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Radical Ring-Opening Polymerization Behavior of 1,1-Dicyano-2-Vinylcyclopropane and Its Copolymerization with 1-Cyano-1-Ester-2-Vinylcyclopropane

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(Additional Supporting Information may be found in the online version of this article.)

ABSTRACT

Radical ring-opening polymerization (RROP) of 1,1-dicyano-2-vinylcyclopropane **1** was performed in benzonitrile to find the corresponding homopolymer **2** soluble in organic solvents was successfully obtained while that in other solvents gave crosslinked and thus insoluble homopolymer. In addition, **1** underwent radical copolymerization with 1-cyano-1-ester-2-vinylcyclopropanes **3** and **4** to afford the corresponding copolymers **7** and **8**. By increasing the content of the **1**-derived unit in the resulting copolymers, the solubility of the copolymers in organic solvents became lower and the residual weights at 600 °C and their glass transition temperatures became higher.

KEYWORDS: vinyl cyclopropane; radical ring-opening polymerization; radical copolymerization.

INTRODUCTION

Cyclopropanes bearing vinyl group (vinylcyclopropanes; VCP) undergo radical ring-opening polymerization (RROP) to afford polymers with carbon-carbon double bonds in main chains and functional groups X and Y inherited from the monomers (Figure 1).¹⁻¹⁰ In the RROP process, the vinyl group of VCP reacts with radical species to give a carbon radical adjacent to the cyclopropane moiety. Then, the cyclopropane moiety undergoes the ring-opening to afford acyclic radical species. The substituents X and Y are often selected from cyano¹¹⁻¹⁴, chloro¹⁴⁻¹⁵, ester^{12-14,16-17}, and amide¹⁸⁻¹⁹ groups, which can stabilize the adjacent radical species. In general, cleavage of C1-C2 bond in VCP is favored than that of C1-C3. When the stabilization of the radical species is insufficient, some pathways to form cyclobutane ring

become possible^{14,17}. The ring-opening process leads to smaller volume shrinkage upon RROPs of VCPs than the conventional vinyl monomers, making us to expect the efficient use of VCPs in coating and dental applications where volume shrinkage should be minimized as much as possible.²⁰⁻²³

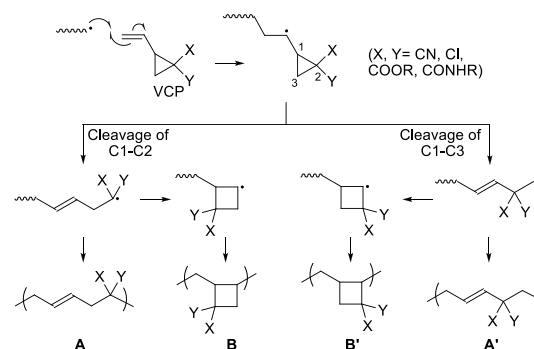


Figure 1. Postulated mechanism for RROP of VCP derivatives

VCP derivative bearing cyano groups **1** undergoes RROP as expected from the strong ability of cyano group to stabilize its adjacent carbon radical (Figure 2). However, the resulting polymer was scarcely soluble in organic solvents due to the formation of crosslinked structures, preventing detailed structural analysis of the polymers.¹⁴ Such crosslinking was not observed in the RROPs of other VCP derivatives bearing ester and amide moieties. A possible mechanism for this crosslinking includes addition of a propagating radical to a carbon-carbon double bond in the main chain, which is possible for a propagating radical center substituted by less hindered cyano groups.

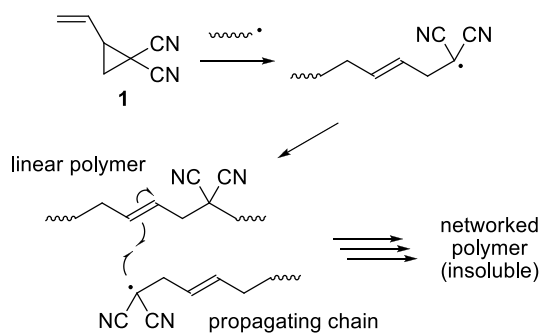


Figure 2. Possible mechanism for the formation of networked polymer by RROP of VCP **1**

Herein, we report a successful synthesis of soluble polymer from **1** by performing its RROP using benzonitrile as the polymerization solvent. In addition, we have also investigated radical copolymerization of **1** with two types of 1-cyano-1-ester-2-VCP derivatives **3** and **4**. Solubilities and thermal properties of the obtained polymers are presented.

EXPERIMENTAL

Materials.

Acetonitrile (99.5%), chlorobenzene (99%), *N,N*-dimethyl formamide (DMF) (99.5%), dimethyl sulfoxide (DMSO) (99%), 1,4-dioxane (99%), ethyl acetate (1st grade), silver oxide (I) (special grade), tetrahydrofuran (THF) (1st grade) were purchased from Wako Pure Chemical Industries Co., Ltd. and used as received.

Azobisisobutyronitrile (AIBN) (98%) was purchased from Wako Pure Chemical Industries Co., Ltd. and recrystallized in the methanol prior to use. Benzonitrile (>99%), *trans*-1,4-dibromo-2-butene (>98%), ethyl cyanoacetate (>99%), isobutyl cyanoacetate (>98%), malononitrile (>99%) and sodium hydride (60%, dispersion in Paraffin Liquid) were purchased from Tokyo Chemical Industries Co., Ltd. and used as received. Chloroform-*d* (99.8%D), dimethyl sulfoxide-*d*₆ (99%D) and hexane (1st grade) were purchased from Kanto Chemical Co., Inc. and used as received.

Instruments.

¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) spectra were recorded with a JEOL ECS-400 spectrometer, and chemical shifts δ and coupling constant *J* were given in ppm and Hz using tetramethyl silane (TMS) or a solvent signal as an internal standard. The solid-state ¹³C-NMR spectra (100 MHz) were recorded with a JNM-ECX 400 spectrometer. IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer equipped with a Smart iTR Sampling Accessory using attenuated total reflection (ATR) method. For the estimation of number average molecular weight (*M_n*) and weight average molecular weight (*M_w*) of the synthesized polymers, size-exclusion chromatography (SEC) was performed on a TOSOH HLC-8220 system equipped with three consecutive polystyrene gel columns [TSK-gels (bead size, exclusion, limited molecular weight); super-AW4000 (6 μ m, >4 \times 10⁵), super-AW3000 (4 μ m, >6 \times 10⁴), and super-AW2500 (4 μ m, >2 \times 10³)] and refractive index and ultraviolet detectors. The system was operated as 40 °C using 10 mM LiBr in DMF as the eluent, at a flow rate of 0.5 mL/min. Polystyrene standards were used for calibration. High-resolution mass spectra (HRMS) were recorded on a JEOL JMN-700 spectrometer. Thermogravimetric analysis (TGA) was performed with a Seiko Instrument TG-DTA 6200 under nitrogen flow rate of 100 mL/min in a range from 50 to 600 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC)

was performed with a Seiko Instrument DSC-6200R under nitrogen flow rate of 50 mL/min.

Synthesis of 1,1-dicyano-2-vinylcyclopropane 1

Malononitrile (3.96 g; 59.9 mmol), silver oxide (13.9 g; 60.0 mmol) and *trans*-1,4-dibromo-2-butene (13.1 g; 61.2 mmol) in THF (20 mL) were added to a 200-mL flask. To a suspension was stirred using mechanical stirrer and heated at 60 °C for 12 h. The reaction mixture was passed through a celite pad, and the obtained filtrate was evaporated under reduced pressure. The residue was distilled using Kugelrohr (100 °C under 0.90 mmHg) and isolated by a silica gel chromatography (eluent : hexane/ethyl acetate = 3/1) to yield **1** as a colorless liquid (2.98 g; 25.2 mmol; 42%). ¹H-NMR (400 MHz, DMSO-*d*₆, at r.t., ppm) δ 5.71-5.54 (m, 2H), 5.45 (dd, *J* = 9.6, 2.0 Hz, 1H), 3.06 (dd, *J* = 16.0, 8.8 Hz, 1H), 2.30-2.21 (m, 2H); ¹³C-NMR (100 MHz, DMSO-*d*₆, at r.t., ppm) δ 130.97, 122.47, 115.61, 114.31, 32.85, 22.52, 5.28; IR (ATR, cm⁻¹) ν 3026, 2248, 1445, 1264, 1074, 986, 931, 706. HRMS *m/z*: [M+H]⁺ Calcd for [C₇H₆N₂]⁺ 118.0531; Found 118.0531.

Radical polymerization of 1

Typical procedure: In a 5-mL ample flask, **1** (118 mg; 1.00 mmol) and AIBN (16 mg; 0.10 mmol) were dissolved in benzonitrile (0.40 mL). The solution was degassed (frozen in liquid nitrogen and warmed in water) three times and heated at 65 °C. After 48 h, the resulting solution was transformed to a yellow solid. The obtained solid was crushed and stirred in methanol (60 mL) for 2 h to precipitate a pale yellow solid. The resulting solid was filtered under reduced pressure and dried under vacuum at 100 °C to yield **2** as a pale yellow solid (109 mg; 89% of the theoretical weight); ¹H-NMR (400 MHz, DMSO-*d*₆, at r.t., ppm) δ 5.88 (brs, 2H), 2.92 (brs, 4H); ¹³C-NMR (CP-MAS, at r.t., ppm) δ 130.29, 117.34, 113.19, 40.40, 28.57; IR (ATR, cm⁻¹) ν 2977, 2930, 2250, 1448, 970. *M*_n=2900, *M*_w=5700, *M*_w/*M*_n=1.97.

Synthesis of 1-cyano-1-ethoxycarbonyl-2-vinylcyclopropane 3

Typical procedure: 60% sodium hydride (900 mg; 37.5 mmol) and hexane (10 mL) were added to a 50 mL flask under nitrogen atmosphere. The suspension was stirred at room temperature for 10 min, and the resulting supernatant liquid was removed via a syringe. After repeating this washing process three times, a solution of ethyl cyanoacetate (1.13 g; 10.0 mmol) in DMF (10 mL) was added to this reaction system at 0 °C via a syringe over 5 min and a suspension was stirred for 10 min at room temperature. Next, a solution of *trans*-1,4-dibromo-2-butene (2.25 g; 10.5 mmol) in DMF (10 mL) was added to this suspension at 0 °C via a syringe over 10 min. After the reaction mixture was stirred at 60 °C for 16 h, the resulting solution was treated with 10% sodium carbonate *aq* (200 mL) and extracted with ethyl acetate (50 mL×2). The obtained organic layer was dried using sodium magnesium over 2 h and evaporated under reduced pressure. The residue was isolated by a silica gel chromatography (eluent : hexane/ethyl acetate = 10/1) to yield **3** as a colorless liquid (852 mg; 5.15 mmol; 52%); ¹H-NMR (400 MHz, CDCl₃, at r.t., ppm) δ 5.69-5.60 (m, 1H), 5.46-5.37 (m, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.56 (dd, *J* = 16.6, 8.8 Hz, 1H), 1.98 (dd, *J* = 8.8, 6.8 Hz, 1H), 1.66 (dd, *J* = 7.6, 5.2 Hz, 1H), 1.35 (t, *J* = 7.0 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃, at r.t., ppm) δ 167.35, 132.36, 120.98, 116.88, 63.06, 33.89, 24.02, 21.25, 14.20; IR (ATR, cm⁻¹) ν 2990, 2244, 1732, 1288, 1257, 1155, 989, 925, 852, 739. HRMS *m/z*: [M+H]⁺ Calcd for [C₉H₁₁NO₂]⁺ 165.0790; Found 165.0791.

Synthesis of 1-cyano-1-isobutylester-2-vinylcyclopropane 4

According to the synthetic procedure of **3**: the reaction of isobutyl cyanoacetate (1.41 g; 10.0 mmol) with *trans*-1,4-dibromo-2-butene (2.24 g; 10.5 mmol) in DMF (20 mL) at 60 °C for 16 h was performed to yield **4** as a colorless liquid (1.12 g; 5.79 mmol; 58%). ¹H-NMR (400 MHz, CDCl₃, at r.t., ppm) δ 5.67-5.59 (m, 1H), 5.42-5.35 (m, 2H), 3.96 (dd, *J* = 6.4 Hz, 4.0 Hz), 2.54 (dd, *J* = 16.8, 8.0 Hz, 1H), 2.05-1.94 (m, 2H), 1.64 (dd, *J* = 8.0, 4.8 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 6H); ¹³C-NMR (100

MHz, CDCl₃, at r.t., ppm) δ 167.32, 132.28, 120.97, 116.76, 72.95, 33.84, 27.81, 23.4, 21.24, 19.05; IR (ATR, cm⁻¹) ν 2963, 2877, 2246, 1731, 1470, 1258, 1169, 985, 923, 739. HRMS *m/z*: [M+H]⁺ Calcd for [C₁₁H₁₅NO₂]⁺ 193.1103; Found 193.1102.

Radical polymerization of 3

According to the synthetic procedure of **2**, **3** (165 mg; 1.00 mmol) using AIBN (16 mg; 0.10 mmol) in benzonitrile (0.40 mL) was performed to yield **5** as a yellow solid (141 mg; 85% of the theoretical weight); ¹H-NMR (400 MHz, CDCl₃, at r.t., ppm) δ 5.65 (brs, 2H), 4.26 (brq, *J* = 14.0, 6.8 Hz, 2H), 2.65-2.49 (brm, 4H), 1.31 (brt, *J* = 6.8 Hz, 3H); ¹³C-NMR (400 MHz, CDCl₃, at r.t., ppm) δ 167.56, 128.69, 127.01, 118.06, 63.18, 49.43, 49.34, 49.26, 39.08, 34.19, 14.18; IR (ATR, cm⁻¹) ν 2984, 2927, 2244, 1733, 1439, 1202, 971, 856. *M_n*=38400, *M_w*=97100, *M_w*/*M_n*=2.53.

Radical polymerization of 4

According to the synthetic procedure of **2**, **4** (193 mg; 1.00 mmol) using AIBN (16 mg; 0.10 mmol) in benzonitrile (0.40 mL) was performed to yield **6** as a yellow solid (116 mg; 60% of the theoretical weight); ¹H-NMR (400 MHz, CDCl₃, at r.t., ppm) δ 5.63 (brs, 2H), 3.95 (brd, *J* = 6.8 Hz, 2H), 2.65-2.49 (brm, 4H), 1.99-1.93 (brm, 1H), 0.95 (brd, *J* = 6.8 Hz, 6H); ¹³C-NMR (100 MHz, CDCl₃, at r.t., ppm) δ 167.59, 128.92, 118.16, 72.87, 49.77, 49.66, 49.55, 49.42, 39.35, 34.49, 27.74, 19.03; IR (ATR, cm⁻¹) ν 2963, 2875, 2241, 1736, 1470, 1206, 972. *M_n*=10900, *M_w*=17900, *M_w*/*M_n*=1.64.

