3$, respectively. All the results measured by SEC and ^{1}H-NMR are summarized in Table I.

Figure 4 shows the ^{1}H-NMR spectra of I-0 and I-50. The characteristic proton resonances corresponding to Ar—CH$_2$—N and O—CH$_2$—N of oxazine ring appeared at 4.8 and 4.0 ppm, respectively. Their integral ratios were 1 : 0.91 of I-0 and 1 : 0.88 of I-50, respectively. The ring-opening ratios of benzoxazine rings during the copolymerization were determined by ^{1}H-NMR. The calculating formula is $R\% = 100(1 - 3I/I')$, where R is the ring-opening ratio of benzoxazine. I is the proton integral intensity of O—CH$_2$—N. I' is all the proton integral intensity of CH$_2$—CH$_2$—CH$_2$. The ring-opening ratios of the oligomers were within 10%, indicating only small amounts of oxazine ring opened. Additionally, a tiny peak of Si—O—CH$_3$ at 3.53 ppm was observed, indicating that the most of Si—O—CH$_3$ groups were consumed.

Figure 2 shows the FTIR spectra of SBZ and I-40. Compared to SBZ, the peak at 1089 cm^{-1} attributed to Si—O—CH$_3$ disappeared in the I-40 spectrum. The new peaks at 1085 cm^{-1} and 1022 cm^{-1} attributed to Si—O—Si emerged, indicating the formation of polysiloxane oligomers.[39] Meanwhile, the characteristic absorptions of benzoxazine structure (926 cm^{-1}) also existed, indicating the incorporation of benzoxazine into the polysiloxane.

Characterization of Poly(benzoxazine-co-siloxane)s

The thermal curing behavior of the polysiloxanes oligomers was studied by DSC (Figure 5). The exothermic behavior was attributed to the ring-opening polymerization of benzoxazine groups. The SBZ monomer and oligomers exhibited exothermic peak temperature at about 185–240°C. It was noteworthy that the maximum exothermic temperature of oligomers was lower than that of SBZ monomer. The reason is that small amount of phenolic hydroxyl group of the ring-opened benzoxazine worked as acid catalyst and lowered the polymerization temperature.

In order to further monitor the progress of the ring-opening polymerization of polysiloxanes oligomers, we chose I-40 as an example (Figure 6). After curing at 140°C for 2 h, the intensities of characteristic absorption bands at 926 cm^{-1} due to the benzoxazine ring and at 1498 cm^{-1} due to disubstituted benzene ring changed little, suggesting that the ring-opening polymerization did not occur at this stage. When the sample was further cured at 200°C for another 2 h, the absorption bands at 926 cm^{-1} nearly disappeared. The intensity of absorption bands at 1498 cm^{-1} due to the disubstituted benzene ring decreased. Meanwhile the intensity of absorption bands at 1456 cm^{-1} due to the tetrasubstituted benzene ring increased, suggesting that the ring-opening polymerization of I-40 occurred and afforded polybenzoxazines.

Properties of Poly(benzoxazine-co-siloxane)s

Poly(benzoxazine-co-siloxane)s were obtained via the ring-opening polymerization of benzoxazine side group. The color of the poly(benzoxazine-co-siloxane) films became shallow with increasing siloxane content. When the mass percent of DEDMS was above 50%, the tensile strengths of poly(benzoxazine-co-siloxane) films were very low. Therefore, we only investigated the mass range of DEDMS from 0% to 50%.

Thermal properties of the cured poly(benzoxazine-co-siloxane)s films were investigated by DMA and TGA. Figure 7 shows the DMA curves for the poly(benzoxazine-co-siloxane)s. The storage modulus (G') was reduced gradually with increasing siloxane content. The glass transition temperature was determined from the maxima of loss modulus (G'') and tan δ curve, and the results are summarized in Table II. T_gs showed the increase firstly (from 145°C for poly(I-0) to 165°C for poly(I-20)) and then the decrease (from 165°C for poly(I-20) to 119°C for poly(I-50)) with increasing siloxane content. When the mass percent of DEDMS was less than 20%, we speculate that the increase of T_gs may be attributed to two factors. One was that the esterification between phenolic hydroxyl group of the ring-opened benzoxazine and Si—OR group improved the crosslinking density.[40] The other was that the plasticizing effect of linear siloxane assisted the polymerization of benzoxazines, which
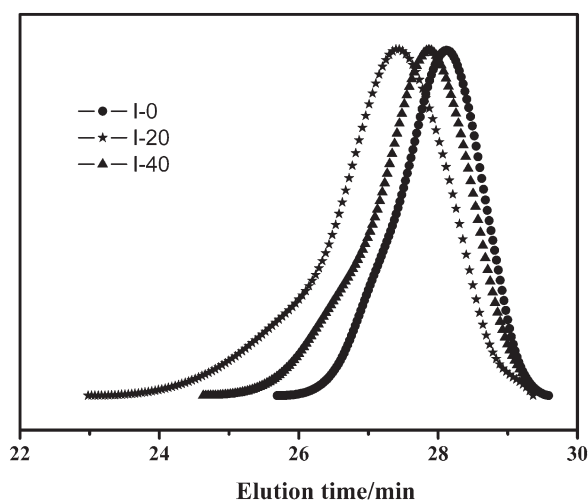

