

SYNTHESIS AND CHARACTERIZATION OF BENZOCYCLOBUTEN-4-YL ACRYLATE MONOMER AND ITS RADICAL POLYMERIZATION*

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Abstract A benzocyclobuten-4-yl acrylate (**1**) monomer was prepared by esterification of 4-hydroxybenzocyclobutene with acryloyl chloride. The radical homopolymerization of **1** and copolymerization of **1** with styrene or *n*-butyl acrylate were carried out to produce linear polymers **2a**, **2b** and **2c**. Heating of these linear polymers under thermal initiation gave corresponding cross-linked polymers **3a**, **3b** and **3c**. The ring-opening reaction in the cross-linking process was confirmed by on-line infrared spectra. Differential scanning calorimetry showed that the glass transition temperatures of linear polymers **2a** and **2b** were 83.2°C and 68.1°C, respectively. Thermogravimetric analysis of the cross-linked polymers showed that they all exhibited good thermal stability.

Keywords: Benzocyclobuten-4-yl acrylate; Polymerization; Cross-linking; Thermal stability.

INTRODUCTION

Benzocyclobutene (BCB) resins have been widely used in the microelectronics industry^[1–6] and possess many excellent properties, including low dielectric constants, low dissipation factors, low water absorption, high thermal stability, acid and alkali resistance. The four member ring of BCB can produce a highly reactive intermediate, *o*-quinodimethane, under thermal initiation which can readily undergo a crosslinking reaction to form polymers^[7, 8]. Recently, BCB units as important building blocks have been reported to form many novel structure materials due to their special structures and have exhibited broad prospects in new material construction^[9–11].

It is well known that polyacrylate and polystyrene possess excellent mechanical and electrical properties and have many important applications in many fields^[12]. The low price of them is also an attractive feature but their glass transition temperatures (T_g) are too low to be useful for most applications^[13].

In this paper, as part of our long-term interest in the study of new BCB materials, we report a new BCB monomer, benzocyclobuten-4-yl acrylate (**1**), which was synthesized by the esterification of acryloyl chloride with 4-hydroxybenzocyclobutene^[14]. Homopolymerization of **1** gave a linear polymer **2a**, while copolymerization^[15–17] of **1** with styrene (St) or *n*-butyl acrylate (BA) gave linear polymers **2b** and **2c** (Scheme 1).

The introduction of a BCB unit with crosslinkable functional groups enables the new BCB resins to achieve high T_g and thermal stability. The results show that these new crosslinked polymers (Scheme 2) have no T_g at temperatures below the onset of thermal degradation, possess good thermal stability and acid-alkali resistance

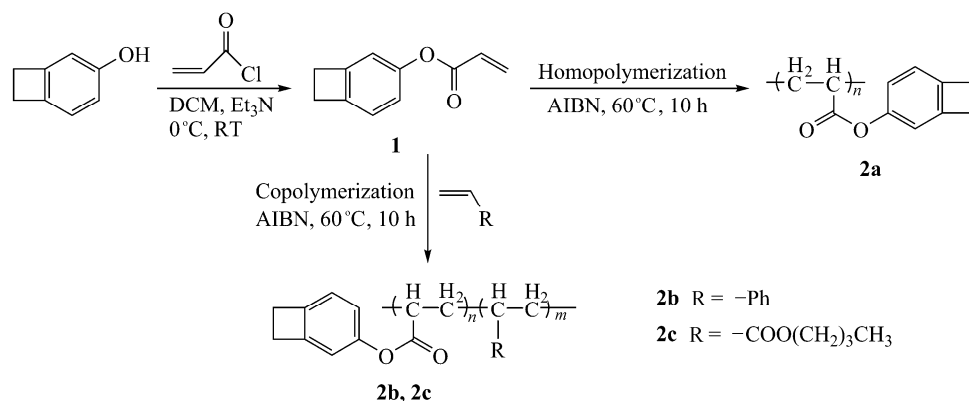
* This work was financially supported by the National Natural Science Foundation of China (Nos. 20571046, 10976024).