Radical copolymerization of 1 with 3

Typical procedure: **1** (35 mg; 0.30 mmol) with **3** (116 mg; 0.700 mmol) using AIBN (16 mg; 0.10 mmol) in benzonitrile (0.40 mL) was performed to yield copolymer **7a** as a yellow solid (97 mg; 64% of the theoretical weight); ¹H-NMR (400 MHz, CDCl₃, at r.t., ppm) δ 5.94-5.65 (brm, 4H), 4.66 (brq, *J* = 6.8 Hz, 2H), 2.78-2.54 (brm, 8H), 1.31 (brt, *J* = 17.5 Hz, 3H) ¹³C-NMR (100 MHz, CDCl₃, at r.t., ppm) δ 167.65, 131.48, 128.89,

126.82, 118.26, 114.79, 63.35, 63.22, 49.65, 49.58, 49.49, 49.42, 43.71, 39.49, 39.30, 39.06, 37.42, 34.32, 26.27, 14.21; IR (ATR, cm⁻¹) ν 2983, 2934, 2246, 1733, 1439, 1206, 971, 856. 753. *M_n*=15700, *M_w*=38200 *M_w*/*M_n*=2.43.

Radical copolymerization of 1 with 4

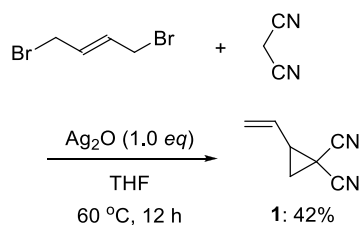
According to the synthetic procedure of **7a**, **1** (35 mg; 0.30 mmol) with **4** (135 mg; 0.700 mmol) using AIBN (16 mg; 0.10 mmol) in benzonitrile (0.40 mL) was performed to yield copolymer **8a** as a yellow solid (86 mg; 51% of the theoretical weight); ¹H-NMR (400 MHz, DMSO-*d*₆, at r.t., ppm) δ 5.86-5.58 (brm, 4H), 3.91 (brd, *J* = 5.2 Hz, 2H), 2.91-2.35 (brm, 8H), 1.93-1.87 (brm, 1H), 0.89 (brd, *J* = 6.8 Hz, 6H). ¹³C-NMR spectra (100 MHz, DMSO-*d*₆, at r.t., ppm) δ 167.20, 130.50, 128.56, 127.28, 118.25, 115.25, 49.45, 38.41, 37.88, 37.49, 37.43, 27.09, 25.43, 18.62; IR (ATR, cm⁻¹) ν 2962, 2876, 2243, 1737, 1439, 1207, 972. *M_n*=22400, *M_w*=38900, *M_w*/*M_n*=1.74.

Other copolymers **7** and **8** were synthesized and their spectroscopic data were summarized in the supporting information (SI), respectively.

RESULTS AND DISCUSSION

Synthesis of 1,1-dicyano-2-vinylcyclopropane 1

1,1-Dicyano-2-vinylcyclopropane (VCP) **1** was synthesized by the reaction of malononitrile with *trans*-1,4-dibromo-2-butene in the presence of silver oxide (Scheme 1). VCP **1** was obtained as a colorless liquid and its structure was confirmed by ¹H- and ¹³C-NMR analyses (Figures 4 and S1). The ¹H-NMR data was identical with the reported one.¹² The ¹³C-NMR spectrum indicated three signals attributable to the three carbons composing the cyclopropane ring at 5.28, 22.52 and 32.85 ppm. Two signals at 122.47 and 130.97 ppm confirmed the presence of the vinyl group. Signals attributable to the two cyano groups were observed at 114.31 and 115.61 ppm. In the IR spectrum, a strong absorption by cyano groups was observed at 2248 cm⁻¹.

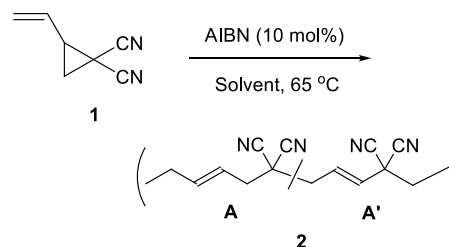


Scheme 1. Synthesis of VCP **1**

Radical ring-opening polymerization of **1**.

RROP behaviors of **1** were investigated with varying solvents (Scheme 2, Table 1). In all the cases, the polymerization was performed using AIBN as a radical initiator at 65 °C. In entry 1, the polymerization was performed in chlorobenzene. After the resulting solution became gelation, the obtained gel was washed in an excess of methanol and collected by a filtration to afford **2** as a white solid in 45% yield. From the filtrate, unreacted **1** was recovered in 37% yield. The resulting polymer was insoluble in various organic solvents such as dimethyl sulfoxide (DMSO), *N,N*-dimethyl acetoamide (DMAc), *N,N*-dimethyl formamide (DMF) and tetrahydrofuran (THF), suggesting the progress of crosslinking. In entry 2, DMF was used as a solvent. In this case, **1** did not undergo RROP and was recovered in 98% yield. In contrast, the uses

of acetonitrile and benzonitrile allowed successful synthesis of polymers soluble in DMSO, DMAc, and DMF (entries 3 and 4). By increasing the amount of AIBN (entry 4 vs. entry 5), by prolonging the polymerization time (entry 5 vs. entry 6), and by increasing the initial concentration of **1** (entry 6 vs. entry 7), the yield of **2** was successfully improved and unreacted **1** was recovered in 6% yield.



Scheme 2. RROP of VCP **1**

A plausible role of nitrile solvents to prevent crosslinking is illustrated in Figure 3. The high dipole moment of cyano group would allow strong interactions of the cyano groups at the propagating end with nitrile solvents. As a result, the steric hinderance around the propagating radical can be increased to prevent its attack to the carbon-carbon double bonds in the main chain.

Table 1. RROP of VCP **1**

| Entry | Solvent | Conc. (M) | AIBN (mol%) | Time (h) | Recovery of unreacted 1 (%) ^a | Yield of 2 (%) ^b | <i>M_n</i> (<i>M_w</i> / <i>M_n</i>) ^c |
|-------|----------------------------------|-----------|-------------|----------|---|------------------------------------|---|
| 1 | C ₆ H ₅ Cl | 1.0 | 1 | 16 | 37 | 45 | N.D. ^e |
| 2 | DMF | 1.0 | 1 | 16 | 98 | 0 | N.D. ^e |
| 3 | CH ₃ CN | 1.0 | 1 | 16 | - ^d | 7 | 2700 (1.50) |
| 4 | C ₆ H ₅ CN | 1.0 | 1 | 16 | - ^d | 25 | 3400 (1.85) |
| 5 | C ₆ H ₅ CN | 1.0 | 10 | 16 | - ^d | 46 | 2700 (1.50) |
| 6 | C ₆ H ₅ CN | 1.0 | 10 | 48 | - ^d | 57 | 3000 (1.77) |
| 7 | C ₆ H ₅ CN | 2.5 | 10 | 48 | 6 | 89 | 2900 (1.97) |

^a Recovered by column chromatography. ^b Methanol-insoluble Parts. ^c Estimated by SEC (calibration = polystyrene standards, eluent = DMF including 10 mM LiBr). ^d Not recovered. ^e Not determined.

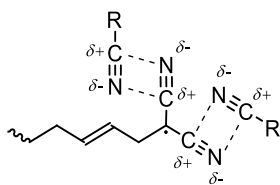


Figure 3. Dipole-dipole interactions between cyano groups

The structure of **2** obtained in entry 7 was studied by ^1H - and solid state ^{13}C -NMR spectroscopies. The resulting spectra are shown in Figure 4 and Figure S1, respectively. The ^1H -NMR spectrum clarified that **2** was consisted of units A and A' containing C-C double bond but not of units bearing cyclobutane ring (represented as B and B' in Figure 1). The absence of units B and B' was confirmed by the absence of the corresponding ^1H -NMR signals in a region 1.6–2.7 ppm.¹⁴ In the ^1H -NMR spectrum, methylene group a'' was observed separately from the other methylene groups a and a'. The comparison of signal intensity between these signals allowed calculation of unit ratio A : A'. The ratio thus calculated was 79 : 21. In the solid state ^{13}C -NMR spectrum, signals attributable to the olefin carbons b, b' and b'' were observed at 140 ppm. Signals appeared in 110–120 ppm were assigned to the carbons β and β' in the cyano groups. A signal of methylene carbon a'' was observed at 28 ppm, and those of other methylene carbons (a, a') and quaternary carbons (α , α') were confirmed around 40 ppm. In the IR spectrum, absorptions by the *trans* carbon-carbon double bond and cyano group were observed at 970 and 2250 cm^{-1} , respectively. Absorption by the *cis* carbon-carbon double bond that should appear at 710 cm^{-1} was negligible (Figure S11).

Copolymerization of VCP 1 with VCPs 3 and 4

Upon confirming the successful progress of RROP of **1** in benzonitrile allowing the formation of soluble homopolymer **2**, we next investigate copolymerization of **1** with vinylcyclopropanes bearing cyano and ester groups **3** and **4** (Scheme 3, Table 2).

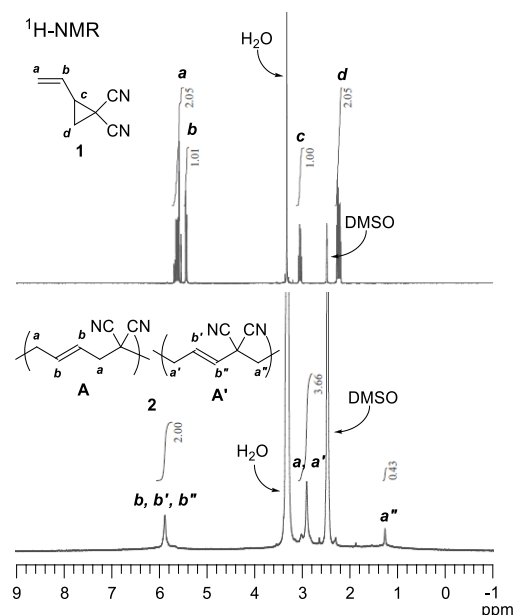
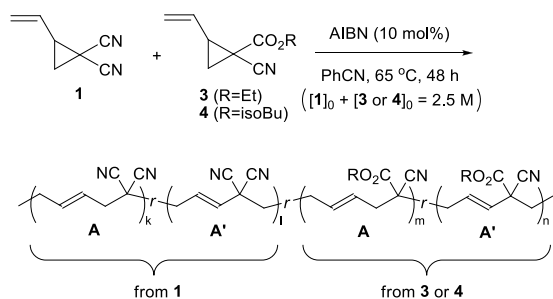


Figure 4. ^1H -NMR spectra of 1,1-dicyano-2-VCP **1** and homopolymer **2**.

According to the reported procedure¹⁶, VCP **3** was synthesized by the condensation reaction of ethyl 1-cyanoacetate with *trans*-1,4-dibromo-2-butene under basic conditions, and the other VCP **4** was synthesized similarly from the corresponding 1-cyanoacetate (Scheme S1). The structures of **3** and **4** were confirmed by their ^1H - and ^{13}C -NMR spectra (Figures S2 and S3). So far, copolymerization of **1** with simple vinyl monomers such as styrene, acrylonitrile and vinyl acetate has been reported.¹² Chiellini *et al.* have reported radical copolymerization of fluorinated and non-fluorinated 1,1-diester-2-VCP derivatives.⁶

Prior to performing copolymerizations of **1** with these VCPs bearing ester group, homopolymerizations **3** and **4** were performed using benzonitrile as a solvent (Table 2, entries 1 and 5). The homopolymerization of **3** proceeded successfully to afford the corresponding polymer **5** in a high yield. Similarly, the homopolymerization of VCP **4** gave homopolymer **6**. The structures of these homopolymers were studied by ^1H - and ^{13}C -NMR spectroscopies. The resulting spectra were shown in Figures S4–S6.

The $^1\text{H-NMR}$ spectra of **5** and **6** revealed that these homopolymers were not contaminated by cyclobutane-containing units, and thus, consisted by units A and A' containing C-C double bond. The unit ratios, [amount of unit A]:[amount of unit A'] were calculated based on the integrations of the corresponding signals. Homopolymer **5** was also analyzed by CH-COSY. The spectrum is shown in Figure S5, where the signal attributable to carbon a'' was distinguished from those attributable to carbons a and a'. Based on this finding, the assignments in the other spectra were corrected. In addition, the IR analyses of the polymers confirmed the presence of *trans* carbon-carbon double bonds, cyano, and ester groups (Figure S11).



Scheme 3. Copolymerization of VCP **1** with VCPs **3-4**

Under the same conditions for the homopolymerizations, copolymerization of **1** with **3** (entries 2-4) and that of **1** with **4** (entries 6-8) were performed. The resulting copolymers **7** and **8** were more soluble in THF, chloroform, and acetone than **2** (= homopolymers of **1**), demonstrating that the solubility of the copolymers was enhanced by the introduction of the **3**- and **4**-derived units (Table S1). The structures of the copolymers were analyzed by NMR spectroscopies (Figures S7-S10). In the resulting spectra, signals derived from cyclobutane ring were not detected. $^1\text{H-NMR}$ spectra of **7** and **8** revealed that these polymers were mainly consisted of structure A formed by the cleavage of C1-C2 bond the cyclopropane moiety.

The composition ratios of **1**-derived unit ($k + l$) to **3**- and **4**-derived unit ($m + n$) in copolymers **7** and **8** were calculated from $^1\text{H-NMR}$ spectra. The ratios indicated that of **3**- and **4**-derived units were incorporated into copolymers **7** and **8** more frequently than those expected from the feed ratios. The ratios of unit A to unit A' were calculated based on the relative intensities of the corresponding $^1\text{H-NMR}$ signals.

Table 2. Radical homopolymerizations and copolymerizations of VCPs

| Entry | Monomer(s) (Feed ratio) | Polymer | Yield (%) ^a | ($k + l$) : ($m + n$) ^b | A : A' ^b | M_n (M_w/M_n) ^c |
|-------|---------------------------------|-----------|------------------------|--|---------------------|----------------------------------|
| 1 | 3 | 5 | 85 | - | 95 : 5 | 38400 (2.53) |
| 2 | 1 and 3 (30 : 70) | 7a | 64 | 18 : 82 | 94 : 6 | 15700 (2.43) |
| 3 | 1 and 3 (50 : 50) | 7b | 52 | 41 : 59 | 92 : 8 | 12500 (2.00) |
| 4 | 1 and 3 (70 : 30) | 7c | 64 | 57 : 43 | 93 : 7 | 9800 (1.94) |
| 5 | 4 | 6 | 60 | - | 88 : 12 | 10900 (1.64) |
| 6 | 1 and 4 (30 : 70) | 8a | 51 | 21 : 79 | 95 : 5 | 22400 (1.74) |
| 7 | 1 and 4 (50 : 50) | 8b | 55 | 43 : 57 | 93 : 7 | 10500 (2.38) |
| 8 | 1 and 4 (70 : 30) | 8c | 68 | 66 : 34 | 88 : 12 | 12400 (1.87) |

^a Methanol-insoluble Parts. ^b Determined by $^1\text{H-NMR}$. ^c Estimated by SEC (calibration = polystyrene standards, eluent = DMF including 10 mM LiBr).

Like homopolymer **2**, the amount of unit A formed by cleavage of C1-C2 bond in VCP was much larger than that of unit A' formed by cleavage of C1-C3 bond in VCP.