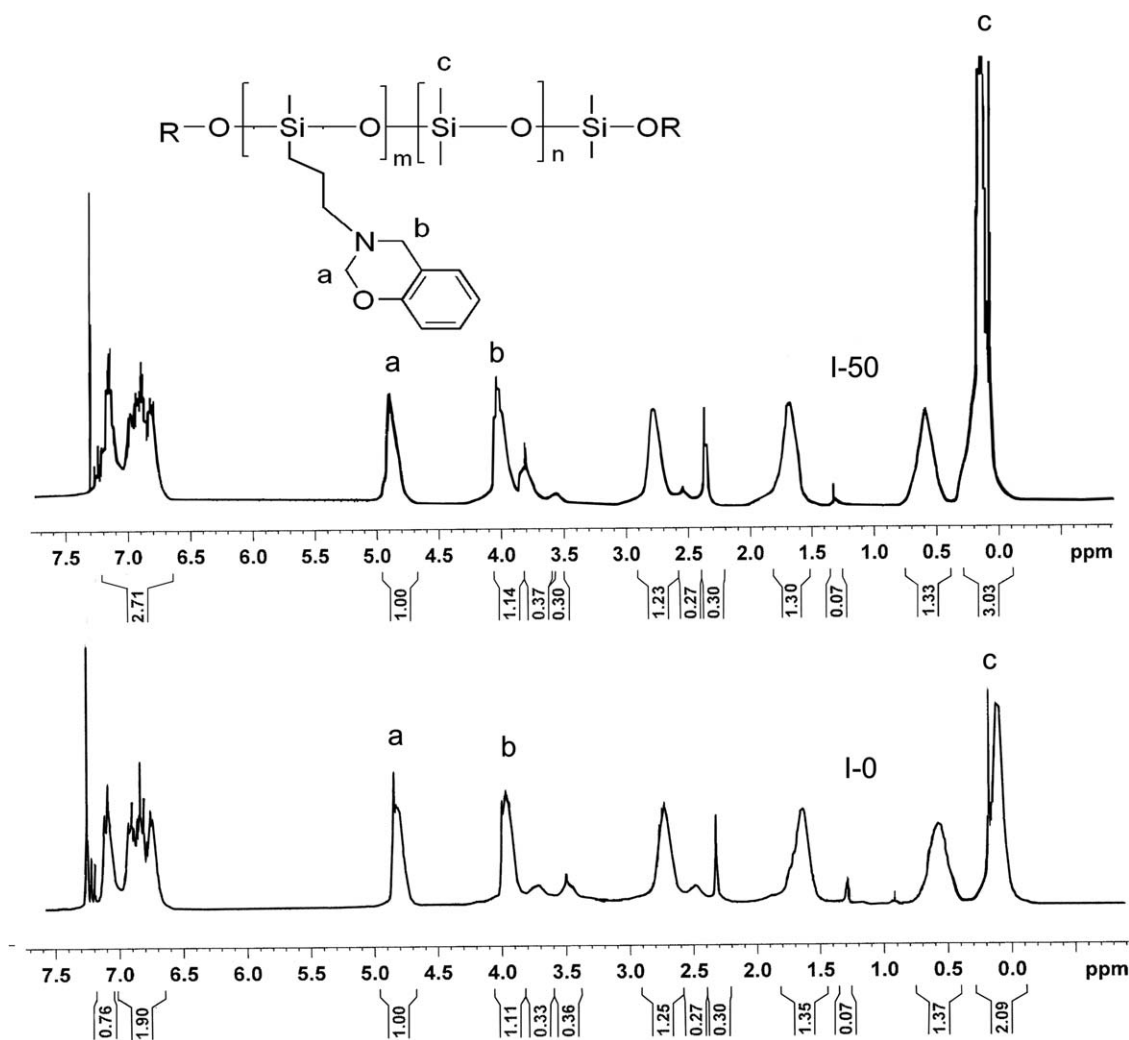**Figure 3.** SEC chromatograms of I-0, I-20, and I-40.