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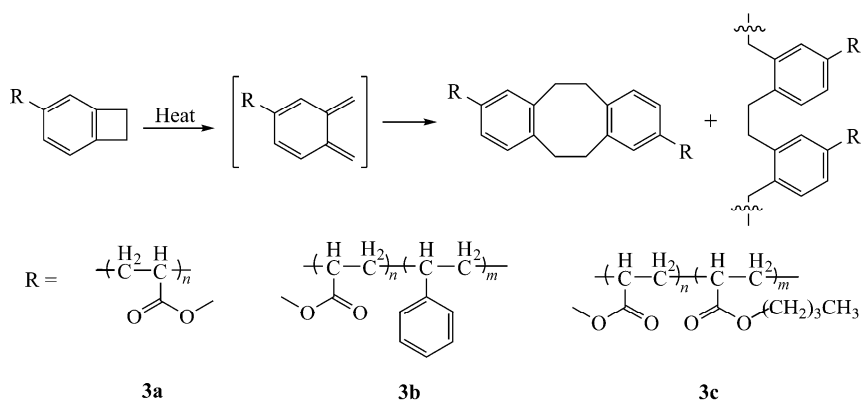
Received October 27, 2009; Revised December 17, 2009; Accepted December 24, 2009

doi: 10.1007/s10118-010-9160-4

and, importantly, they are insoluble in usual solvents. This method is simple which could be applied in the synthesis of many new polymers. We also expect that these new polymers will be able to be used as high-performance coating materials or functional membranes.



Scheme 1 Synthesis of benzocyclobuten-4-yl acrylate and polymerization using AIBN as an initiator



Scheme 2 The conceivable crosslinking process of the linear polymers

EXPERIMENTAL

Materials and Measurements

4-Hydroxybenzocyclobutene (> 97%) and acryloyl chloride (96%) were purchased from Chemtarget Technologies Co., Ltd. (Mianyang, China) and Alfa Aesar Co., respectively, and used without further purification. Styrene and *n*-butyl acrylate were dried over calcium hydride, distilled under vacuum and stored under nitrogen, and solvents were purified by distillation.

Fourier transform infrared (FTIR) measurements were conducted on a Nicolet FTIR 5700 spectrophotometer at room temperature and detected at 400–4000 cm^{-1} by the liquid-film method. On-line infrared spectra were recorded on a Nicolet FIT-IR 6700 at a heating rate of 5 K/min, recorded per 10 min between room temperature and 250°C and then at a constant temperature of 250°C for 40 min. $^1\text{H-NMR}$ spectra were obtained with a Bruker Avance-600 and $^{13}\text{C-NMR}$ spectra were obtained with a Bruker Avance-400, using deuterated chloroform as the solvent and tetramethylsilane as the internal reference. Mass spectra (MS) were obtained on a 3900 GC-Saturn 2100 Gas-Mass spectrometer, using electron ionization as the ion source. High resolution mass spectra (HRMS) were conducted on a Bruker Daltonics Bio-TOF-QIII Mass instrument, using electron spray ionization as the ion source. Gel permeation chromatography (GPC) was performed on a Wyatt

Dawn Heleos instrument, test portions of 0.0500 g polystyrene standards and samples were dissolved in 10 mL THF at room temperature, a 200 mL injection sample loop was filled with polystyrene standards and samples, tetrahydrofuran served as an eluent. The flow rate was set at 1.0 mL/min, the two analytical columns were connected in series at room temperature. M_w and M_n represented weight average molecular weight and number average molecular weight, respectively. M_w/M_n represented molecular weight distribution. Differential scanning calorimetry (DSC) was performed on powdered samples using a TA Q200 differential scanning calorimeter at a heating rate of 10 K/min under a nitrogen atmosphere. A SDT-2960 TG-DSC thermogravimetric analyzer was used to investigate the thermal stability of the cured BCB resins. All thermal analyses were conducted in a nitrogen atmosphere from 20°C to the desired temperature. The thermal degradation temperature was taken as the onset temperature at which 5% weight loss occurred.