Thermal properties of homopolymers and copolymers

Thermal properties of obtained polymers were evaluated by TG and DSC analyses (Figures S13-S18). From the resulting TG thermograms, 10% weight loss temperature (T_{d10}) and the residual weight at 600 °C were extracted and summarized in Table 3. The thermal degradability of the homopolymers **2**, **5**, and **6** were compared with each other to find that the corresponding T_{d10} values were quite similar (entries 1-3); however, there was a significant difference in the residual weight at 600 °C: those of **5** and **6** were approximately 20%, whilst that of **2** was 57%, suggesting that the higher content of cyano group contributed to the efficient suppression of the thermal degradation at elevated temperatures ranging from 350 to 600 °C. At such high temperatures, the cyano groups would undergo thermally induced trimerization into

triazine rings to enhance the thermal stability of polymers.²⁴⁻²⁶ We attempted to confirm the presence of triazine rings by measuring IR spectrum of **2** after heating it at 600 °C (Figure S12); however, the spectrum did not show decisively clear absorption at around 1560 cm^{-1} . The residual weights at 600 °C of copolymers **7**, obtained by the copolymerization of **1** and **3**, were higher than that of homopolymer **5**, obtained by the homopolymerization of VCP **3** bearing ester group (entries 4-6 vs. entry 2). In addition, the increase of the content of **1**-derived units in copolymer **7** resulted in the increase of their residual weights at 600 °C, suggesting that the thermal stability of the copolymers was improved by the increase of cyano groups. A similar tendency was observed in the case of copolymers of **8**, obtained by the copolymerization of **1** and **4**. DSC analysis of homopolymer **2** revealed that it was a crystalline polymer, of which melting temperature (T_m) was observed at 210 °C. Such crystallinity of **2** would be arisen by the high content of highly polar cyano groups in the side chains.

Table 3. Thermal properties of homopolymers and copolymers

| Entry | Polymer | T_{d10} (°C) ^a | Residual weight at 600 °C (%) ^a |
|-------|---|-----------------------------|--|
| 1 | 2 (homopolymer of 1) ^b | 350 | 57 |
| 2 | 5 (homopolymer of 3) | 350 | 21 |
| 3 | 6 (homopolymer of 4) | 350 | 17 |
| 4 | 7a (copolymer of 1 and 3 , 30:70) | 340 | 23 |
| 5 | 7b (copolymer of 1 and 3 , 50:50) | 340 | 33 |
| 6 | 7c (copolymer of 1 and 3 , 70:30) ^c | 330 | 38 |
| 7 | 8a (copolymer of 1 and 4 , 30:70) | 350 | 23 |
| 8 | 8b (copolymer of 1 and 4 , 50:50) | 350 | 31 |
| 9 | 8c (copolymer of 1 and 4 , 70:30) ^d | 350 | 39 |

^a Determined by TGA. ^b $T_m=210$ °C. ^c $T_g=181$. ^d $T_g=199$.

Copolymers **7c** and **8c**, of which contents of the **1**-derived unit were higher than the other copolymers, exhibited high glass transition temperatures as **181 °C** and **199 °C** (entries 6 and 9), suggesting that the motion of the polymer chains was efficiently suppressed by the strong dipolar interaction between cyano groups in the side chains.

CONCLUSIONS

RROP of 1,1-dicyano-2-VCP **1** using benzonitrile as the solvent successfully gave the corresponding homopolymer **2** soluble in a wide range of organic solvents. The use of benzonitrile for the copolymerizations of **1** with 1-cyano-1-ester-2-VCP derivatives **3** and **4** allowed also their successful progress affording the corresponding copolymers **7** and **8**, whose solubilities in organic solvents were much higher than that of **2**. The homopolymer **2** and the copolymers **7** and **8** showed higher thermal stability than the homopolymers of **3** and **4**, leading to the improved residual weights at 600 °C. This improvement should be due to the thermally induced trimerization of the cyano groups in the side chains of the polymers. The homopolymer **2** exhibited crystallinity presumably due to the dipole interactions between the cyano pendants. Such a high degree in the dipole interactions between side chains resulted in the high glass transition temperatures of **7c** (copolymer of **1** and **3**, feed ratio = 70 : 30) and **8c** (copolymer of **1** and **4**, feed ratio = 70 : 30), suggesting the potential applicability of VCP **1** as a monomer for synthesizing high performance polymers by radical processes.

ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

1. T. Endo, Y. Yoshida, *J. Network Polym., Jpn.*, **2019**, 40, 45.
2. Y. Catel, P. Fässler, U. Fischer, C. Gorsche, R. Liska, S. Schörpf, S. Tauscher, N. Moszner, *European Polymer Journal*, **2018**, 98, 439.
3. T. Endo, A. Sudo, *ACS Symposium Series*, **2015**, 187, 19.
4. S. Ata, D. Mal, N. K. Singha, *RSC. Adv.*, **2013**, 3, 14486.
5. D. H. Seuyep, N. Gerrit, A. Luinstra, P. Theato, *Polym. Chem.*, **2013**, 4, 2724.
6. G. Gallo, M. Ragnoli, M. Bertolucci, C. K. Ober, E. J. Kramer, E. Chiellini, *Macromol. Symp.*, **2004**, 218, 303.
7. A. de Meijere, V. Bagutski, F. Zeuner, U. K. Fischer, V. Rheinberger, N. Moszner, *Eur. J. Org. Chem.* **2004**, 17, 3669.
8. N. Moszner, T. Völkel, F. Zeuner, V. Rheinberger, *Macromol. Symp.*, **2000**, 153, 151.
9. I. Cho, *Prog. Polym. Sci.*, **2000**, 25, 1043.
10. F. Sanda, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.*, **2000**, 39, 265.
11. I. Cho, J.-Y. Lee, *J. Polymer Sci. Polymer Chem. Ed.*, **1980**, 18, 639.
12. I. Cho, K.-D. Ahn, *J. Polymer Sci. Polymer Chem. Ed.*, **1979**, 17, 3169.
13. I. Cho, K.-D. Ahn, *Polymer Letters Edition*, **1977**, 15, 751.
14. F. Sanda, T. Takata, T. Endo, *Macromolecules*, **1993**, 26, 1818.
15. T. Takahashi, *J. Polym. Sci. A-1*, **1970**, 8, 617.
16. H. Chiba, K. Kitazume, S. Yamada, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.*, **2016**, 54, 39.
17. F. Sanda, T. Takata, T. Endo, *Macromolecules*, **1994**, 27, 3982.
18. N. Takahashi, S. Yamada, A. Sudo, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.*, **2017**, 55, 3996.
19. N. Takahashi, A. Sudo, T. Endo, *Macromolecules*, **2017**, 50, 5679.
20. P. P. Contreras, S. Agarwal, *Polym. Chem.*, **2016**, 7, 3100.

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65
21. Y. Catel, U. Fischer, P. Fässler, N. Moszner, *Macromol. Chem. Phys.*, **2016**, 217, 2686.
 22. P. P. Contreras, P. Tyagi, S. Agarwal, *Polym. Chem.*, **2015**, 6, 2297.
 23. P. P. Contreras, C. Kuttner, A. Fery, U. Stahlschmidt, V. Jérôme, R. Freitag, S. Agarwal, *Chem. Commun.*, **2015**, 51, 11899.
 24. Y. Liu, S. Zhao, H. Zhang, M. Wang, M. Run, *Thermochim. Acta*, **2012**, 549, 42.
 25. G. P. Cao, W. J. Chen, J. J. Wei, W. T. Li, X. B. Liu, *Express Polym. Lett.*, **2007**, 1, 512.
 26. Z. Brunovska, H. Isida, *J. Appl. Polym. Sci.*, **1999**, 73, 2937.

Supporting Information for

Radical Ring-Opening Polymerization Behavior of 1,1-Dicyano-2-Vinylcyclopropane and
Its Copolymerization with 1-Cyano-1-Ester-2-Vinylcyclopropane

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Spectroscopic data for copolymers **7** and **8**

Synthesis of **7b**

According to the synthetic procedure of **7a**, **1** (59 mg; 0.50 mmol) with **3** (83 mg; 0.50 mmol) using AIBN (16 mg; 0.10 mmol) in benzonitrile (0.40 mL) was performed to yield copolymer **7b** as a yellow solid (73 mg; 52% of the theoretical weight); $^1\text{H-NMR}$ (400 MHz, CDCl_3 , at r.t., ppm) δ 5.94-5.65 (brm, 4H), 4.66 (brq, $J = 6.8$ Hz, 2H), 2.78-2.54 (brm, 8H), 1.31 (brt, $J = 17.5$ Hz, 3H); $^{13}\text{C-NMR}$ (CP-MAS) δ 168.25, 130.05, 118.08, 64.34, 50.90, 40.59, 15.33; IR (ATR, cm^{-1}) ν 2984, 2938, 2244, 1734, 1440, 1215, 971, 856. 760. $M_n=12500$, $M_w=25000$, $M_w/M_n=2.00$.

Synthesis of **7c**

According to the synthetic procedure of **7a**, **1** (83 mg; 0.70 mmol) with **3** (50 mg; 0.300 mmol) using AIBN (16 mg; 0.10 mmol) in benzonitrile (0.40 mL) was performed to yield **7c** as a yellow solid (97 mg; 64% of the theoretical weight); $^1\text{H-NMR}$ (400 MHz, CDCl_3 , at r.t., ppm) δ 5.94-5.65 (brm, 4H), 4.66 (brq, $J = 6.8$ Hz, 2H), 2.78-2.54 (brm, 8H), 1.31 (brt, $J = 17.5$ Hz, 3H); $^{13}\text{C-NMR}$ (CP-MAS) δ 168.40, 130.43, 117.00, 64.43, 50.27, 40.40, 15.48; IR (ATR, cm^{-1}) ν 2983, 2934, 2246, 1737, 1441, 1215, 969, 856. 756. $M_n=9800$, $M_w=19000$, $M_w/M_n=1.94$.

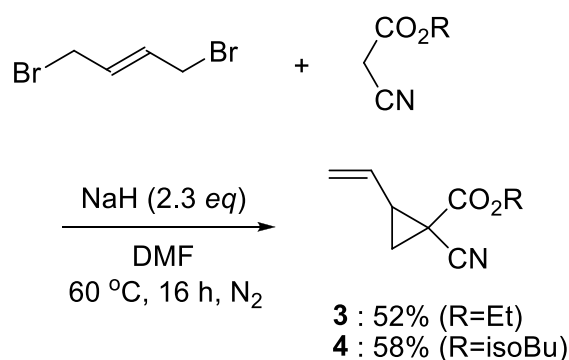
Synthesis of **8b**

According to the synthetic procedure of **8a**, **1** (59 mg; 0.50 mmol) with **4** (97 mg; 0.50 mmol) using AIBN (16 mg; 0.10 mmol) in benzonitrile (0.40 mL) was performed to yield copolymer **8b** as a yellow solid (86 mg; 55% of the theoretical weight); $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, at r.t., ppm) δ 5.87-5.58 (brm, 4H), 3.91 (brd, $J = 5.2$ Hz, 2H), 2.92-2.49 (brm, 8H), 1.94-1.87 (brm, 1H), 0.89 (brd, $J = 6.8$ Hz, 6H). $^{13}\text{C-NMR}$ spectra (CP-MAS)

δ 168.30, 130.54, 117.93, 73.91, 50.56, 40.54, 28.87, 20.17; IR (ATR, cm^{-1}) ν 2966, 2877, 2245, 1737, 1439, 1208, 971. $M_n=10500$, $M_w=25000$, $M_w/M_n=2.38$.

Synthesis of **8c**

According to the synthetic procedure of **8a**, **1** (83 mg; 0.70 mmol) with **4** (58 mg; 0.30 mmol) using AIBN (16 mg; 0.10 mmol) in benzonitrile (0.40 mL) was performed to yield **8c** as a yellow solid (96 mg; 68% of the theoretical weight); $^1\text{H-NMR}$ (400 MHz, CDCl_3 , at r.t., ppm) δ 5.89-5.60 (brm, 4H), 3.92 (brd, $J = 6.0$ Hz, 2H), 2.93-2.60 (brm, 8H), 1.95-1.88 (brm, 1H), 0.90 (brd, $J = 6.8$ Hz, 6H). $^{13}\text{C-NMR}$ spectra (CP-MAS) δ 168.25, 130.24, 118.08, 73.81, 51.24, 40.54, 28.96, 20.27; IR (ATR, cm^{-1}) ν 2966, 2875, 2247, 1737, 1440, 1215, 969. $M_n=12400$, $M_w=23200$, $M_w/M_n=1.87$.



Scheme S1. Synthesis of VCPs **3-4**

NMR Spectra

^{13}C -NMR

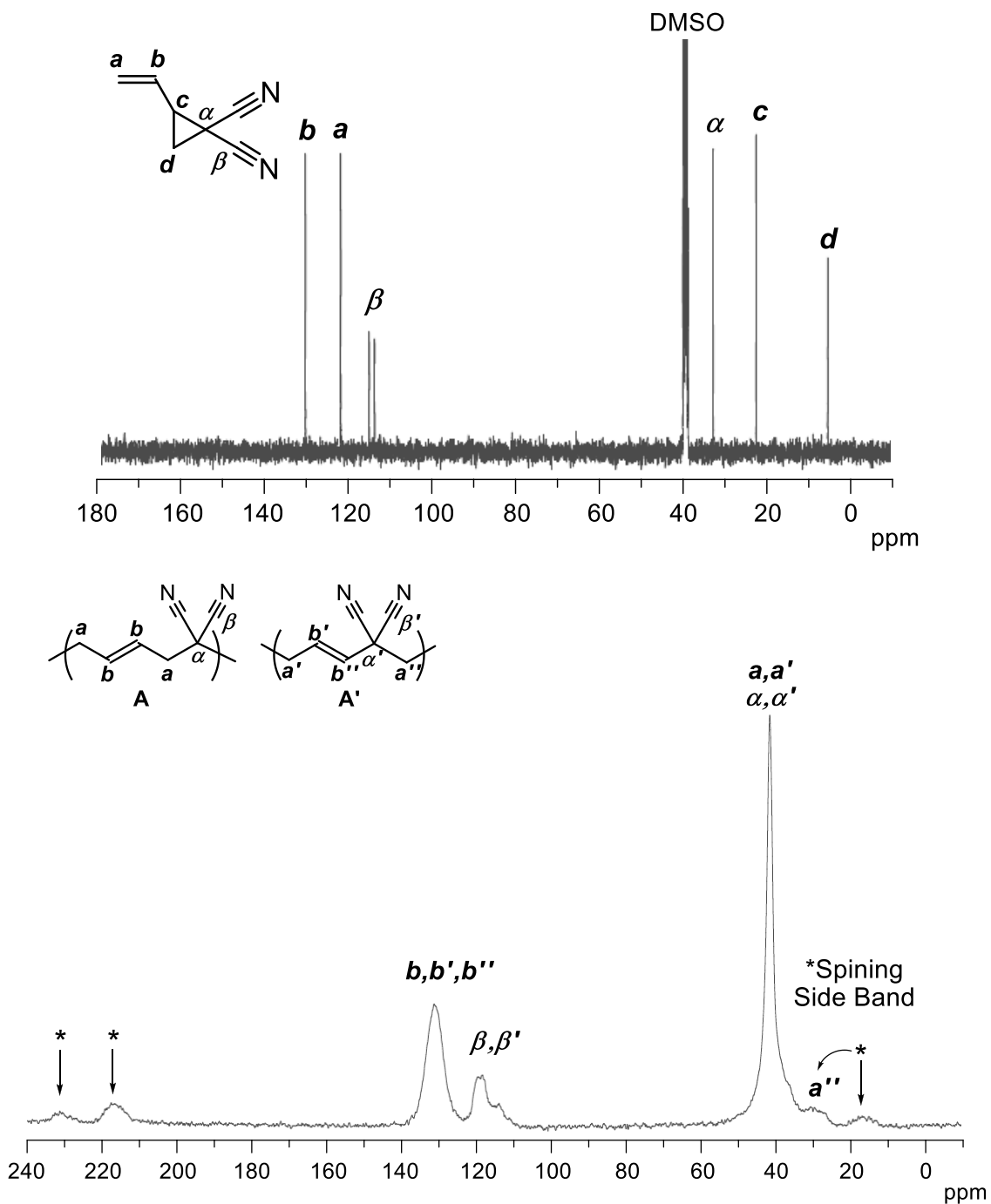
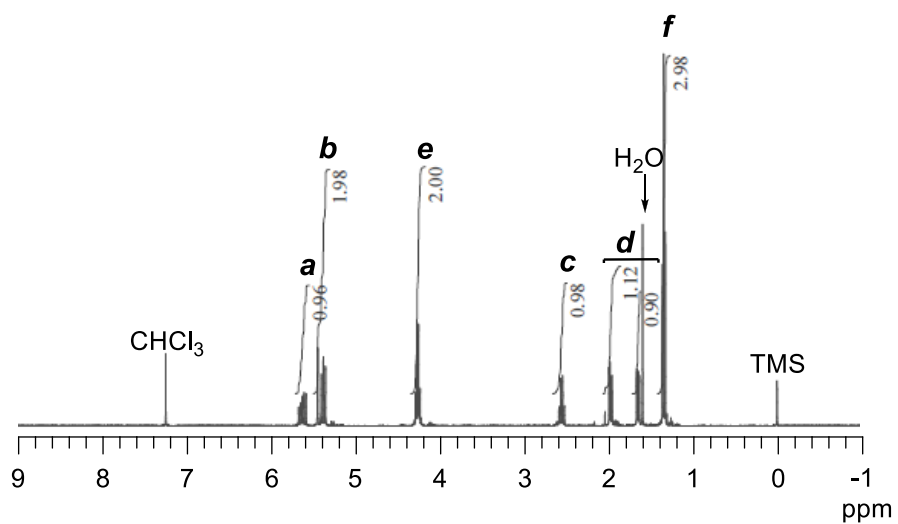
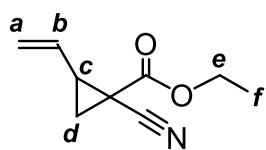