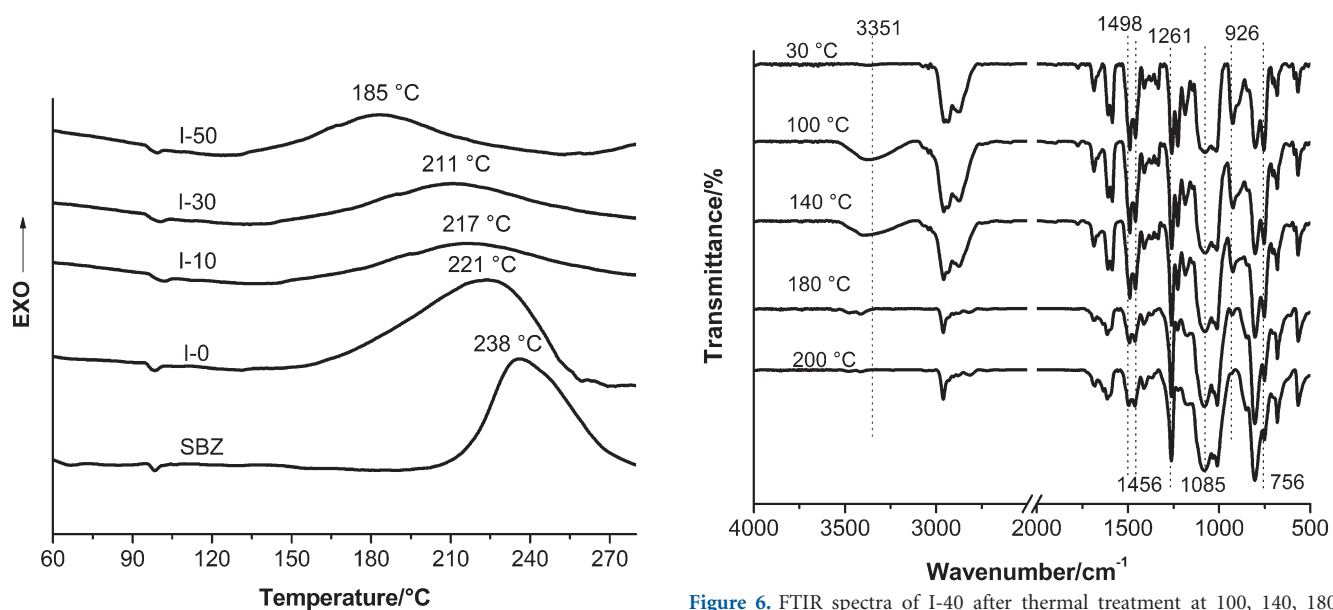**Figure 4.** ^{1}H-NMR spectra of I-0 and I-50.

Figure 5. DSC thermograms of SBZ and polysiloxanes oligomers.

Figure 6. FTIR spectra of I-40 after thermal treatment at 100, 140, 180, and 200°C.
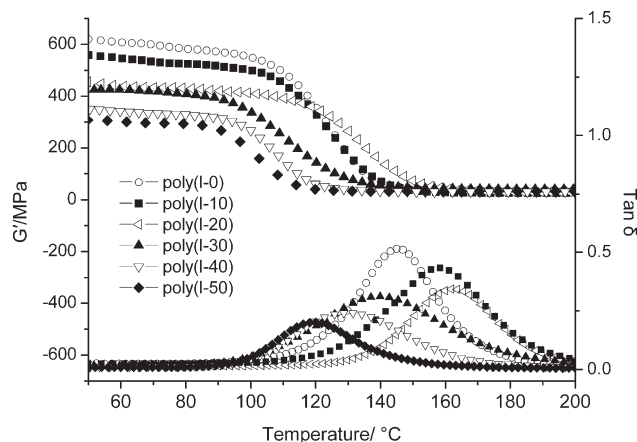
Figure 7. DMA curves for the poly(benzoxazine-*co*-siloxane)s.

Table II. Thermal Properties of Poly(benzoxazine-*co*-siloxane)s

	DMA		TGA		
	G''_{max} (°C)	tan δ_{max} (°C)	T_{d5} (°C)	T_{d10} (°C)	Char yield (wt %)
Poly(I-0)	130	145	363	404	47.3
Poly(I-10)	136	159	377	417	50.1
Poly(I-20)	140	165	381	429	51.7
Poly(I-30)	125	138	378	430	51.1
Poly(I-40)	114	131	391	433	54.3
Poly(I-50)	108	119	390	443	55.6

resulted in increasing the crosslinking density.[30,34] The decrease of T_gs was due to higher molecular chain flexibility when the siloxane content increased. Therefore, poly(I-50) showed the lowest T_g of all the polymers.