Synthesis of Benzocyclobutene-4-yl Acrylate

A dry double-necked round-bottomed flask was charged with a solution of 4-hydroxybenzocyclobutene (2.0 g, 17 mmol) in dichloromethane (5 mL). Triethylamine (16.6 mL, 67 mmol) was added and the reaction mixture was cooled to 0°C and stirred for 30 min before a mixture of acryloyl chloride (2.7 mL, 33 mmol) and dichloromethane (10 mL) was added dropwise. After reaction at 0°C for 2 h, the reaction medium was warmed to room temperature over 6 h and complete conversion of 4-hydroxybenzocyclobutene was achieved. The dark red filtrate was washed three times with NaHCO₃ (5%) and distilled water respectively. The organic layer was dried over anhydrous sodium sulfate and the product was purified by column chromatography, using dichloromethane-petroleum ether (1:1 *V/V*) as eluant. The corresponding eluent was collected and concentrated under reduced pressure to afford **1** as a colorless oil. Yield: 2.2 g (76%). ¹H-NMR (600 MHz, CDCl₃, δ): 3.15 (d, J = 3.1 Hz, 4H), 5.9 (dd, J = 1.2, 10.4 Hz, 1H), 6.3 (dd, J = 10.6, 17.4 Hz, 1H), 6.6 (dd, J = 1.1, 17.2 Hz, 1H), 6.8 (s, 1H), 6.9 (s, 1H), 7.0 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃, δ): 29.0, 29.1, 116.5, 120.2, 123.6, 128.1, 132.3, 143.1, 146.4, 149.8, 165.0. IR (KBr), ν/cm^{-1} : 3035, 2933, 1742, 1634, 1592, 1244, 1117, 983, 902, 822, 777. EI-MS for C₁₁H₁₀O₂: m/z 174.0, 120.0, 91.0, 55.0. HRMS molar mass calculated for C₁₁H₁₀O₂: m/z 197.0534 [M + Na]⁺. Found: m/z 197.0582 [M + Na]⁺.

General Procedures for Polymerization of 1

Homopolymerization of 1

A dry Schlenk flask, equipped with a magnetic stir bar, was sealed with a plug cock and cycled between vacuum and nitrogen three times to remove oxygen. **1** (300.0 mg, 1.72 mmol), AIBN (5.65 mg, 0.034 mmol) and toluene (2.0 mL) were added under a nitrogen atmosphere. Subsequently, the flask was immersed in an oil bath at 60°C for 10 h. The reaction mixture was then poured into adequate methanol to form a white precipitate. The precipitate was washed thoroughly with methanol and dried under vacuum to yield 289.2 mg (96.4%) of polymeric product. M_n = 6900, M_w/M_n = 2.03. ¹H-NMR (400.13 MHz, CDCl₃, δ): 2.01–2.04 (br, 2H), 2.35–2.41 (br, 1H), 3.00–3.06 (br, 4H), 6.74–6.84 (br, 3H). IR (KBr): 2930 $\nu(\text{Csp}^3\text{-H})$, 1752 $\nu(\text{C=O})$, 1605 $\nu(\text{C=C})$, 1591 $\nu(\text{C=C})$, 1465 $\nu(\text{Csp}^3\text{-H})$, 1212 $\nu(\text{C-O})$, 1146 $\nu(\text{C-O})$, 890, 815, $\nu(\text{Csp}^3\text{-H})$.

Radical copolymerization of 1 with St

A mixture of **1** (100.0 mg, 0.575 mmol), St (0.595 mL, 5.172 mmol), AIBN (2.86 mg, 0.017 mmol) and toluene (1.0 mL) was placed in a polymerization tube, which was degassed under vacuum and sealed under nitrogen. After stirring at 60°C for 10 h, the reaction mixture was poured into adequate methanol to form a colorless precipitate. The precipitate was then dried under vacuum for 12 h to yield 303 mg (47.5%) as a hard white solid. The incorporation ratio of **1** was estimated to be 32.31% by ¹H-NMR. ¹H-NMR (400.13 MHz, CDCl₃, δ): 1.25–1.76 (br, aliphatic), 1.76–2.05 (br, m, aliphatic), 3.12 (br, alicyclic), 6.46–6.82 (br, aromatic), 6.94–7.23 (br, aromatic). IR (KBr): 2923 $\nu(\text{Csp}^3\text{-H})$, 1753 $\nu(\text{C=O})$, 1602 $\nu(\text{C=C})$, 1591 $\nu(\text{C=C})$, 1465 $\nu(\text{Csp}^3\text{-H})$, 1135 $\nu(\text{C-O})$, 1029 $\nu(\text{C-O})$, 766, 701 $\nu(\text{Csp}^3\text{-H})$.