Figure S1. ^{13}C -NMR spectrum of 1,1-dicyano-2-vinylcyclopropane **1** and a solid state ^{13}C -NMR spectrum of homopolymer **2**

¹H-NMR



¹³C-NMR

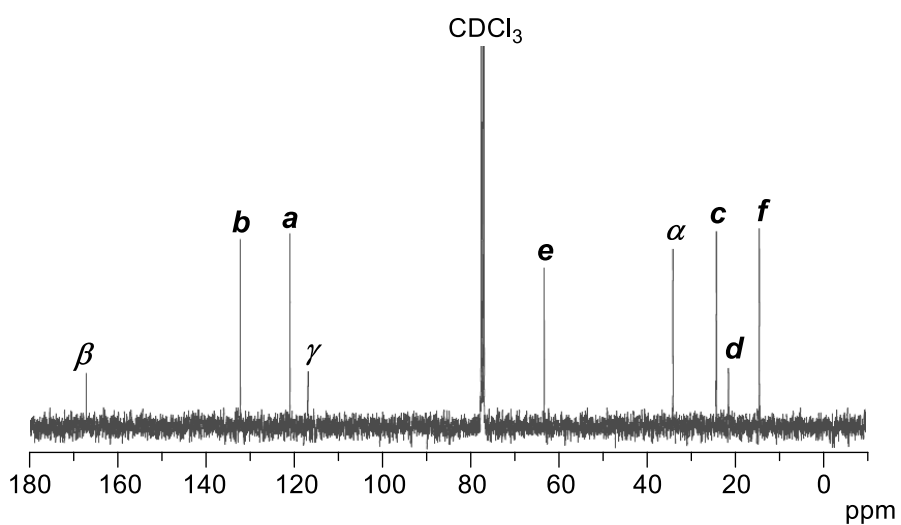
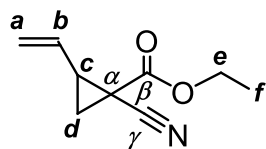


Figure S2. ¹H- and ¹³C-NMR spectra of 1-cyano-1-ethoxycarbonyl-2-vinylcyclopropane **3**

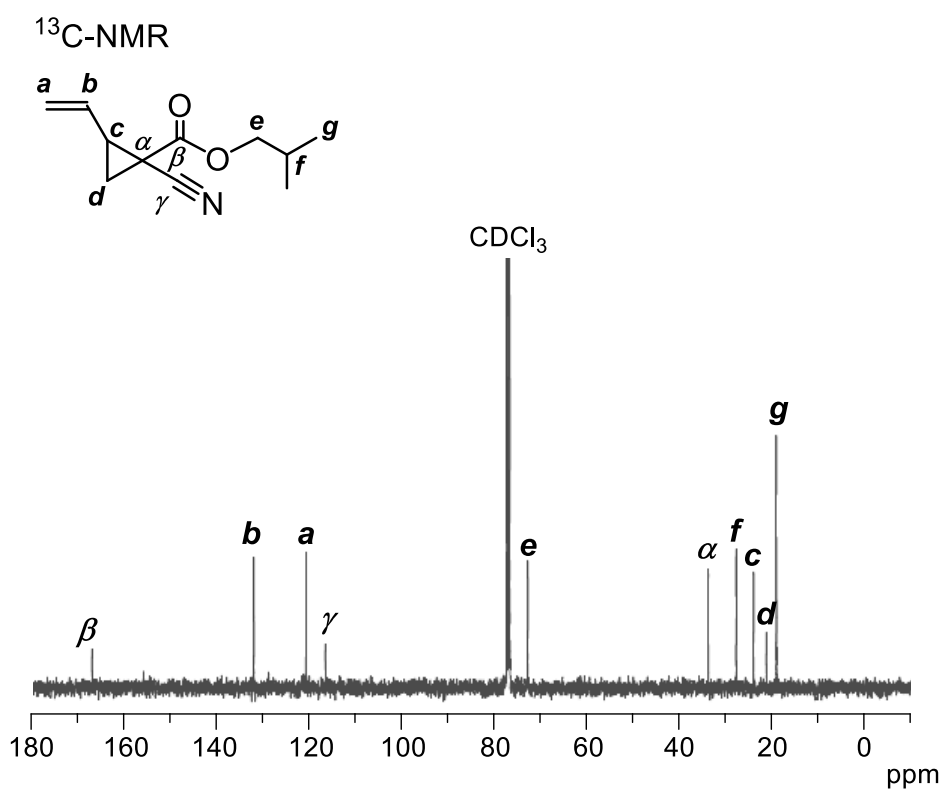
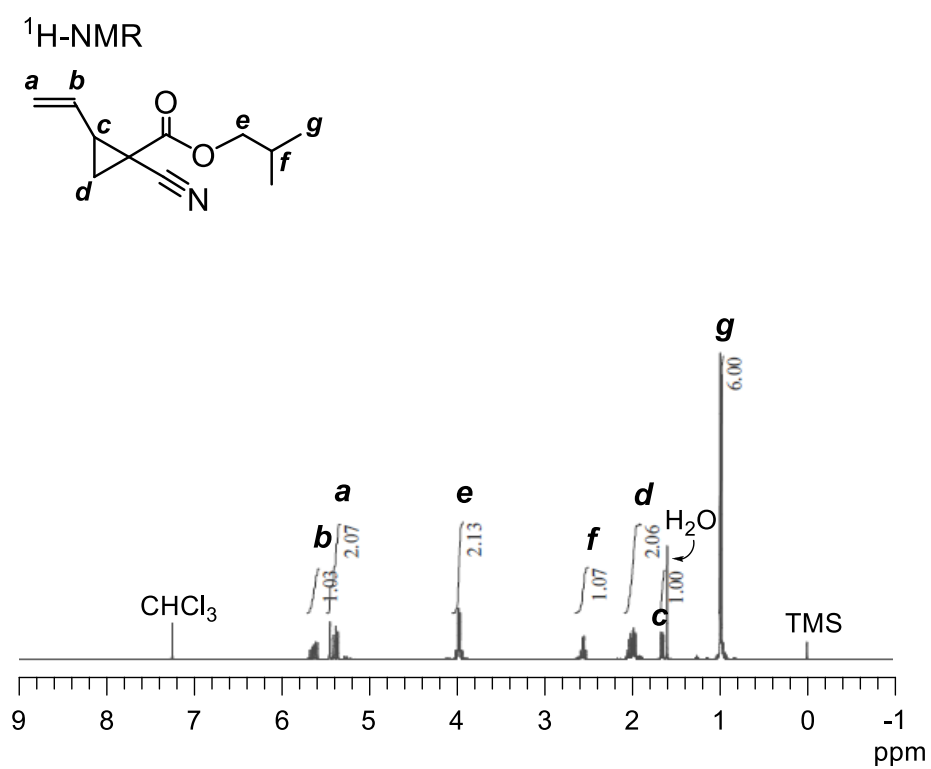
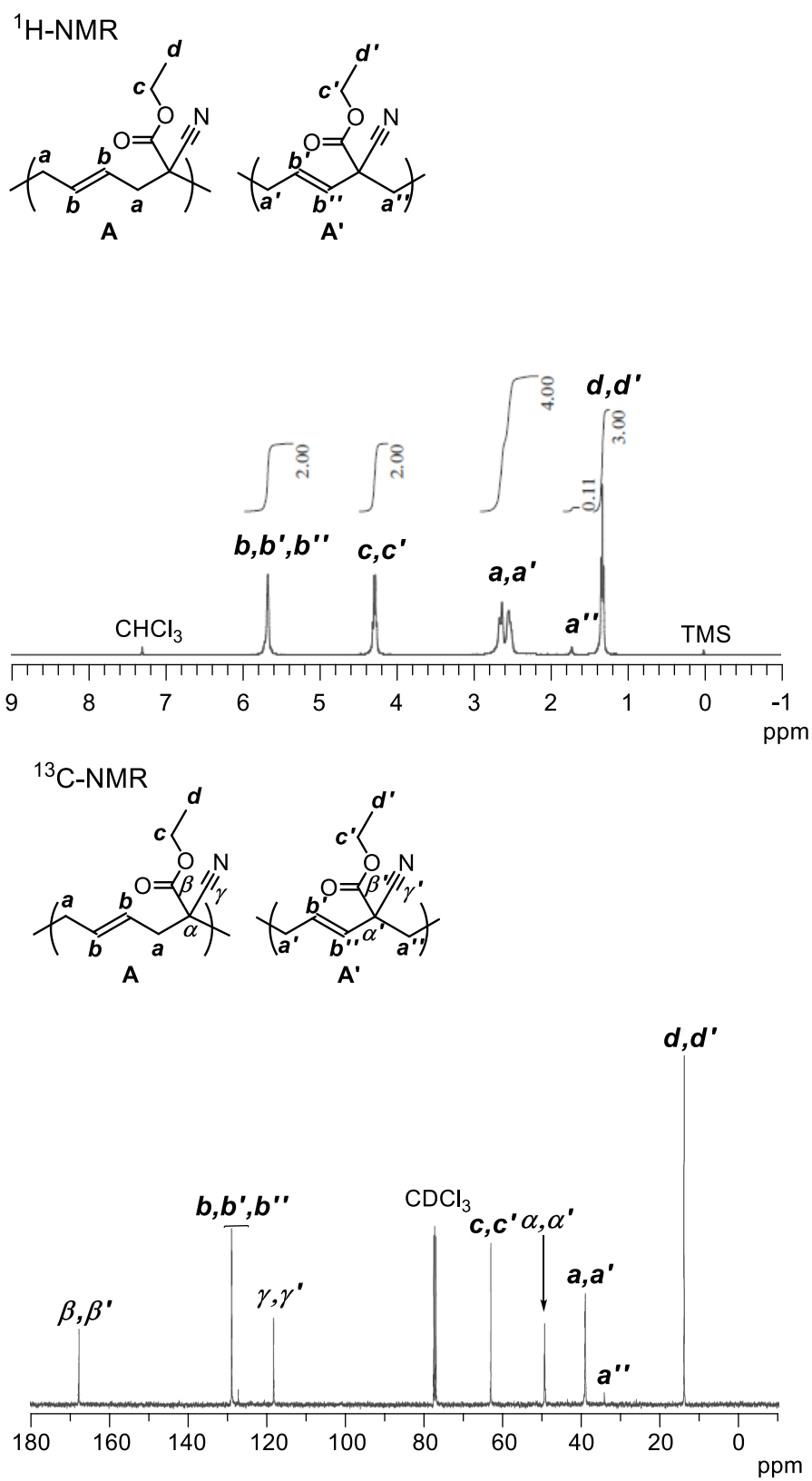


Figure S3. ¹H- and ¹³C-NMR spectra of 1-cyano-1-isobutylester-2-vinylcyclopropane **4**



