Synthesis of Reactive Poly(norbornene): Ring-Opening Metathesis Polymerization of Norbornene Monomer Bearing Cyclic Dithiocarbonate Moiety

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ABSTRACT: A norbornene monomer bearing cyclic dithiocarbonate moiety (NB-DTC) was successfully synthesized from the corresponding precursor having epoxy moiety by its reaction with carbon disulfide. NB-DTC underwent the ring-opening metathesis polymerization (ROMP) catalyzed by a ruthenium carbene complex to give the corresponding poly(norbornene). The dithiocarbonate moiety incorporated into the side chain of the obtained poly(norbornene) reacted with amine to afford the corresponding thiourethane moiety with thiol group, which underwent oxidative S-S coupling and/or addition reaction to the C-C double bond in the main chain, leading to formation of a cross-linked polymer. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1097–1103, 2011

KEYWORDS: copolymerization; functionalization of polymers; ROMP

INTRODUCTION One of the current growing interests in the field of transition-metal catalyzed polymerization has been focused on development of new norbornene-type monomers bearing various functional groups and their ring-opening metathesis polymerization (ROMP).[1,2] Recently, highly efficient catalysts for ROMP that are compatible with those functional groups have been developed to permit successful synthesis of various functionalized poly(norbornene)s.[3] By introducing functional groups into the side chains of poly(norbornene)s, their intrinsic high thermal stability, high transparency, low birefringence, and low dielectric constant can be combined with additional advantages such as high processing ability, compatibility with other materials, and improved adhesion strength. In particular, ROMP of norbornenes bearing reactive groups would give reactive poly(norbornene)s,[4] which are expected as polymeric scaffolds for immobilization of functional molecules, for further functionalization by chemical transformation of the side chains, and for cross-linking reactions to obtain cross-linked poly(norbornene)s with improved thermal stability, mechanical properties, and chemical resistance.

Previously, we reported a new straightforward synthesis of a norbornene derivative bearing epoxy group (2-bicyclo[2.2.1]-hept-5-en-2-yl oxirane; NB-EP) (Fig. 1).[5] With using this functionalized norbornene as a precursor, its epoxy moiety was converted into the corresponding five-membered cyclic carbonate moiety to give a new monomer NB-CC, based on the cycloaddition reaction of epoxide with carbon dioxide under atmospheric pressure with using lithium chloride as a catalyst.[6] The norbornene moiety of NB-CC underwent ROMP successfully to afford the corresponding poly(norbornene) bearing cyclic carbonate moiety in the side chain, of which intrinsic high reactivity with amine allowed highly efficient chemical modification of this new poly(norbornene).

The successful utilization of NB-EP for development of a new norbornene monomer made us to demonstrate another chemical transformation of NB-EP based on the reaction of epoxide with carbon disulfide,[7] a sulfur-containing analogue of carbon dioxide, to afford a new norbornene monomer bearing cyclic dithiocarbonate moiety (NB-DTC) bearing five-membered cyclic dithiocarbonate (DTC). So far, we have clarified that DTC undergoes the ring-opening reaction by amine that proceeds readily and highly chemoselectively,[8] and this intriguing reactive feature of DTC has enabled its application to our polymer synthesis.[9] Besides, DTC undergoes the isomerization to afford another type of cyclic dithiocarbonate[10] and the cationic ring-opening polymerization to afford the corresponding polydithiocarbonate.[11] These backgrounds motivated us to synthesize NB-DTC as a monomer for synthesizing new poly(norbornene)s that would be endowed with the unique reactivity of DTCs. In general, sulfur atom exhibits high affinity to various metals at the centers of catalysts to deactivate them. So far, there have been only a few successful examples of ROMP of norbornenes bearing sulfur-containing functional groups such as dithioacetal and trithiocarbonate moieties.[12] This background encouraged us to investigate ROMP of NB-DTC. Herein we report the details of the synthesis of NB-DTC and its ROMP

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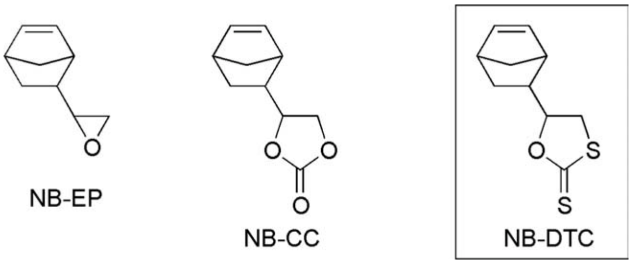


FIGURE 1 Norbornenes bearing reactive groups.

catalyzed by a ruthenium carbene complex. A polymer reaction of the resulting poly(norbornene) based on the reactivity of DTC with amine was also demonstrated.