Radical copolymerization of **1** with BA

A mixture of **1** (100.0 mg, 0.575 mmol), BA (0.737 mL, 5.172 mmol), AIBN (2.86 mg, 0.017 mmol) and toluene (1.0 mL) was placed in a polymerization tube, which was degassed under vacuum and sealed under nitrogen. After stirring at 60°C for 10 h, the reaction mixture was poured into adequate methanol to form a colorless precipitate. The precipitate was then dried under vacuum for 12 h to form 736.97 mg (96.7%) as a gummy solid. The incorporation ratio of **1** was estimated to be 11.95% by ¹H-NMR. ¹H-NMR (400.13 MHz, CDCl₃, δ): 0.88–0.97 (br, aliphatic), 1.35–1.48 (br, aliphatic), 1.74 (br, aliphatic), 1.91–1.92 (br, aliphatic), 2.29–2.53 (br, aliphatic), 3.14–3.16 (br, alicyclic), 3.97–4.06 (br, aliphatic), 6.82–7.03 (br, aromatic). IR (KBr): 2960 ν(Csp³–H), 2874 ν(Csp³–H), 1735 ν(C=O), 1598 ν(C=C), 1466 ν(Csp³–H), 1258 ν(C–O), 1163 ν(C–O), 810, 700 ν(Csp³–H).

General Procedures for Crosslinking

Three dry Schlenk flasks were charged with 100 mg of the linear polymers **2a**, **2b** and **2c**, respectively, then cycled between vacuum and nitrogen three times to remove oxygen. Subsequently, the flasks were immersed in a sand bath at 200°C. After 4 h, the polymerization was stopped by cooling the Schlenk tubes to room temperature and pale yellow polymers of polymer **3a**, polymer **3b** and polymer **3c** were obtained as transparent solids (Scheme 2) and hundred percent yields (there were no volatile small molecule polymers).

RESULTS AND DISCUSSION

Synthesis and Characterization of **1**

The synthesis of compound **1** was achieved as shown in Scheme 1, using the esterification reaction between 4-hydroxybenzocyclobutene and acryloyl chloride to produce **1** as a 76% yield. FTIR analysis showed that, after esterification, a peak corresponding to the stretching vibration of carbonyl groups appeared at 1742.7 cm⁻¹ and a sharp peak corresponding to the vibration absorption of the C–O bonds in **1** appeared at 1190.0 cm⁻¹. Moreover, the vibration peaks of a phenyl group at 1405.3 cm⁻¹ and 1456.7 cm⁻¹ were observed. Furthermore, the vibration peak of terminal olefin appeared at 1634.5 cm⁻¹, and the characteristic vibration peak of terminal