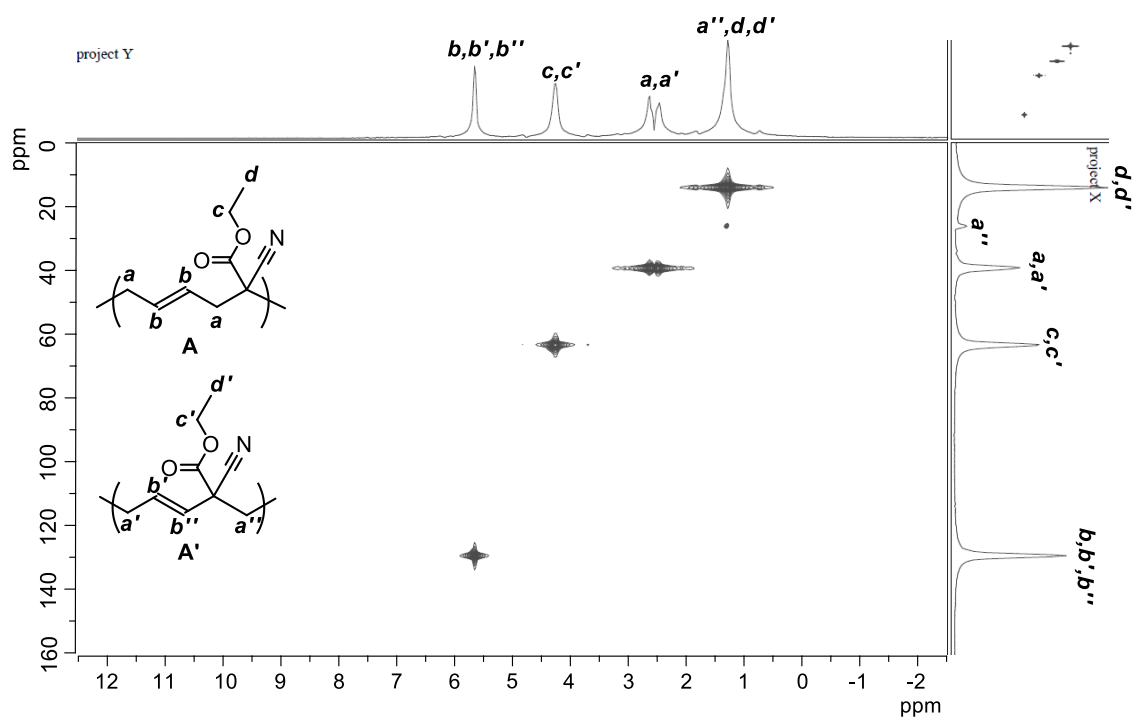


Figure S5. ^1H - ^{13}C -NMR spectrum of homopolymer **5**

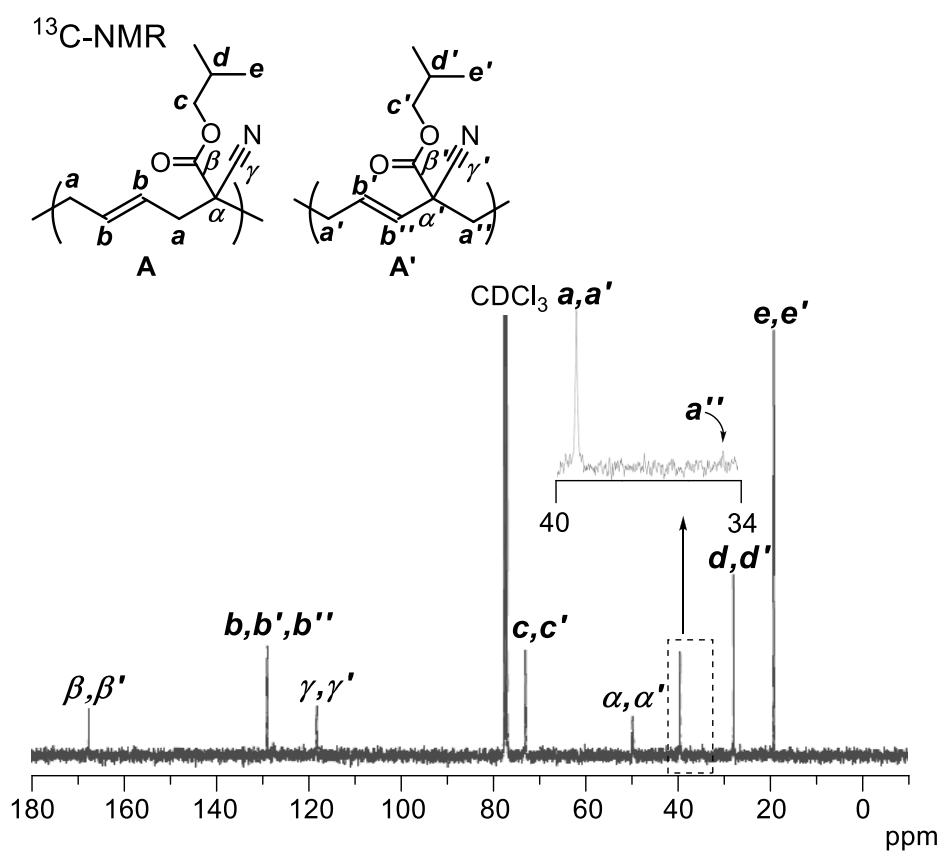
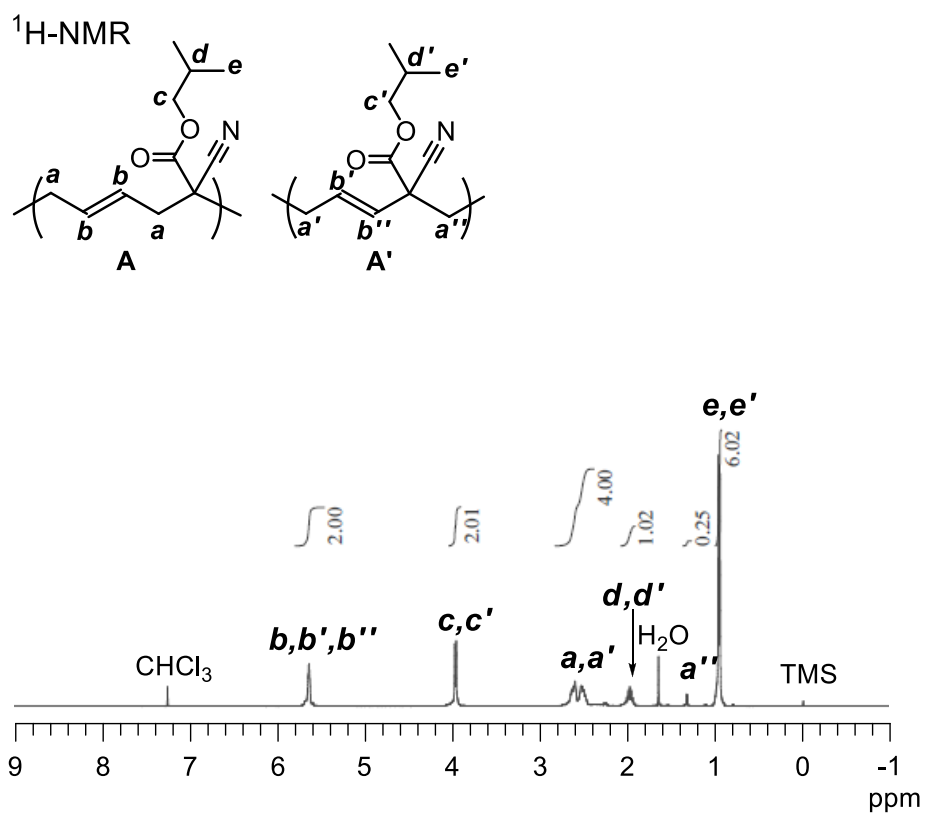
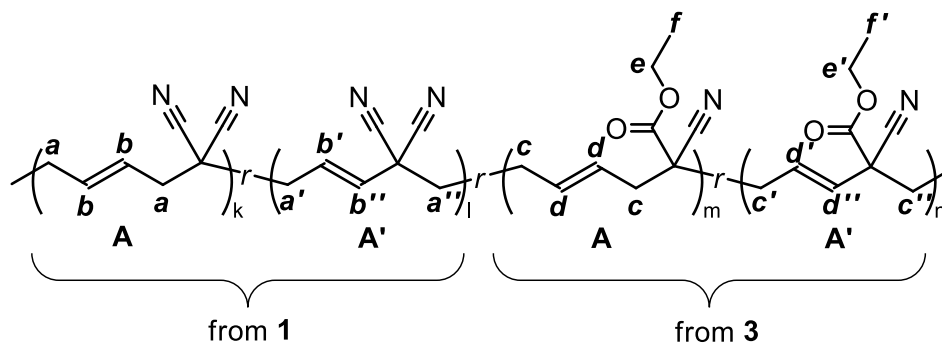
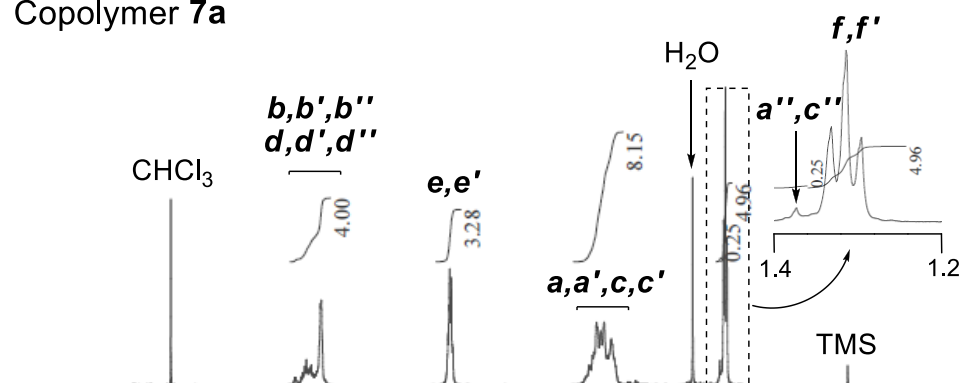


Figure S6. ¹H- and ¹³C-NMR spectra of homopolymer 6

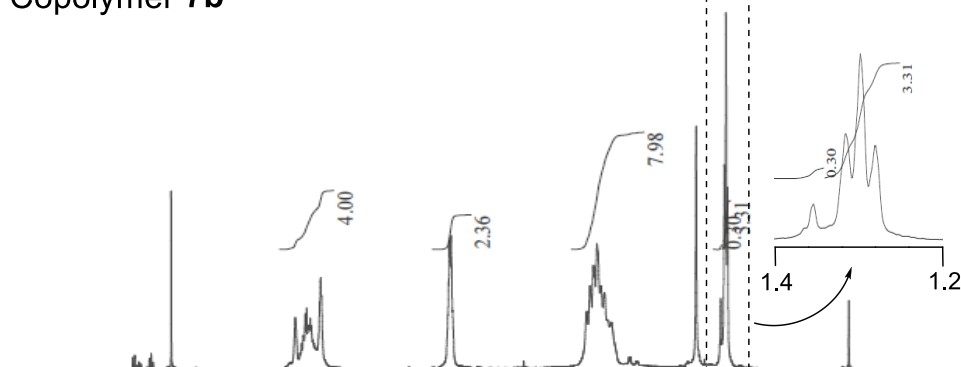
$^1\text{H-NMR}$



Copolymer **7a**



Copolymer **7b**



Copolymer **7c**

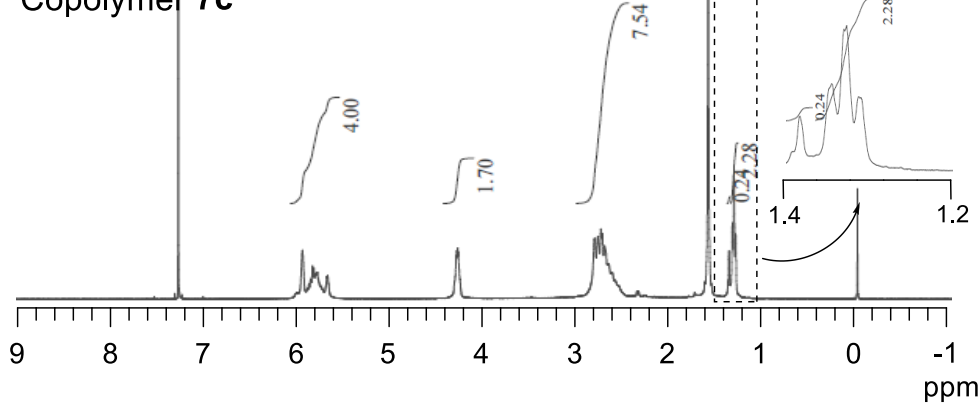
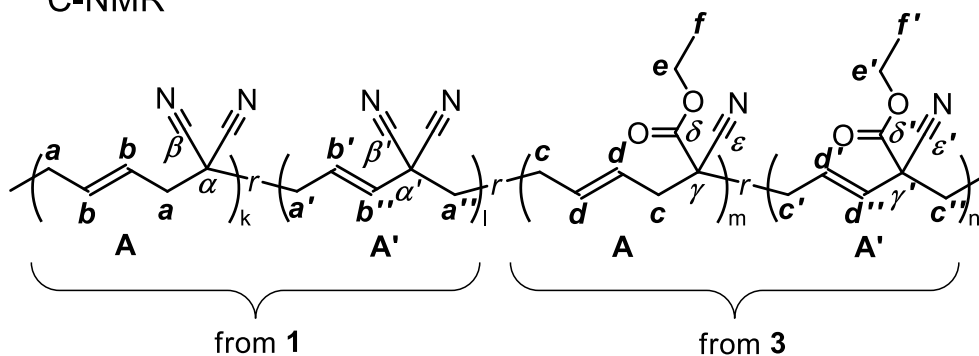
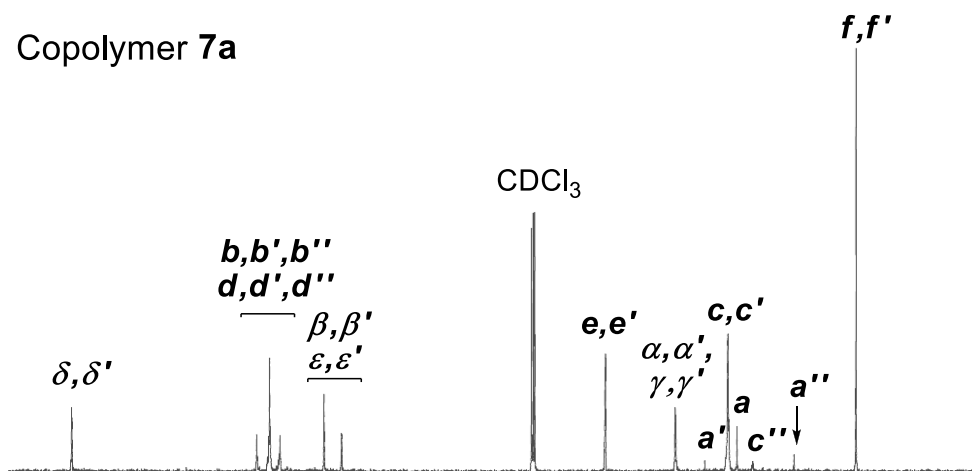


Figure S7. $^1\text{H-NMR}$ spectra of copolymers **7a-c**

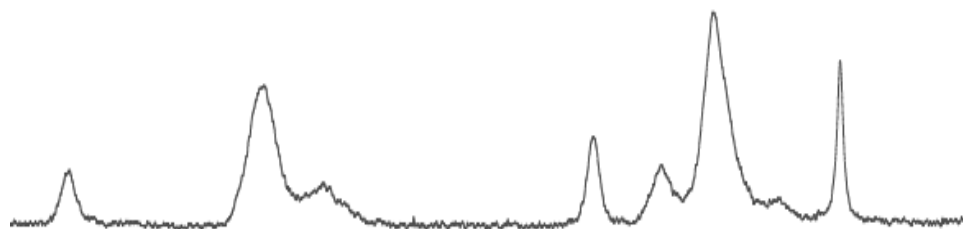
^{13}C -NMR



Copolymer **7a**



Copolymer **7b**



Copolymer **7c**

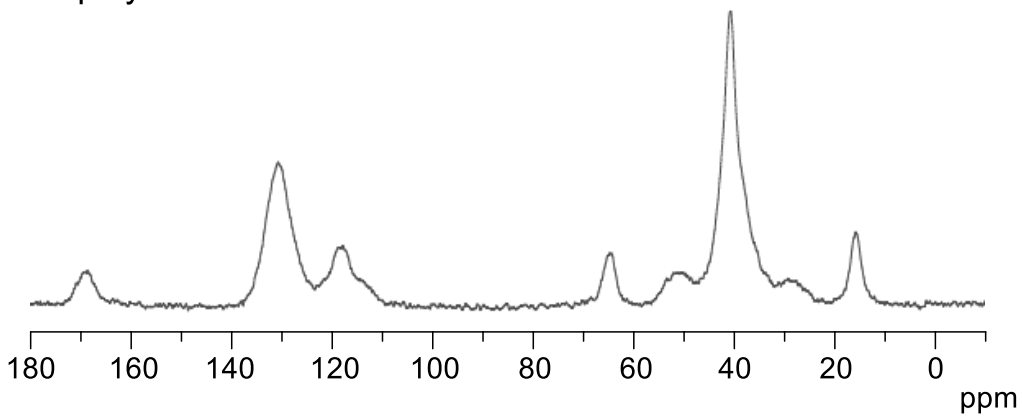
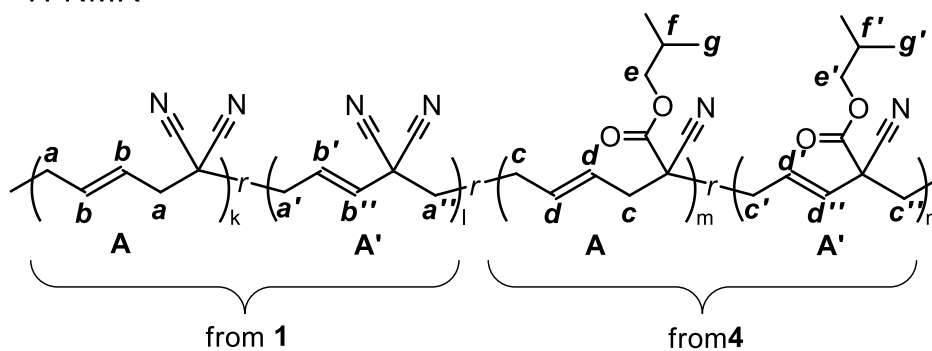