Figure 8 shows TGA thermogram of poly(benzoxazine-*co*-siloxane)s in N_2. The 5% and 10% weight-loss temperatures (T_{d5} and T_{d10}) and char yields at 800°C are shown in Table III. T_{d5} and T_{d10} of poly(benzoxazine-*co*-siloxane)s in N_2 were all above 350°C and 400°C, respectively, indicating excellent thermal
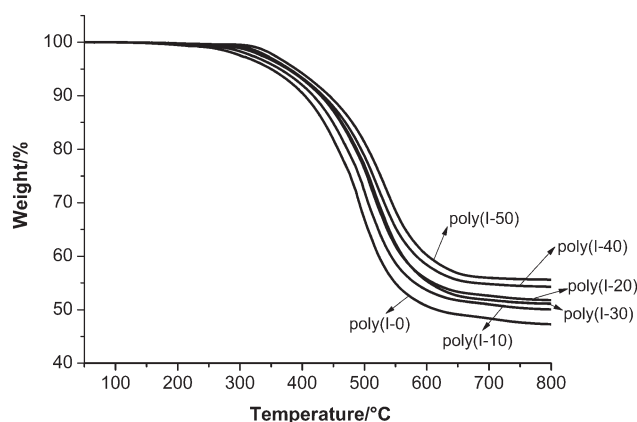
Table III. Tensile Properties of Poly(benzoxazine-*co*-siloxane)s

Code	Modulus (GPa)	Strength (MPa)	Elongation (%)
poly(I-0)	1.56	19	2.6
poly(I-10)	1.36	23	4.6
poly(I-20)	0.92	24	6.1
poly(I-30)	0.66	22	7.1
poly(I-40)	0.51	14	8.5
poly(I-50)	0.39	10	12.1

stability of poly(benzoxazine-*co*-siloxane)s. Moreover, T_{d5}, T_{d10}, and char yields at 800°C were increased with increasing siloxane content because of the good thermal stability of polysiloxanes.

Figure 9 shows stress–strain curves of poly(benzoxazine-*co*-siloxane)s. The tensile modulus, tensile strength, and elongation at break are summarized in Table III. The tensile modulus gradually decreased while the elongation at break increased with increasing siloxane content. Poly(I-0) showed the highest tensile modulus. Poly(I-50) showed the highest elongation at break of 12.1%. The tensile strength of poly(benzoxazine-*co*-siloxane)s increased firstly and decreased afterward with increasing siloxane content. Poly(I-20) showed the highest tensile strength. The results suggested that the new way to prepare poly(benzoxazine-*co*-siloxane)s was an effective approach to improve the flexibility of polybenzoxazine without excessively scarifying their thermal properties.

CONCLUSIONS

We successfully synthesized a series of polysiloxanes oligomers bearing benzoxazine side groups. Thermally ring-opening polymerization of these oligomers provided flexible, uniform polybenzoxazine films.

DSC analysis of the ring-opening polymerization showed that the polymerization temperature gradually reduced with increasing siloxane content. Thermomechanical properties of
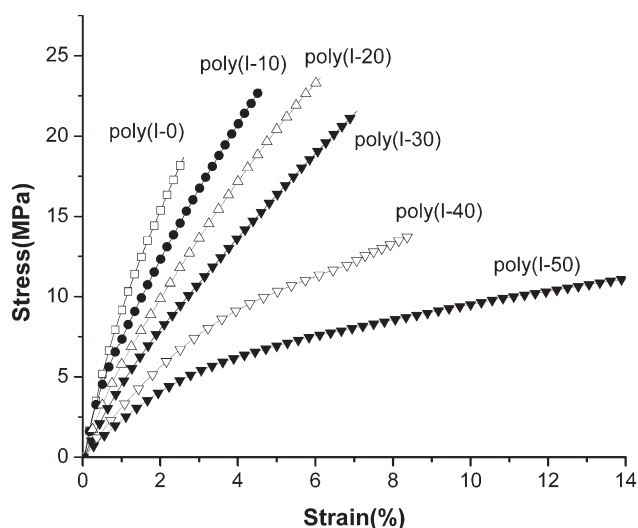

Figure 8. TGA thermogram of poly(benzoxazine-*co*-siloxane)s in N_2.

Figure 9. Stress–strain curves of poly(benzoxazine-*co*-siloxane)s.

poly(benzoxazine-*co*-siloxane)s, such as storage modulus and glass transition temperature, showed a strong dependence on siloxane content. In particular, glass transition temperatures of poly(benzoxazine-*co*-siloxane) series had a temperature range of 46°C simply by changing siloxane content. Tensile properties of poly (benzoxazine-*co*-siloxane) series showed that Young's modulus decreased and elongation at break increased with increasing siloxane content. It is important to note that polysiloxane played an important role in improving the flexibility of materials. Regarding thermal stability, the polymers all showed high 5% and 10% weight loss temperatures and additionally an increase in char yields with increasing siloxane content crosslinked network. The flexible poly(benzoxazine-*co*-siloxane) films will be beneficial in membrane and coating applications because of their improved thermal and tunable flexibility properties.

ACKNOWLEDGMENTS

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