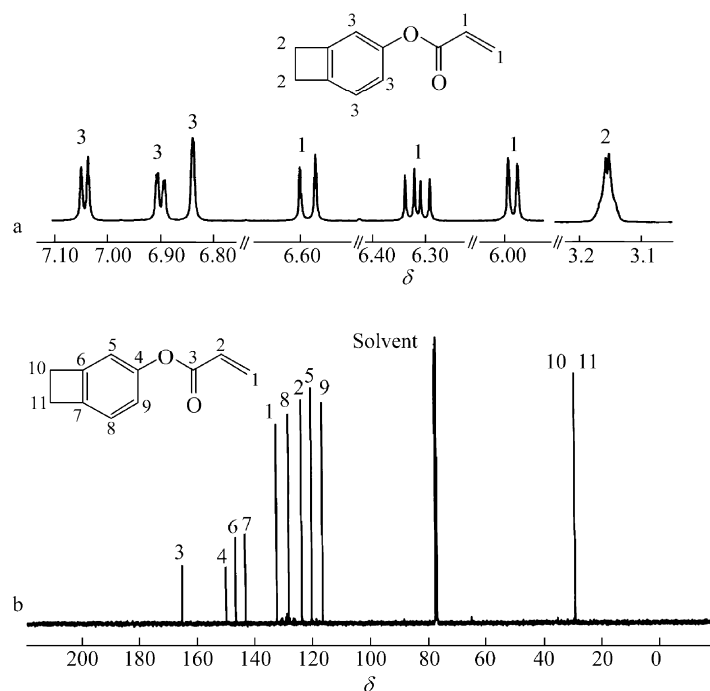


Fig. 1 ¹H-NMR (a) and ¹³C-NMR (b) spectra of **1** at room temperature using CDCl₃ as the solvent

olefinic C—H bonds at 902.3 cm^{-1} was observed. These results indicate that the esterification between 4-hydroxybenzocyclobutene and acryloyl chloride was successful and that the resulting product should be **1**.

To identify the molecular structure of **1**, MS and HRMS analyses were conducted. The molecular ion peak of **1** was located at 174.0. The peak at 91.1 was the fragment of the benzyl group, and that at 55.0 was the fragment of acryloyl. The result of HRMS showed that $[M+Na]^+$ was located at 197.0534. The molecular structure of **1** was also confirmed by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$, as shown in Fig. 1.

In Fig. 1(a), the characteristic alicyclic proton resonances of **1** occur at around $\delta = 3.15$, the signals for aromatic protons are present between $\delta = 6.8$ and $\delta = 7.1$, and terminal vinyl group proton resonances are present between $\delta = 5.95$ and $\delta = 6.65$. The $^{13}\text{C-NMR}$ reveals that the proton signals at $\delta = 29$ belong to the alicyclic carbon atom, and the unsaturated carbons' proton signals are presented between $\delta = 116$ and $\delta = 149$, the substituted aromatic carbons' proton signals are presented at lower field, the characteristic carbonyl carbon' proton signal is presented at even lower field ($\delta = 165$). The chemical shifts of the proton on the unsaturated carbon and the unsaturated carbon of **1** are calculated by empirical equation. There is an error compared with the experimental results.

Radical Polymerization of **1** and Characterization of Their Linear Polymers

1 was subsequently employed as a monomer for the synthesis of linear polymers **2a**, **2b** and **2c** by free radical polymerization (Scheme 1). These reactions were carried out in toluene at 60°C using a molar ratio 100:3 of **1** to AIBN as a model reaction. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the linear polymers were detected by gel permeation chromatography (GPC) (the results are shown in Table 1).

Table 1. GPC and DSC results of linear polymers **2a**, **2b** and **2c**

	M_n	M_w/M_n	Incorporation ratio (%)	T_g ($^\circ\text{C}$)	Initial ring-opening temperatures ($^\circ\text{C}$)	Exotherm peak temperatures ($^\circ\text{C}$)
2a	6900	2.03	100	83.2	200	273.92
2b	23800	1.76	32.3	68.1	202	247.66
2c	61585	2.42	11.95	—	—	—

$^1\text{H-NMR}$ of the linear polymers

The structures of the linear polymers were characterized by $^1\text{H-NMR}$, as shown in Fig. 2, Fig. 3 and Fig. 4. In these figures^[18], the characteristic alicyclic proton resonances of **1** occur at around $\delta = 3.1$, the signals for aromatic protons are present between $\delta = 6.7$ and $\delta = 6.8$ and aliphatic proton resonances are present between $\delta = 2.0$ and $\delta = 2.4$. However, there are obvious aromatic proton resonances from St at $\delta = 7.0$ – 7.2 in Fig. 3, and in Fig. 4 the signals of the methylene protons adjacent to oxygen atoms in BA, present at $\delta = 4.0$.