EXPERIMENTAL

Materials

Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs 1st generation catalyst) (Aldrich), was used as received. NB-EP was synthesized according to the procedure reported by us.[5] 5-Butyl-2-norbornene (BNB) was provided by JSR Co. and was purified prior to use by passing through alumina column and distillation under vacuum. Carbon disulfide, ethyl vinyl ether, dichloromethane, benzylamine, and chlorobenzene were purchased from Wako Pure Chemical Industries and were distilled over calcium hydride prior to use. Anhydrous lithium bromide and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. and used as received.

Measurements

Fourier-transfer IR measurement was carried out at room temperature by casting a sample solution on a prism of an ATR measurement unit on a Perkin-Elmer spectrum-one spectrophotometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were obtained with Varian NMR spectrometer, a model Unit INOVA in CDCl$_3$ with tetramethylsilane as an internal standard. Number- and weight average molecular weights (M_n and M_w) were estimated by size exclusion chromatography (SEC), performed on a Tosoh chromatograph model HLC-8120GPC equipped with Tosoh TSK gel-Super HM-H styrogel columns (6.0 mm ϕ × 15 cm), using CHCl$_3$ as an eluent at a flow rate of 1.0 mL/min after calibration with polystyrene standards. Mass spectroscopy was performed on a Shimadzu GCMS-QP5050A in electron impact (EI) mode. Gas chromatography (GC) was performed on a Agilent Technologies 6850 Network GC system equipped with J and W Scientific HP-1 (0.25 mm × 30 m) capillary column and a Shimadzu GC-18A gas chromatograph equipped with J and W Scientific DB-WAXETR (1 mm × 30 m) capillary column. Thermo-gravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) were performed with a SEIKO EXSTAR6000 (Seiko Instruments).

Synthesis of 5-Bicyclo[2.2.1]hept-5-en-2-yl-[1,3]oxathiolane-2-thione (NB-DTC)

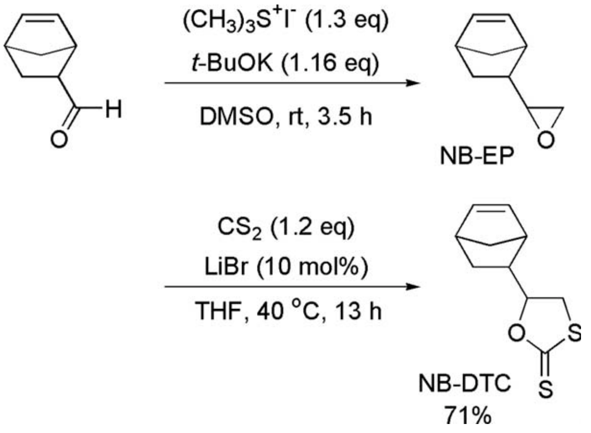
To a solution of NB-EP (4.09 g, 30.0 mmol) and lithium bromide (0.25 g, 2.9 mmol) in THF (15 mL), a solution of carbon disulfide (2.9 g, 38 mmol) in THF (25 mL) was added dropwise for 20 min. The resulting solution was stirred at 40 °C for 12 h. After cooling, the solution was concentrated under reduced pressure, and the resulting residue was dissolved in chloroform (150 mL), washed with distilled water (200 mL) three times. The chloroform layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was fractionated with column chromatography (silica gel, eluent = dichloromethane) to obtain a diasteromeric mixture of NB-DTC as a yellow liquid (4.53 g, 21.3 mmol, 71%): IR (neat) 3053, 2961, 2865, 1432, 1330, 1182, 1054, 707 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.34–5.89 (m, 2H, vinyl), 5.00–4.42 (m, 1H, cyclic-dithiocarbonate-CH), 3.75–3.37 (m, 2H, cyclic-dithiocarbonate-CH2), 3.25–2.67 (m, 2H, 1,4-CH), 2.66–0.60 ppm (m, 5H, 2-CH, 3-CH2, 7-CH2); ^{13}C NMR (CDCl$_3$) δ (mixture of four diastereomers) 212.05, 212.24, 212.26, 212.28, 139.48, 138.31, 137.71, 136.88, 136.10, 135.41, 132.49, 130.30, 97.25, 96.35, 95.60, 95.22, 49.59, 49.08, 49.05, 45.57, 44.96, 44.63, 44.32, 44.26, 43.97, 43.11, 43.06, 43.02, 42.68, 42.31, 42.11, 41.83, 39.11, 38.80, 38.70, 38.62, 30.30, 30.19, 29.13, 28.51 ppm; EI-MS m/z 212 (M^{+}).