Figure S8. ^{13}C -NMR spectra of copolymers **7a-c**

$^1\text{H-NMR}$



Copolymer **8a**

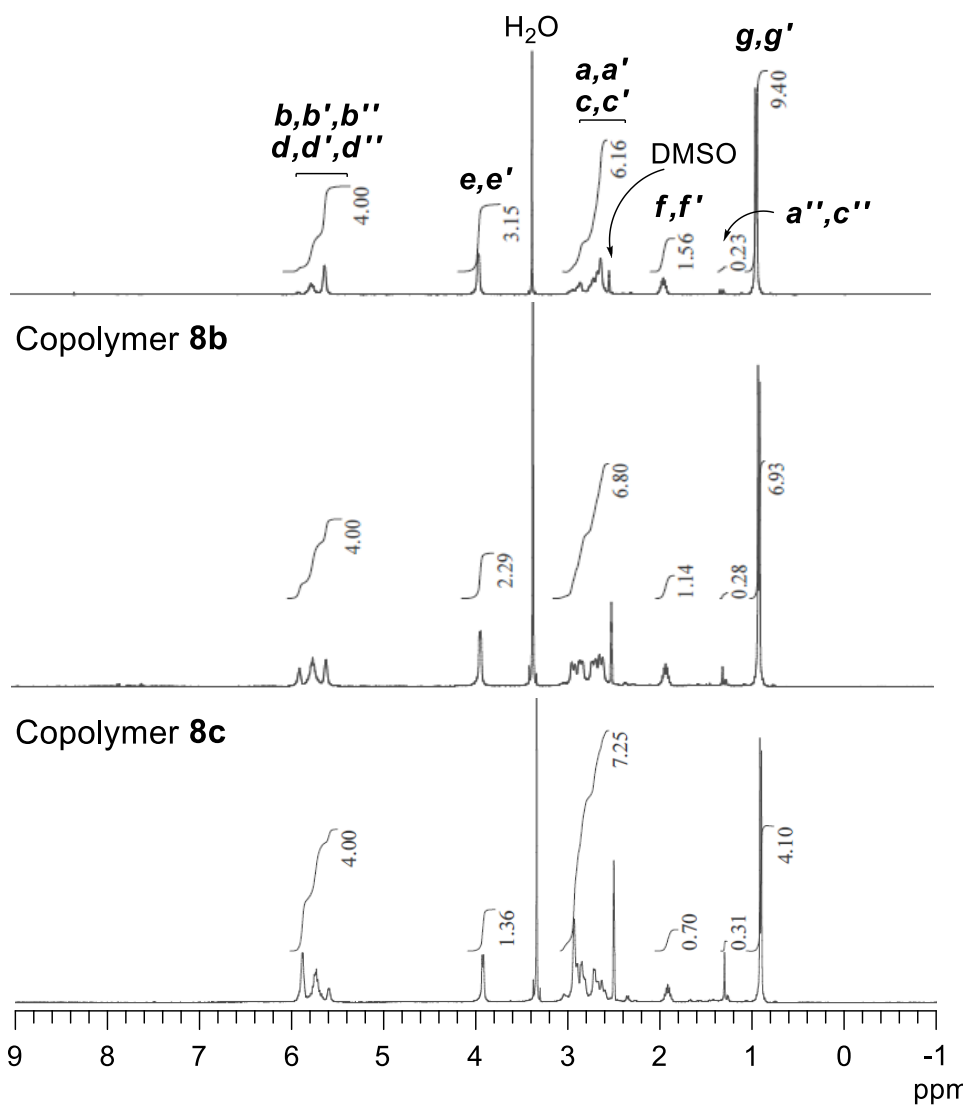
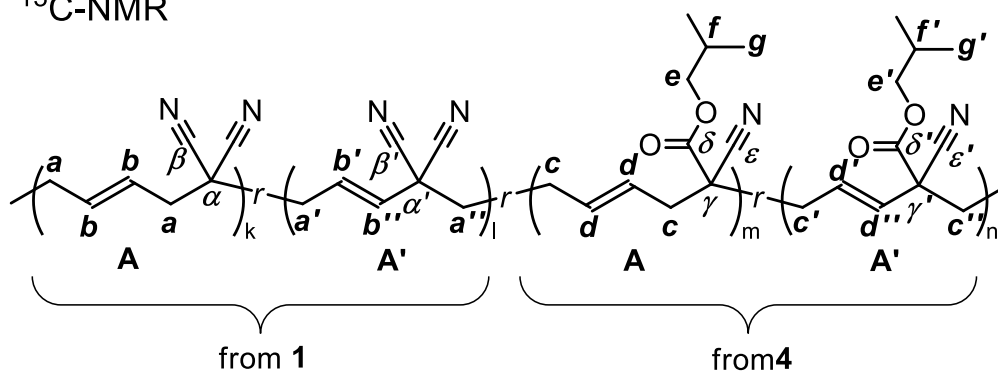
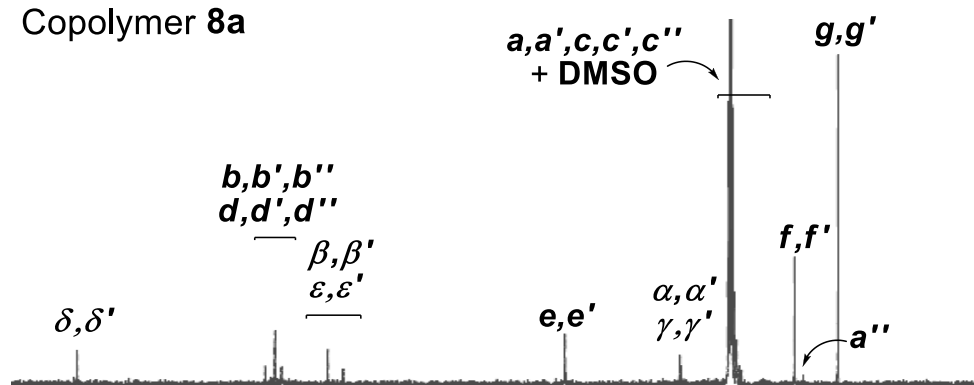


Figure S9. $^1\text{H-NMR}$ spectra of copolymers **8a-c**

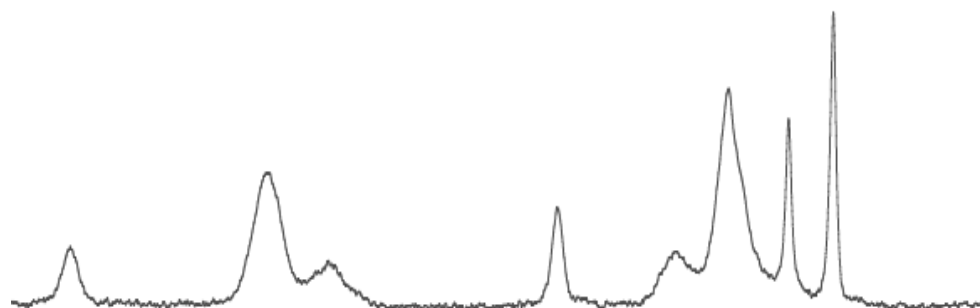
^{13}C -NMR



Copolymer **8a**



Copolymer **8b**



Copolymer **8c**

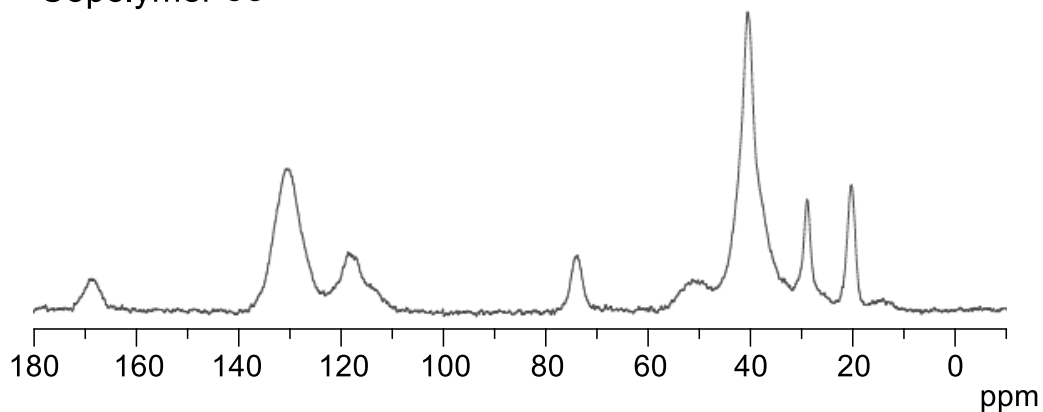


Figure S10. ^{13}C -NMR spectra of copolymers **8a-c**

IR spectra

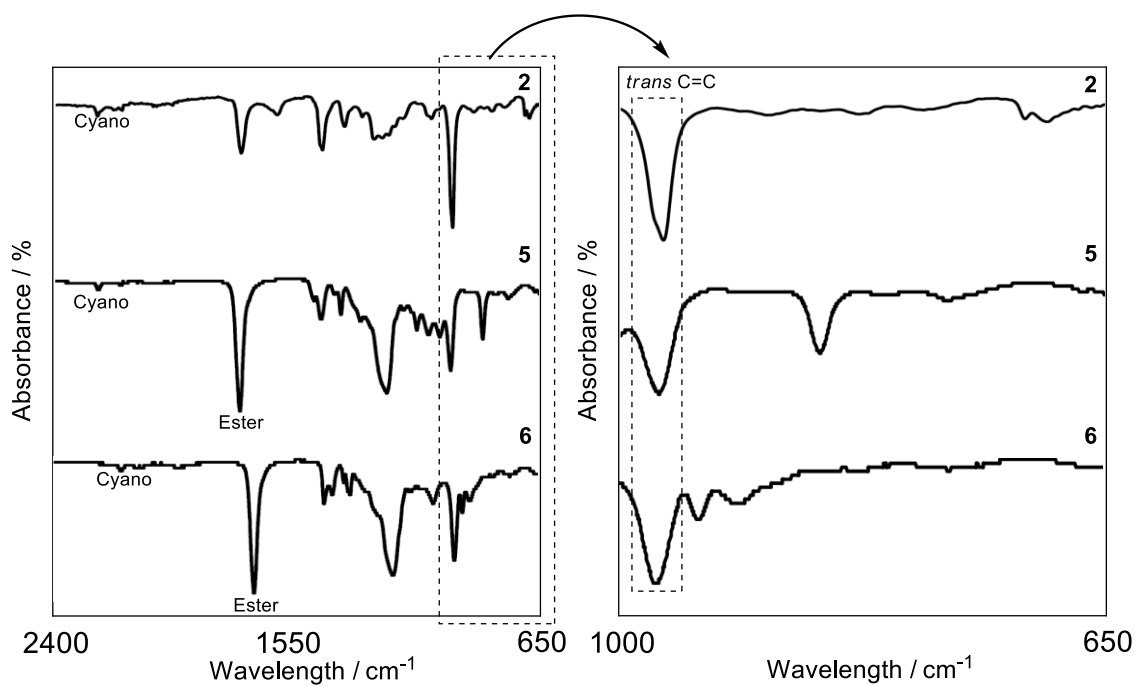


Figure S11. IR spectra of homopolymers 2, 5 and 6

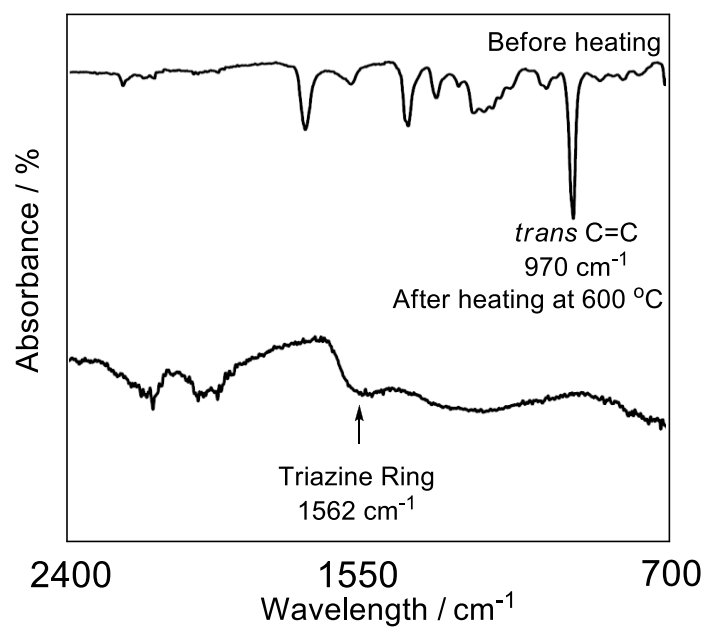


Figure S12. IR spectra of 2 before and after heating at 600 °C.