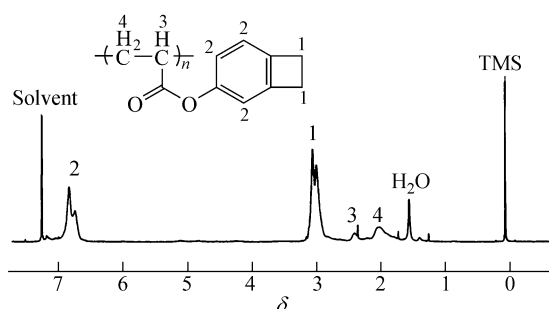


Fig. 2 $^1\text{H-NMR}$ spectrum of linear polymer **2a** at room temperature using CDCl_3 as the solvent

The molar feed ratio in the copolymerization process was $n(\mathbf{1}):n(\text{BA or St}) = 1:9$. We calculated the molar ratio of **1**:BA in linear polymer **2c** to be 1:10 by $^1\text{H-NMR}$ spectra (using $^1\text{H-NMR}$ to calculate molar feed ratio according to the peak of alicyclic proton resonances in benzocyclobutene and the peak of methylene protons adjacent to oxygen atoms in BA), but the molar ratio of **1** to St in linear polymer **2b** was about 1:3.5 (using

$^1\text{H-NMR}$ to determine molar feed ratio according to the peak of alicyclic proton resonances in benzocyclobutene and the peak of aromatic proton resonances in St). This result indicates that there was a large difference between **1** and St in their reactivity ratios^[19]. Additionally, it was more difficult to copolymerize **1** with St than **1** with BA. This behavior is explained by molecular structure, because **1** and BA contain the same acrylic group.

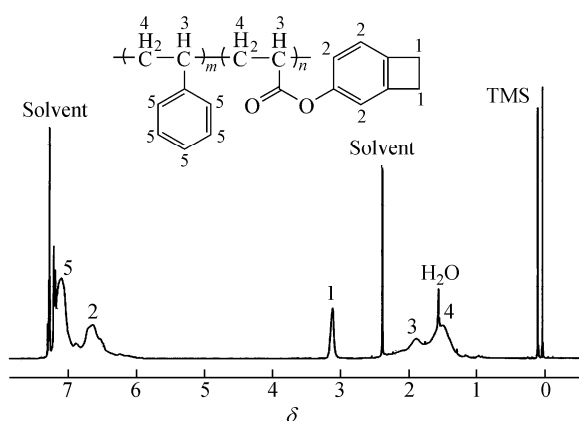


Fig. 3 $^1\text{H-NMR}$ spectrum of linear polymer **2b** at room temperature using CDCl_3 as the solvent

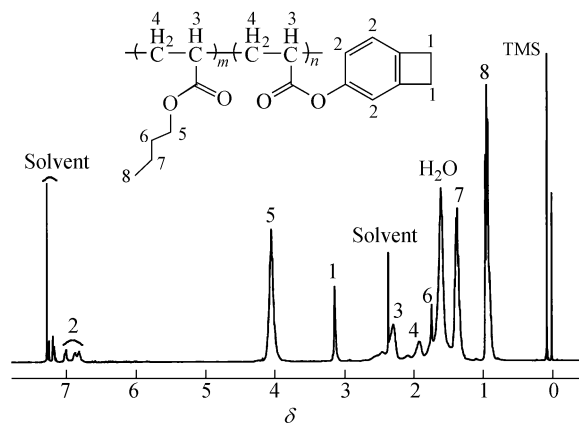


Fig. 4 $^1\text{H-NMR}$ spectrum of linear polymer **2c** at room temperature using CDCl_3 as the solvent

DSC of the linear polymers

Figure 5 shows the DSC curves of linear polymers **2a** and **2b** from 20°C to the desired temperature. Each curve showed a small endothermic peak, indicating that the glass transition temperatures (T_g) of **2a** and **2b** were 83.2°C and 68.1°C , respectively (See Table 1). Besides, the only endothermic peak in the curve of linear polymers **2b**, indicates that there is no homopolymer in the copolymer. Furthermore, there was a large exothermic peak in each curve, related to the ring-opening reaction of BCB, and 247.7°C and 273.9°C were the temperatures at the maximum reaction rates. In addition, there was a small exothermic peak at 127.7°C which corresponds to the cold crystallization temperature of the linear polymer **2b**.