Ring-Opening Metathesis Polymerization of NB-DTC (Homopolymerization)

To a solution of **NB-DTC** (425 mg, 2.00 mmol) and 1,2,3,4-tetrahydronaphthalene (added as an internal standard for GC analysis; 107 mg, 0.809 mmol) in dichloromethane (2.6 mL), a solution of Grubbs 1st generation catalyst in dichloromethane (0.05 M; 0.4 mL, 0.02 mmol) was added at room temperature. At 10 and 30 min, a small portion of the solution was taken and analyzed by GC to determine the conversions of NB-DTC. After 90 min, ethyl vinyl ether (0.25 mL) was added to terminate the polymerization, and the mixture was stirred at room temperature for 40 min. The mixture was poured into methanol (50 mL), and the resulting precipitate was filtered with suction, and dried under vacuum at 50 °C to obtain the homopolymer **1a** (178 mg, 42%): IR (neat) 2930, 2852, 1436, 1334, 1180, 1045, 965 cm^{-1}.

Ring-Opening Metathesis Polymerization of NB-DTC (Copolymerization with BNB)

NB-DTC (212 mg, 1.00 mmol), BNB (150 mg, 1.00 mmol), and 1,2,3,4-tetrahydronaphthalene (added as an internal standard for GC analysis; 107 mg, 0.809 mmol) were dissolved in dichloromethane (2.6 mL). To the obtained solution, a solution of Grubbs 1st generation catalyst in dichloromethane (0.05 M; 0.4 mL, 0.02 mmol) was added at room temperature. At 5 min, 10 min, 20 min, 30 min, 45 min, 60 min, and 90 min, a small portion of the solution was taken and analyzed by GC to determine the conversions of NB-DTC and BNB. After 90 min, ethyl vinyl ether (0.25 mL) was added to terminate the polymerization, and the solution was stirred at room temperature for 40 min. The solution was poured into methanol (50 mL), and the resulting precipitate was filtered with suction, and dried under vacuum to obtain the comopolymer **1b** (283 mg): IR (neat) 2922, 2851, 1453, 1189, 1048, 966 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 5.70–5.20 (broad m, 2H; vinyl protons), 5.20–4.90 (broad m, 0.47H; methine proton of DTC), 3.20–3.80 (broad m, 0.94H; methylene



SCHEME 1 Synthesis of NB-DTC.

protons of DTC), 3.10–0.70 ppm (broad m, including a broad singlet signal at 0.85 ppm for the methyl protons of the BNB-derived unit). $M_n = 14{,}000$, $M_w = 26{,}000$ (estimated by SEC, eluent = chloroform, polystyrene standards).

Reaction of the DTC-Moiety of 2b with Benzylamine

To a solution of copolymer **2b** (49.7 mg, amount of cyclic carbonate moiety = 0.28 mmol) in chlorobenzene (0.30 mL), benzylamine (49 mg; 0.46 mmol) was added at ambient temperature. The resulting solution was stirred at ambient temperature for 16 h under air. The solution was poured into methanol (25 mL), and the resulting precipitate was filtered with suction and dried under vacuum to obtain the resulting polymer **2** (40 mg) as a white powder: IR (neat) 3410, 2928, 2855, 1662, 1511, 1455, 1392, 1343, 1170, 970, 733, 698, 528 cm^{-1}.