TG-DTA Chart

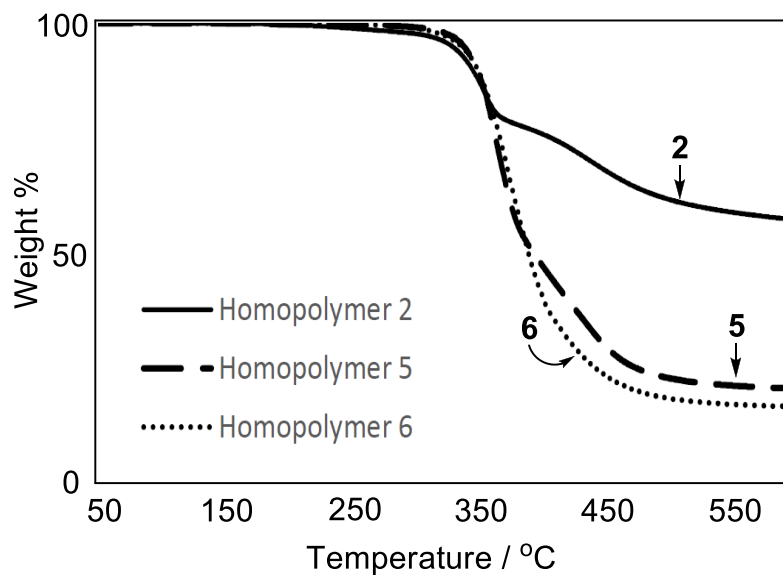


Figure S13. TG-Thermograms of homopolymers 2, 5 and 6

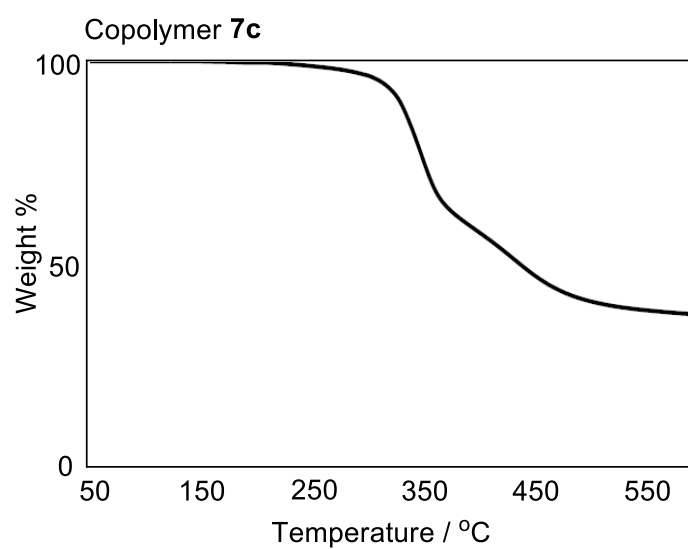
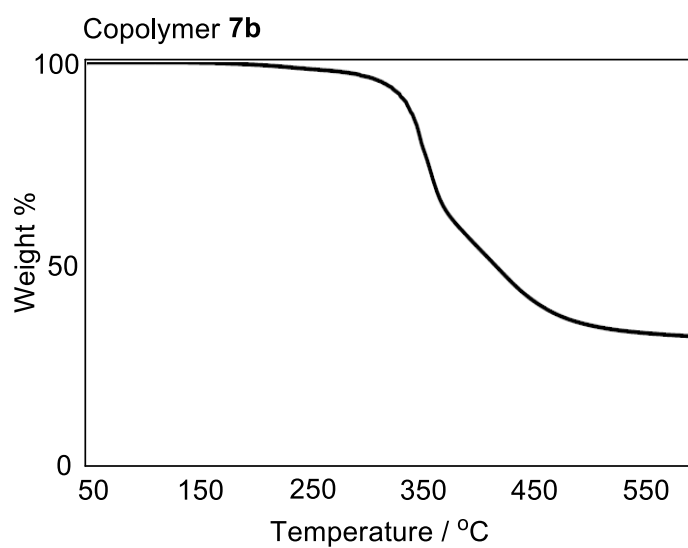
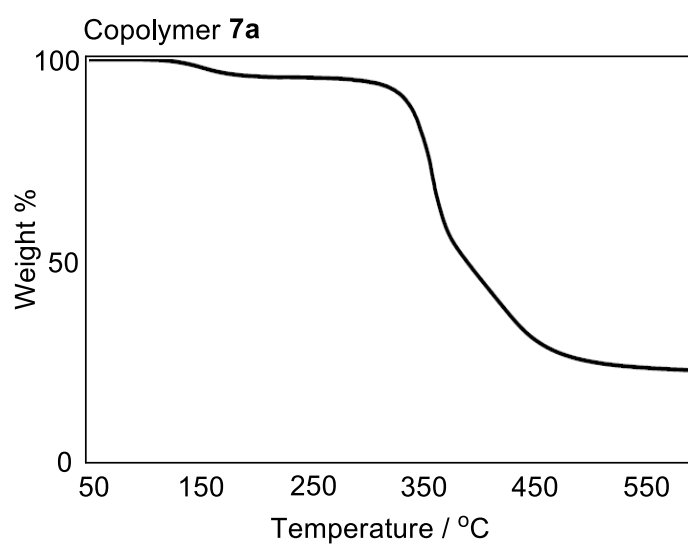


Figure S14. TG-thermograms of copolymers **7a-c**

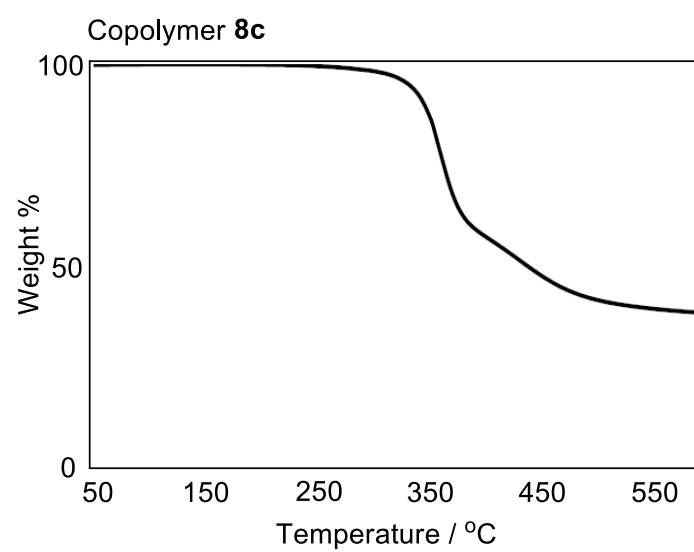
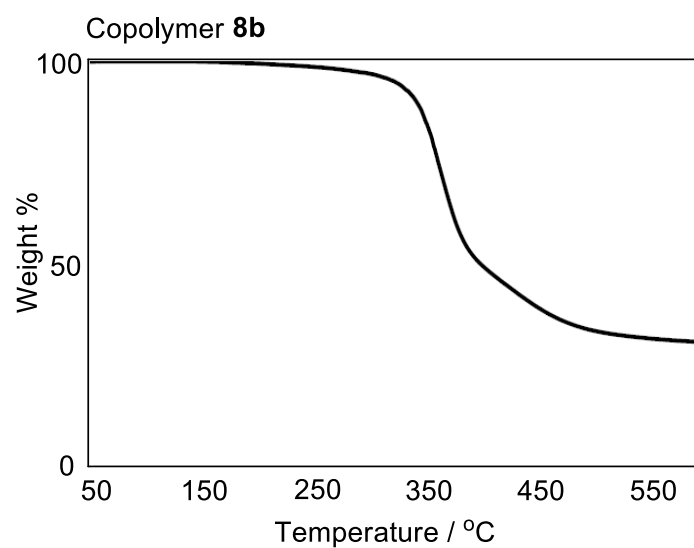
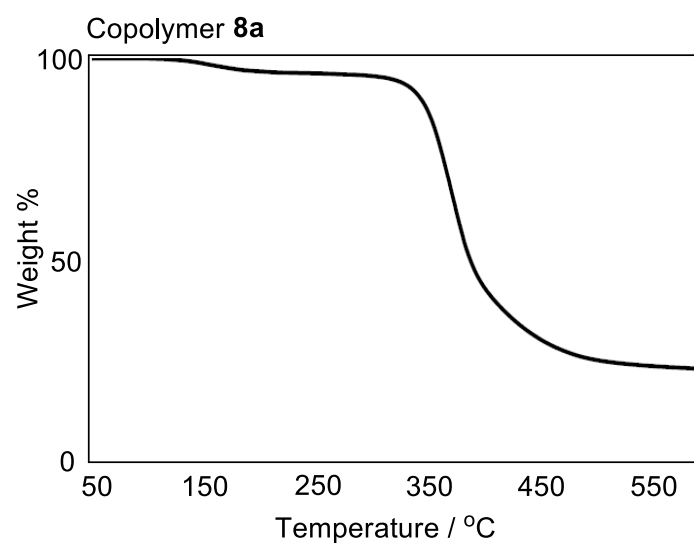


Figure S15. TG-thermograms of copolymers **8a-c**

DSC-Thermograms

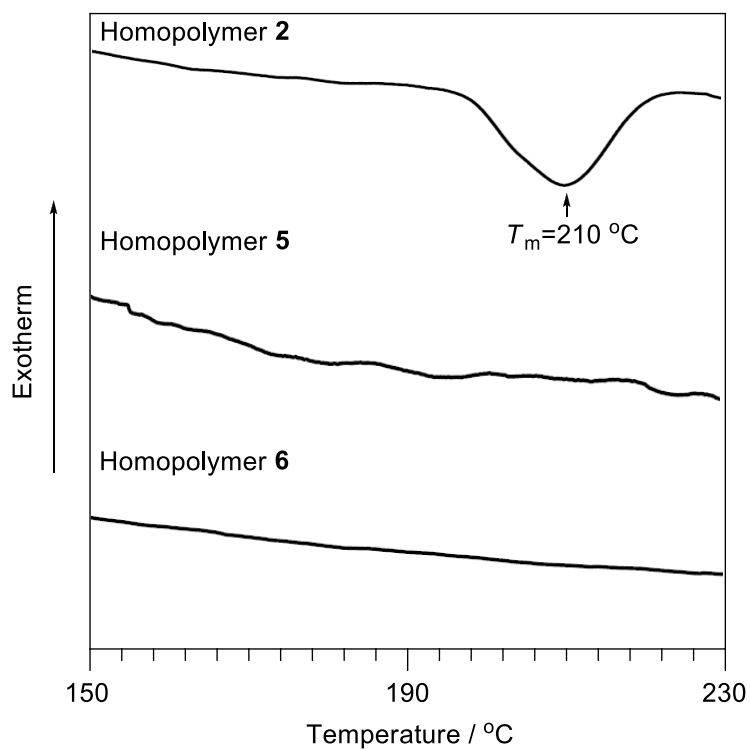


Figure S16. DSC-Charts of homopolymers **2**, **5** and **6**

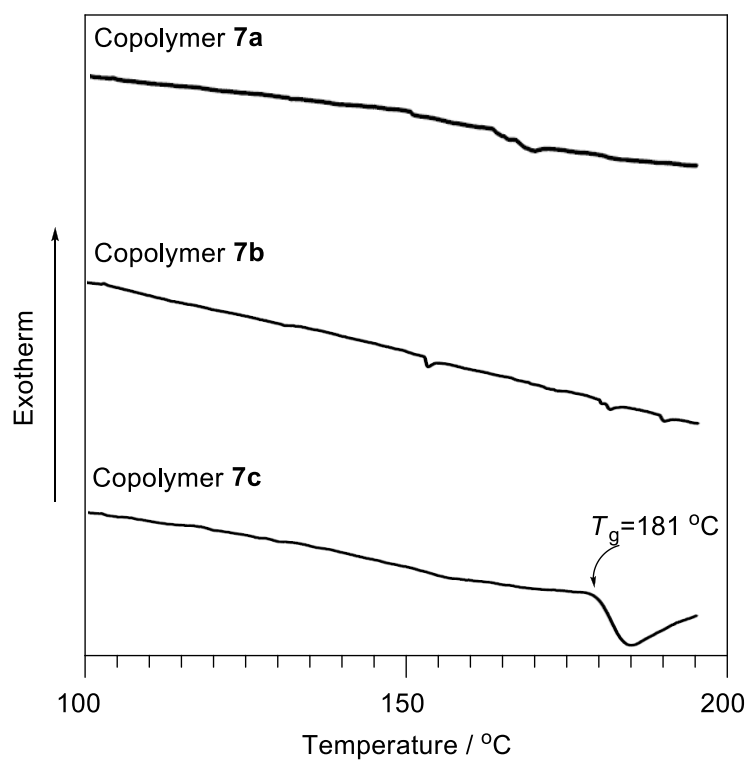


Figure S17. DSC-Charts of copolymers **7a-c**

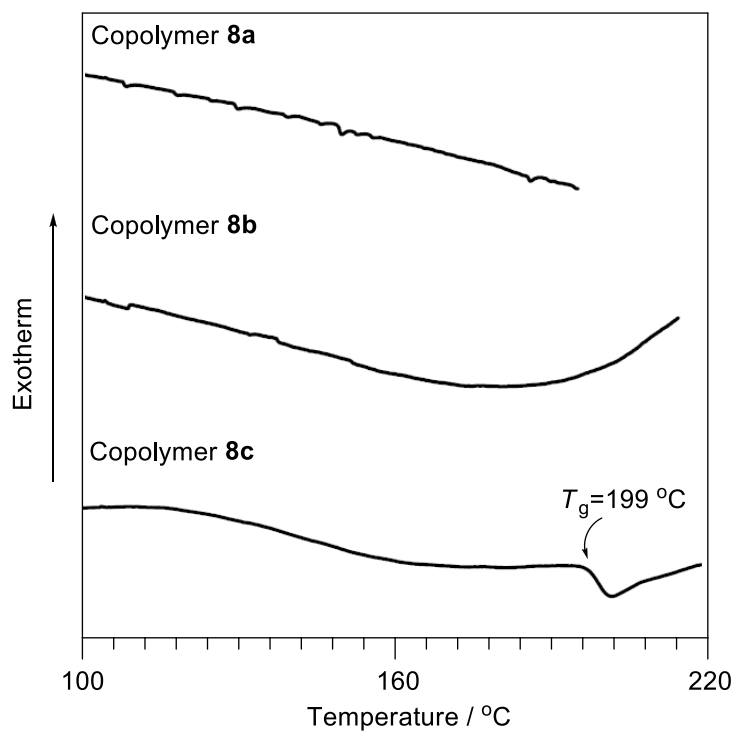
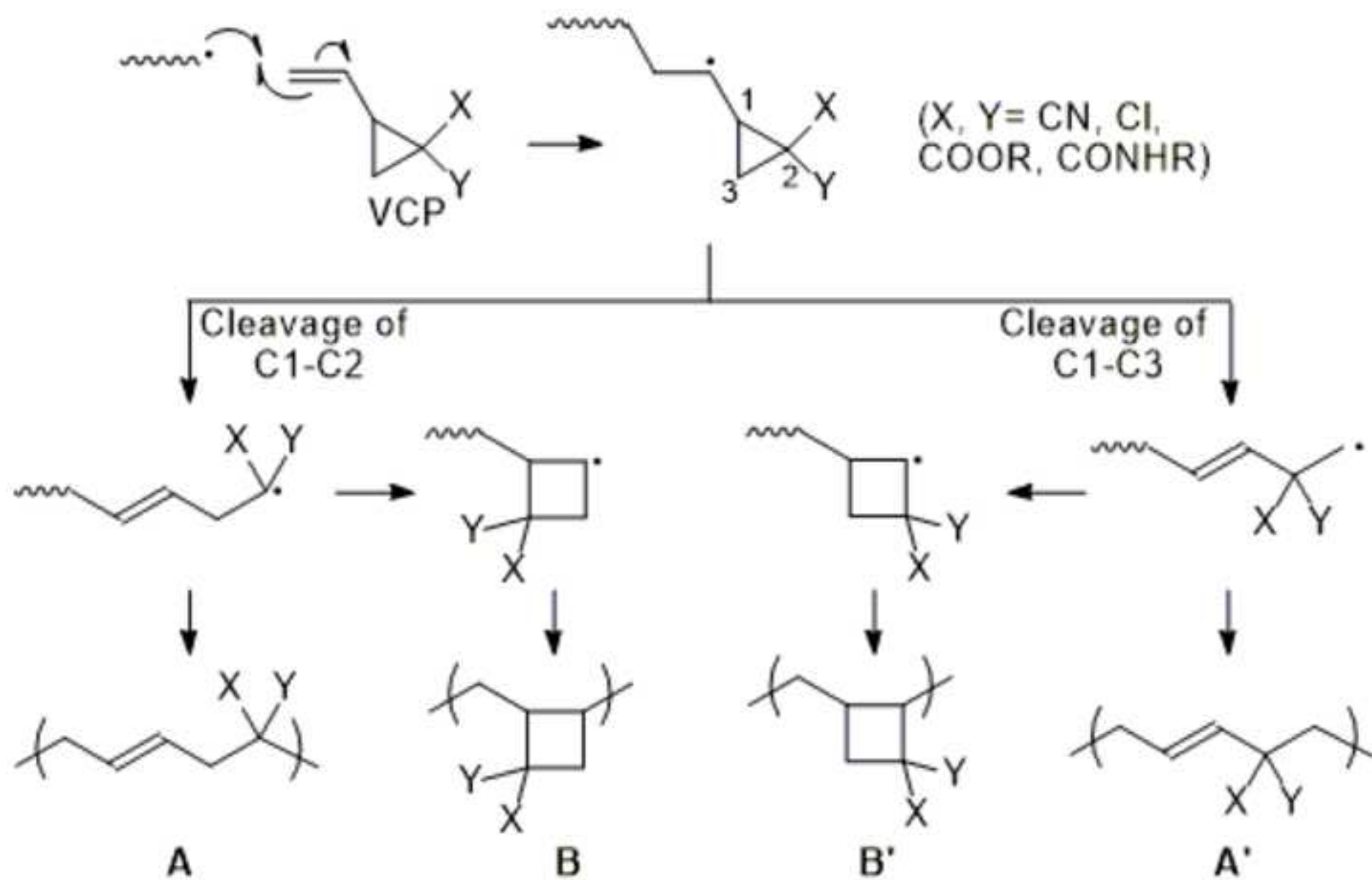