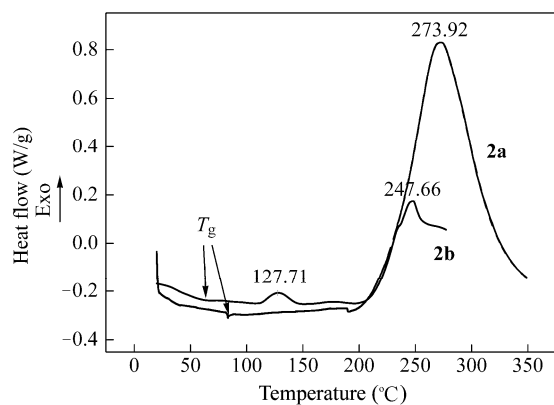


Fig. 5 DSC curves of the linear polymers **2a** and **2b** in nitrogen at a heating rate of 10 K/min

The DSC curves indicate that different co-monomers significantly affected the T_g and ring opening temperature of the BCB resins. However, linear polymers **2a** and **2b** exhibited the same initial ring-opening temperature of about 200°C , possibly due to the absence of a substitution group in the cyclobutene. In particular, linear polymer **2c** was a glutinous substance at room temperature, which has been attributed to the long alkyl chain in BA.

Crosslinking

Thermal stability

The linear polymers **2a**, **2b** and **2c** were subsequently employed for the synthesis of intermolecular or intramolecular crosslinking *via* the route proposed in Scheme 2. Figure 6 shows the changes in the infrared absorption spectra for oligomers with increasing temperature under the protection of pure nitrogen. The characteristic absorption of cyclobutene at 1465 cm^{-1} decreased with increasing time and temperature, indicating that cyclobutene could undergo a thermal initiation reaction.

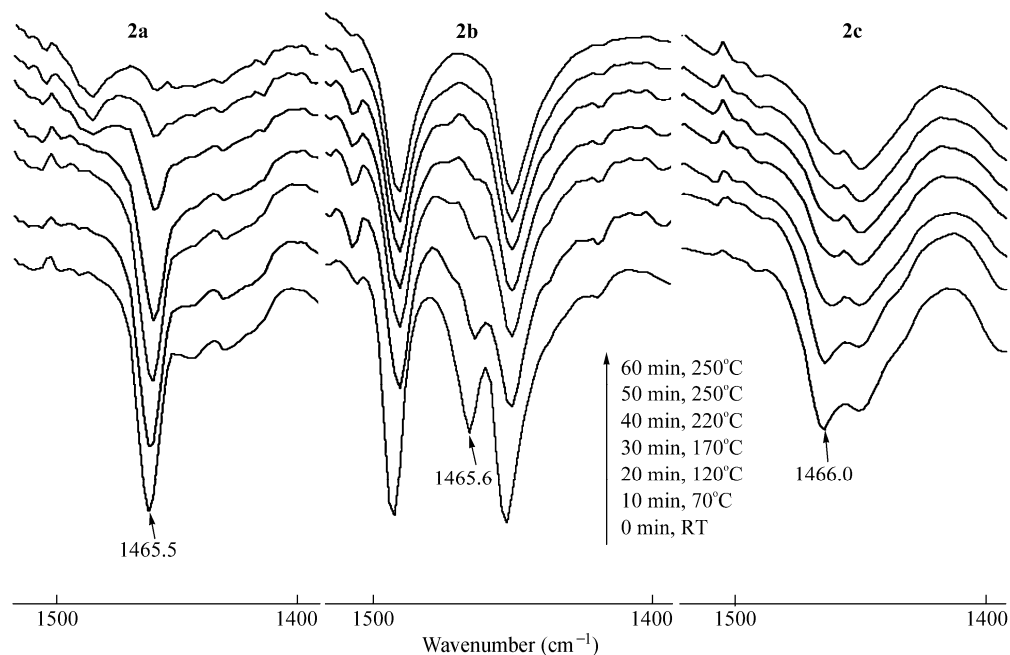


Fig. 6 On-line Infrared Spectra of linear polymers **2a**, **2b**, **2c** in nitrogen at a heating rate of 5 K/min, and then keep the temperature of 250°C for 40 min