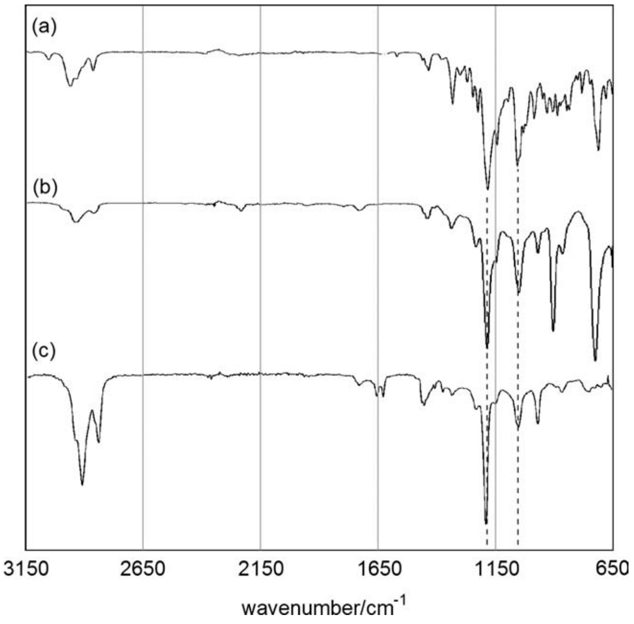


FIGURE 2 IR spectra of (a) NB-DTC, (b) polymer **1a** (= the homopolymer of NB-DTC), and (c) polymer **1b** (the copolymer of NB-DTC and BNB; composition ratio = 47.53).

RESULTS AND DISCUSSION

Synthesis of NB-DTC

Scheme 1 shows the synthetic route to NB-DTC. The precursor NB-EP bearing epoxy moiety was synthesized from 5-norbornene-2-carbaldehyde (a diastereomeric mixture of the *endo* and *exo* isomers) according to our previous report.[5] The obtained NB-EP was mixed with carbon disulfide and lithium bromide in THF, and the resulting solution was heated at 40 °C. As a result, the epoxide moiety of NB-EP was converted successfully to the corresponding five-membered cyclic carbonate moiety to afford NB-DTC. The dithiocarbonate structure was confirmed by its characteristic IR-absorptions at 1182 and 1054 cm^{-1} [Fig. 2(a)]. Figure 3(a) shows the ^{1}H-NMR spectrum of the obtained NB-DTC. The complexity of the spectrum suggested that NB-DTC was obtained as a mixture of diastereomers due to the presence of two chiral centers. It was difficult to resolve them by GC because of the serious overlapping of the corresponding peaks; however; during the GC-MS analysis, they were ionized in EI mode to indicate the same m/z value of 212, which was identical with the calculated molecular weight of NB-DTC.

Ring-Opening Metathesis Polymerization (ROMP) of NB-DTC (Homopolymerization)

ROMP of **NB-DTC** was performed with employing benzylidene-bis(tricyclohexyl phosphine)dichlororuthenium (Grubbs 1st generation catalyst) (Scheme 2), which was efficiently used for ROMP of NB-CC[6] and those of monomers bearing sulfur-containing functional groups.[12] When the catalyst was added to a dichloromethane solution of NB-DTC, its ROMP