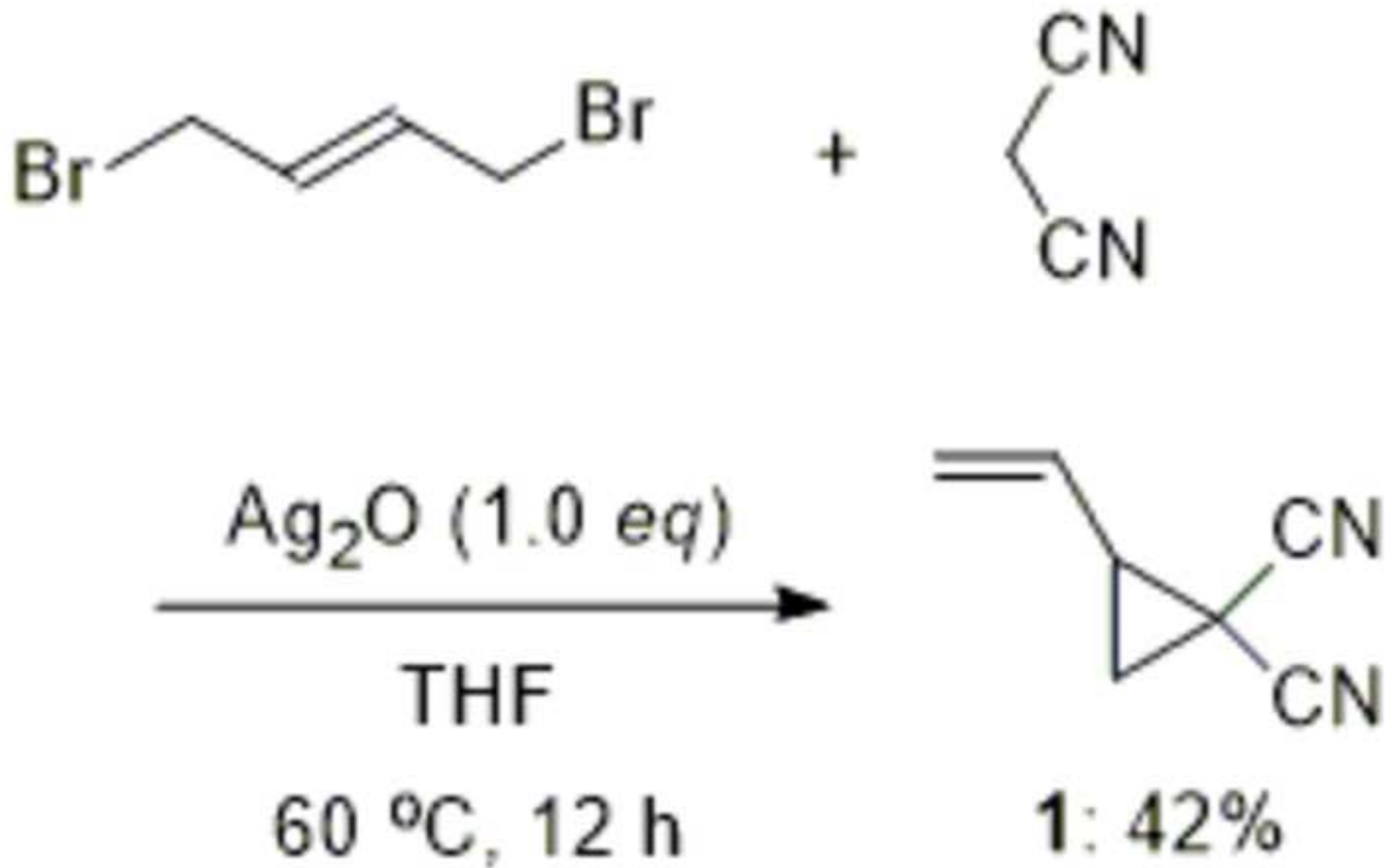
Figure S18. DSC-Charts of copolymers **8a-c**

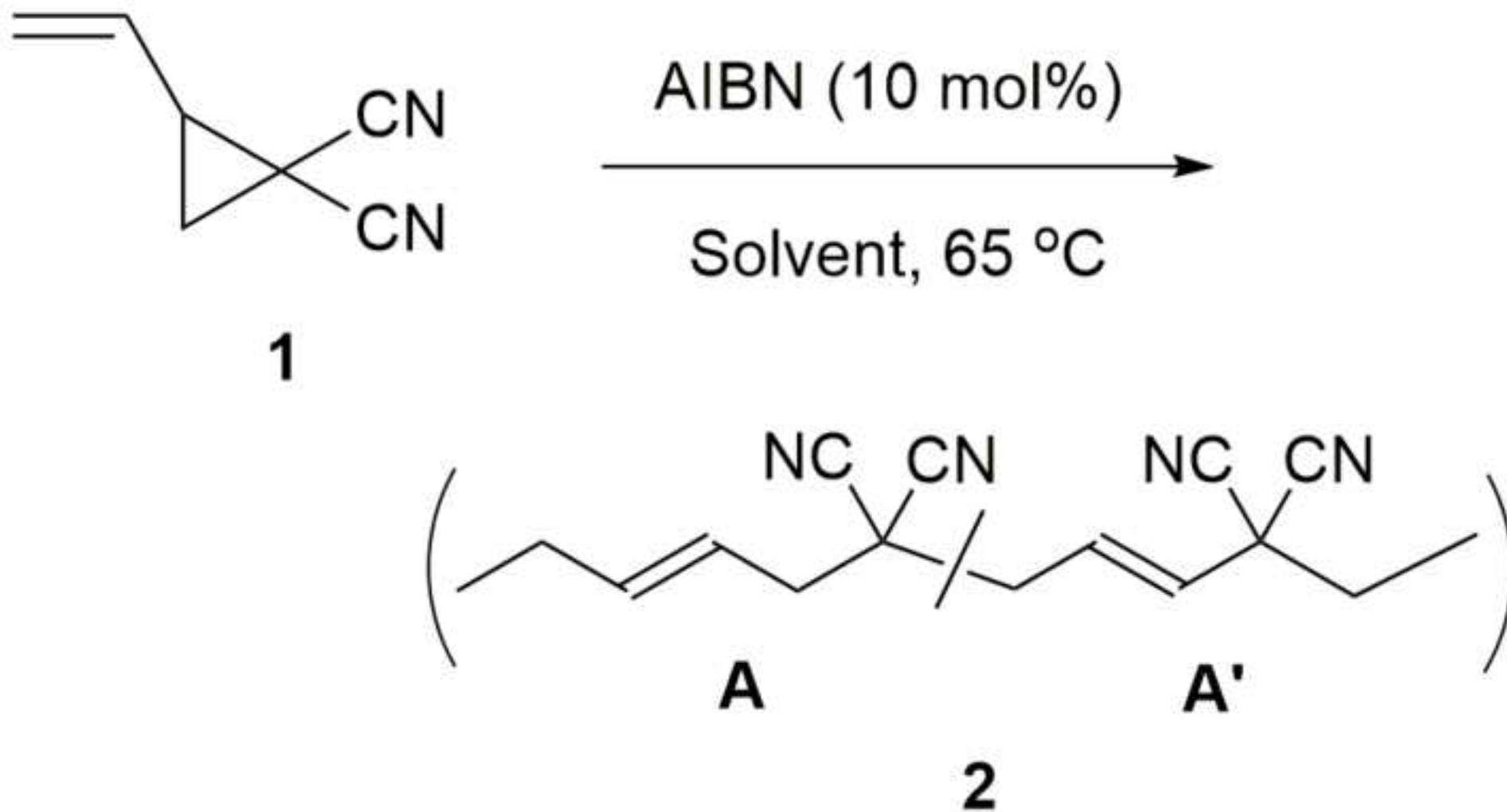
Table S1. The solubility of polymers in organic solvents

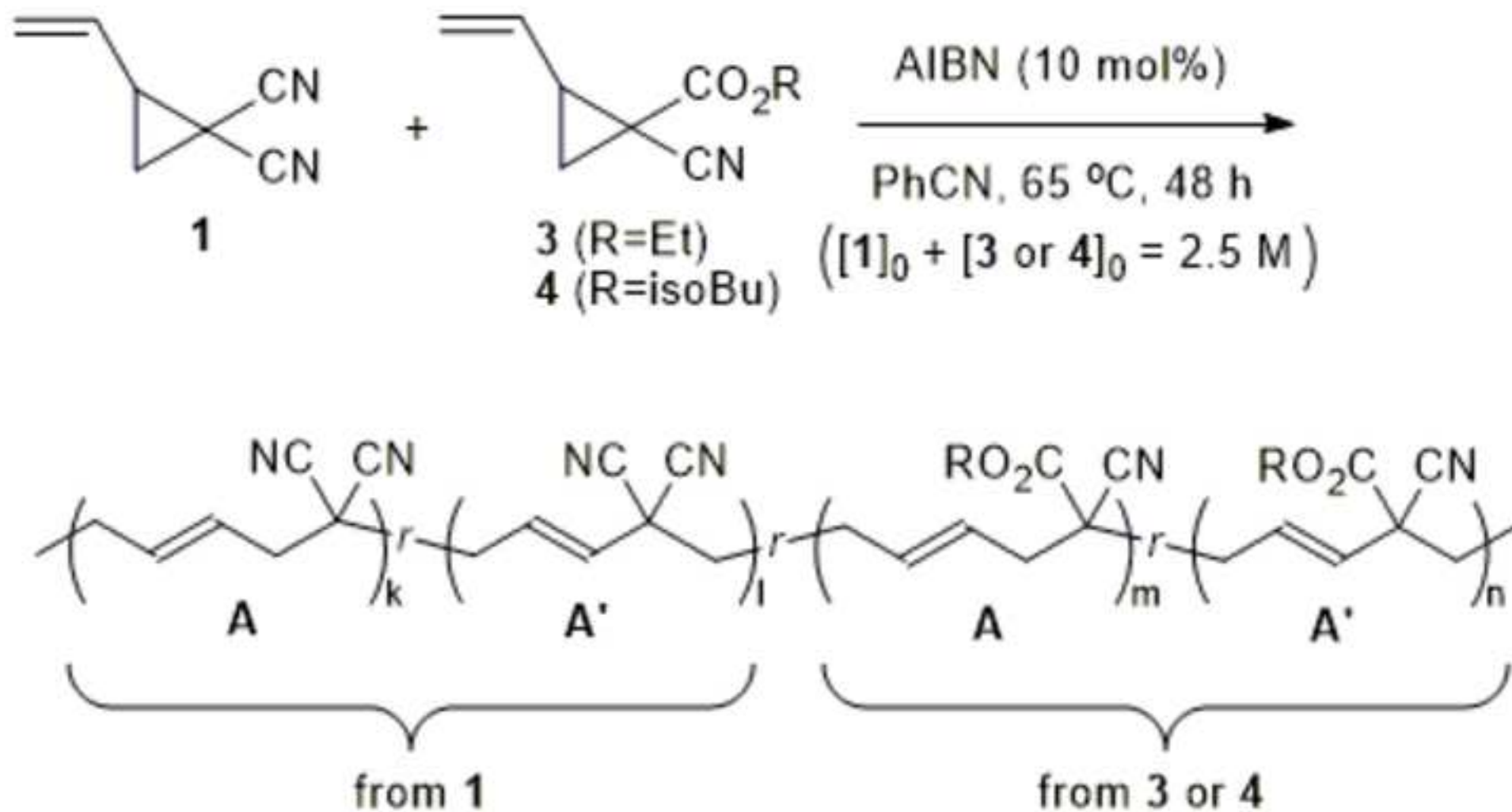
| Entry | polymer | DMSO | DMAc | DMF | THF | CHCl ₃ | Acetone |
|----------------|-----------|------|------|-----|-----|-------------------|---------|
| 1 ^a | 2 | + | + | + | - | - | - |
| 2 | 5 | ++ | ++ | ++ | ++ | ++ | ++ |
| 3 | 6 | ++ | ++ | ++ | ++ | ++ | ++ |
| 4 | 7a | ++ | ++ | ++ | ++ | ++ | ++ |
| 5 | 7b | ++ | ++ | ++ | + | + | + |
| 6 | 7c | ++ | ++ | ++ | - | + | + |
| 7 | 8a | ++ | ++ | ++ | ++ | ++ | ++ |
| 8 | 8b | ++ | ++ | ++ | ++ | ++ | ++ |
| 9 | 8c | ++ | ++ | ++ | - | + | + |

The solubility conditions: 2.0 mg/mL, ++: It's soluble at r.t., +: It's not completely soluble at r.t., -: It's insoluble. ^a the obtained **2** in benzonitrile (Table 1, entry 7).









GRAPHICAL ABSTRACT

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Radical Ring-Opening Polymerization Behavior of 1,1-Dicyano-2-Vinylcyclopropane and Its Copolymerization with 1-Cyano-1-Ester-2-Vinylcyclopropane

Radical ring-opening polymerization (RROP) using benzonitrile of 1,1-dicyano-2-vinylcyclopropane **1** was performed to yield the corresponding homopolymer **2** which was soluble in organic solvents. In addition, **1** underwent radical copolymerization with 1-cyano-1-ester-2-vinylcyclopropanes **3** and **4** to yield the corresponding copolymers **7** and **8**. By increasing the content of **1** in the resulting copolymers, their residual weights at 600 °C and glass transition temperatures became higher.