As expected, the crosslinked polymers showed excellent thermal stability. The TG-DSC curve of crosslinked polymer **3a** (Fig. 7) shows that the decomposition temperature (T_d) was 406.0°C, and no glass transition temperature was detected. The TGA curves (Fig. 8) of crosslinked polymers **3b** and **3c** show that their T_d 's were 378.2°C and 335.5°C, respectively. The order of thermal stabilities, according to TGA (N_2) results, was **3a** > **3b** > **3c**. This result can be attributed to the crosslinking density of the polymers. $^1\text{H-NMR}$ analysis of the linear polymers showed that crosslinked polymer **3a** possessed the most BCB units and **3c** possessed the least, so crosslinked polymer **3a** had the highest crosslinking density. A high density network space is unfavorable to decomposition.

Acid and alkali resistance

A preliminary experiment on the chemical stabilities of the crosslinked polymers was carried out using concentrated sulfuric acid (98%) and concentrated alkali (40% aqueous NaOH). The results show that the polymers did not degrade in concentrated alkali after two months and the shape and color of crosslinked polymers **3a** and **3b** showed little change in concentrated acid. However, crosslinked polymer **3c** was dissolved in concentrated sulfuric acid within about one minute. This behavior is probably related to molecular structure but it is beyond the scope of this paper which will be investigated further. These qualitative results are merely intended to be indicative of the application range of the polymers.

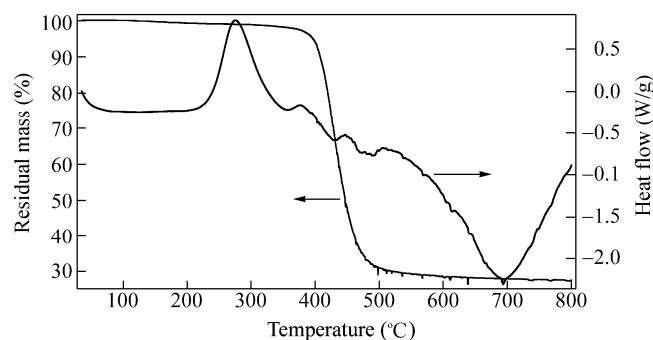


Fig. 7 TG-DSC curve of crosslinked polymer **3a** in nitrogen at a heating rate of 10 K/min

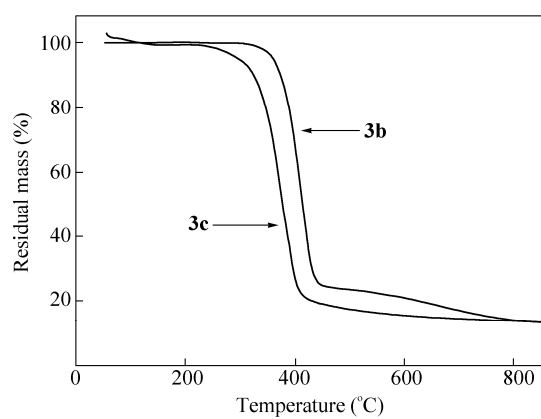


Fig. 8 TGA curves of crosslinked polymers **3b** and **3c** in nitrogen at a heating rate of 10 K/min

CONCLUSIONS

As an extension of our efforts to develop new thermoset resins, we have successfully synthesized a new acrylate monomer, containing benzocyclobutene units, and its derivative polymers. The monomer could be synthesized in good yield from 4-hydroxybenzocyclobutene and acryloyl chloride. Homopolymerization and copolymerization of the monomer were investigated under the radical polymerization using AIBN as initiator. Linear polymers made from the monomer were cured by thermal initiation at about 200°C and the cured polymers exhibited relatively high thermal stabilities. It is worth noting that these polymers could not be dissolved in usual organic solvents, and that **3a** and **3b**, especially, had good corrosion resistance in acid and alkali. Finally, thermal analysis of the thermosetting systems suggests that they have potential use as high temperature macromolecular materials.

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