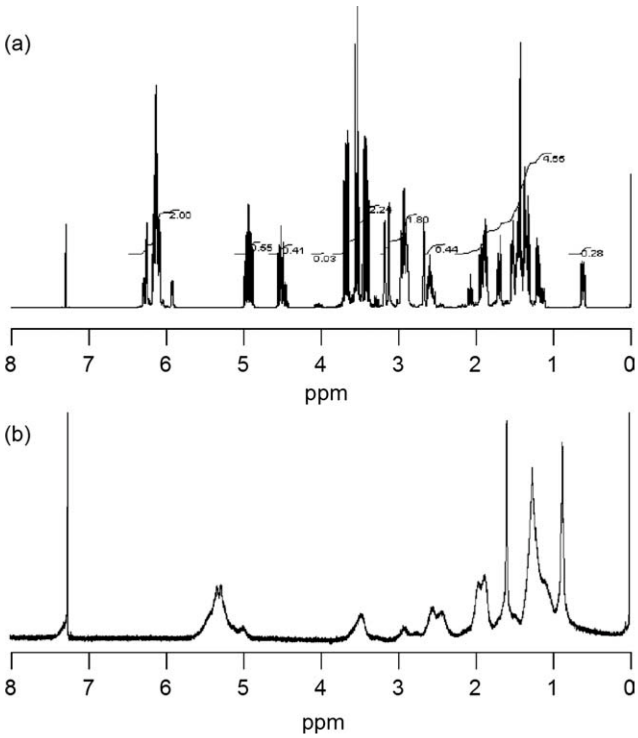
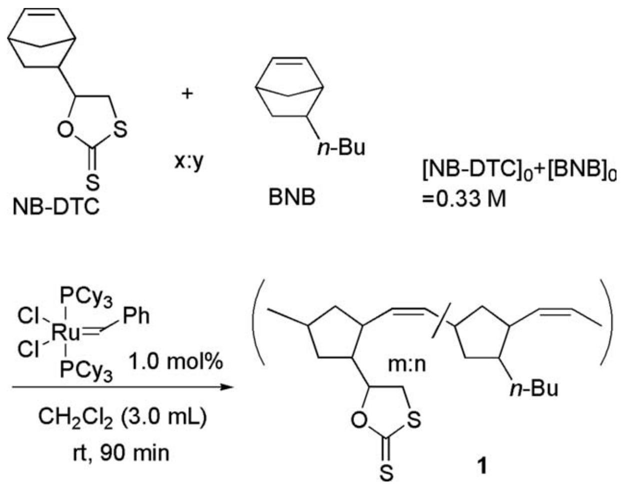


FIGURE 3 ^{1}H NMR spectra of (a) NB-DTC and (b) polymer **1b**.



SCHEME 2 ROMP of NB-DTC.

proceeded slowly [Fig. 4(a)]. The resulting homopolymer **1a** was insoluble in dichloromethane and thus precipitated out from the solution during the polymerization. After adding ethyl vinyl ether to terminate ROMP, the mixture was poured into methanol, and the precipitate was isolated by filtration to obtain **1a** in 42% (Table 1, entry 1). **1a** was insoluble not only in dichloromethane but also in other organic solvents such as toluene, chloroform, THF, acetone, ethyl acetate, dimethyl sulfoxide, and *N*,*N*-dimethylformamide. One of the reasons for the insoluble nature may be the high polarity of DTC moieties. Although this insoluble nature led to only a limited structural analysis, IR was effectively employed to confirm the structure of **1a**. Figure 2(b) shows the IR spectrum of **1a** which indicated characteristic absorptions at 1180 and 1045 cm^{-1}, which clarified that the side chain of **1a** inherited the cyclic dithiocarbonate moiety from the monomer NB-DTC.

The homopolymerization of NB-DTC was slower than that of NB-CC, an analogous monomer having cyclic carbonate moiety. In the homopolymerization of NB-DTC, as shown in Figure 3(a), the conversion of NB-DTC did not reach 50% even when the polymerization time was prolonged to 90 min. On the other hand, in the homopolymerization of NB-CC, NB-CC was completely consumed within 120 min to afford the corresponding homopolymer almost quantitatively. This tendency implied that the sulfur atoms of the cyclic dithiocarbonate exhibited higher affinity to the ruthenium catalyst to interfere approach of the C-C double bond of NB-DTC to the central metal of the catalyst.

Ring-Opening Metathesis Polymerization (ROMP) of NB-DTC (Copolymerization)

Copolymerization of NB-DTC and BNB in a feed ratio of 50:50 was performed (Scheme 2, Table 1, entry 2). The resulting copolymer **1b** was soluble in various organic solvents such as dichloromethane, chloroform, acetone, and THF, due to the incorporation of less polar *n*-butyl group in the side chain. By virtue of this soluble nature, **1b** was analyzed not only by IR but also by NMR and SEC. Figure 2(c) shows the IR spectrum, which clearly indicated two absorptions at 1189 and 1048 cm^{-1} attributable to the cyclic dithiocarbonate moiety in the side chain. In the ^{1}H NMR spectrum [Fig. 3(b)], signals attributable to the methine proton of DTC and the vinyl protons of the main chain appeared in the region from 5 to 6 ppm. Comparison of the integrated signal intensity with that of the other signals allowed calculation of composition ratio [NB-DTC-derived unit]:[BNB-derived unit], which was 47:53. SEC analysis of **1b** permitted estimation of its number average molecular weight (M_n) and weight average molecular weight (M_w), which were 14,000 and 26,000, respectively.

Figure 4(b) shows the corresponding time-dependences of conversions of NB-DTC and BNB, which revealed a significant difference in polymerization ability between the two monomers. Within 20 min, BNB was completely consumed, while the conversion of NB-DTC at 20 min was 70%. From these copolymerization behaviors, formation of segments rich in BNB-derived unit in the early stages and that of segments rich in NB-DTC-derived unit in the late stages to give a gradient copolymer can be assumed.[13] In fact, after the complete consumption of BNB, formation of insoluble polymer by homopolymerization of NB-DTC was not observed, implying that NB-DTC molecules consumed after 20 min until 90

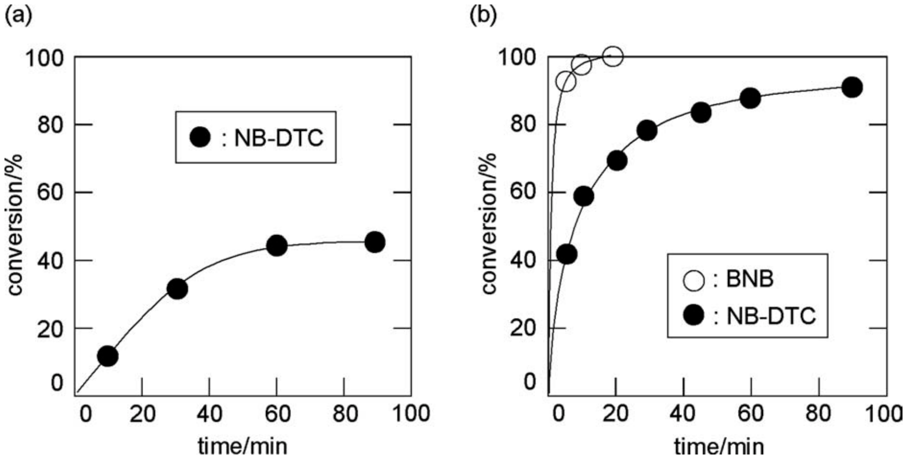


FIGURE 4 Time-conversion relationships for (a) the homopolymerization of NB-DTC and (b) the copolymerization of NB-DTC and BNB (feed ratio = 50:50).

TABLE 1 ROMP of NB-DTC

Entry	Feed Ratio $[NB\text{-}DTC]_0:[BNB]_0$	Polymer	Yield of Polymer/%[a]	M_n (M_w/M_n)[b]	Composition Ratio m:n[c]
1	100:0	**1a**	42	–[d]	100:0[e]
2	50:50	**1b**	78	14,000 (1.86)	47:53

[a] Methanol-insoluble parts.
[b] Estimated by SEC (eluent = $CHCl_3$, polystyrene-standards).
[c] Determined by ^1H NMR.
[d] SEC-analysis was not carried out because **1a** was insoluble in $CHCl_3$.
[e] ^1H NMR was not measured because **1a** was insoluble in $CDCl_3$ and dimethylsulfoxide-d_6.

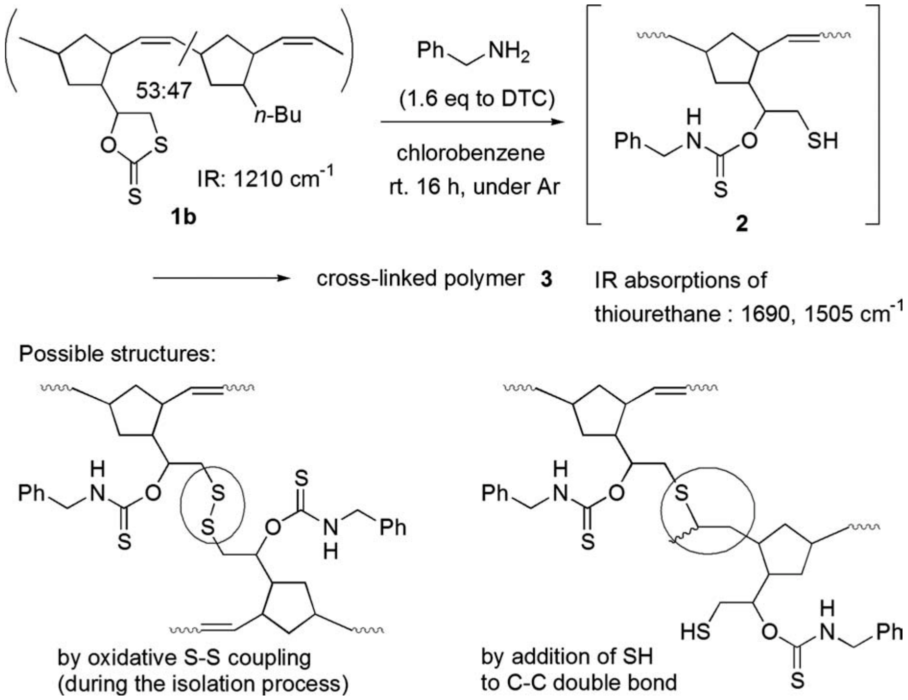
min were successfully converted into homo-sequences of NB-DTC into the tails of the gradient copolymers.

Reaction of the Cyclic Dithiocarbonate Moiety in the Side Chain with Amine

So far, we have reported the reaction of five-membered cyclic dithiocarbonate (DTC) with amines, which affords the corresponding thiourethanes having thiol group:[8] The characteristic feature of this reaction is its chemoselectivity, which permits the nucleophilic addition of primary amine exclusively in the presence of other nucleophiles such as water, alcohols, carboxylic acids, and thiols. In addition, the reaction of DTC with amine is much faster than the analogous reaction of five-membered cyclic carbonate.

To investigate the reactivity of the cyclic moiety in the side chain of poly(norbornene), the copolymer **1b** was treated with benzylamine ($[\text{DTC moiety}]_0:[\text{benzylamine}]_0 = 1:1.6$) in chlorobenzene at ambient temperature (Scheme 3). Upon adding benzylamine, the characteristic yellow color of DTC disappeared to suggest its successful ring opening reaction. In addition, there was no formation of insoluble fraction throughout the reaction to let us expect the formation of a linear poly(norbornene) **2** bearing thiourethane and thiol moieties. The solution was poured into an excess amount of methanol to attempt isolation of **2**; however, the isolated polymer was not soluble in chloroform, THF, DMSO, or DMF, implying that **2** was crosslinked into the corresponding cross-linked polymer **3**. Figure 5 shows the IR spectrum of **3** along with that of polymer **1b**, which confirmed the successful conversion of DTC moiety by its reaction with benzylamine into the corresponding thiourethane moiety. Although the crosslinking process is not clear at present, the cross-linked polymer **3** would bear two possible structures at the crosslinking points: One possible structure is S-S linkage, which can be formed by oxidative coupling of the thiol group in the side chain of **2** during the isolation process. The other one is S-C bond, which can be formed by addition reaction of the thiol group to the C-C double bond in the poly(norbornene) main chain.

In Figure 6, TGA profiles of the precursor polymer **1b** and the resulting cross-linked polymer **3** are shown. Upon



SCHEME 3 Reaction of **1a** with benzylamine and possible structures of cross-linking points.

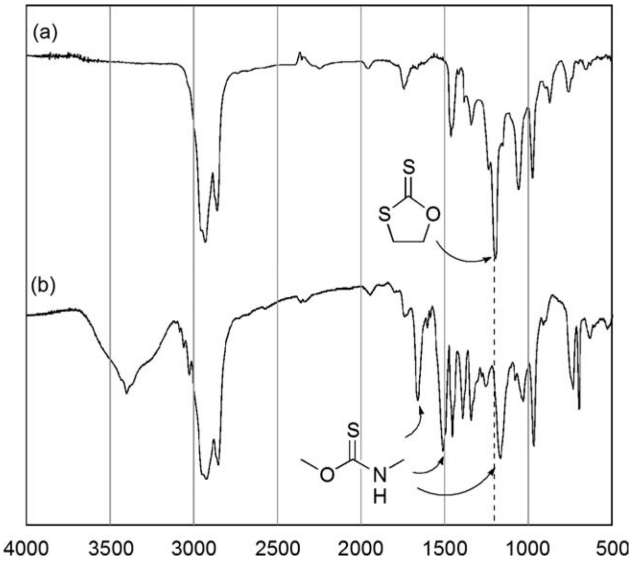


FIGURE 5 IR spectra of (a) copolymer **1b** and (b) cross-linked polymer **3**.

heating **1b** up to 310 °C, it lost 20% of the initial weight, presumably due to the thermally induced transformation of DTC moiety into the corresponding episulfide with releasing COS gas.[14] On the other hand, the temperature for 20% weight loss of **3** was 260 °C, which was much lower than that of **1b**. In Figure 7, DSC profiles of the two polymers are shown, in which glass transition temperatures (T_g) were observed. T_g of **3** was 49 °C. It was slightly higher than that of **1b**, 46 °C, to suggest the more restricted motion of the polymer chain by cross-linking in the cross-linked polymer **3**.

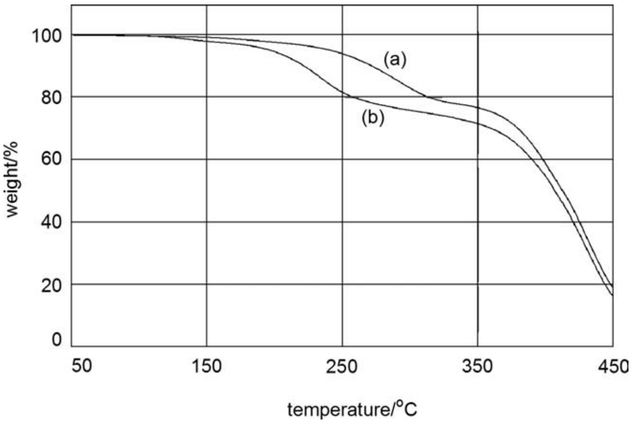


FIGURE 6 TGA profiles of (a) copolymer **1b** and (b) cross-linked polymer **3**.

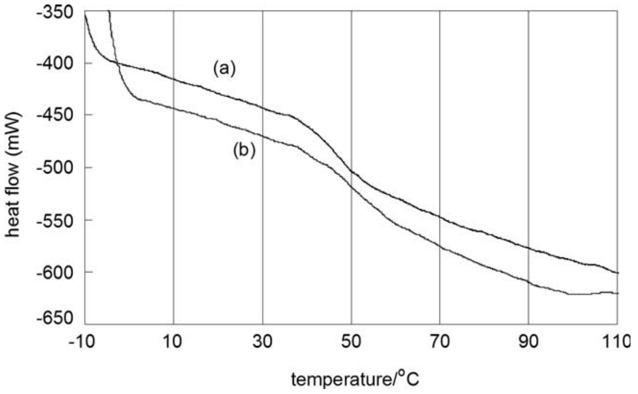


FIGURE 7 DSC thermograms of (a) copolymer **1b** and (b) cross-linked polymer **3**.

SUMMARY

A new norbornene monomer bearing five-membered cyclic dithiocarbonate moiety (=NB-DTC) was synthesized and polymerized readily via ROMP to afford the corresponding reactive poly(norbornene), of which side chain was endowed with the highly reactive nature of DTC with amine.

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