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Dynamic Covalent Polymerization of Chalcogenide Hybrid Inorganic/Organic Polymer Resins with Norbornenyl Comonomers

Minho Kwon[1]
Hongchan Lee[1]
Seo-Hui Lee[2]
Heung Bae Jeon[2]
Min-Cheol Oh[3]
Jeffrey Pyun*[,4]
Hyun-jong Paik*[,1]

[1] Department of Polymer Science, Pusan National University, Pusan 46241, Korea
[2] Department of Chemistry, Kwangwoon University, Seoul 01897, Korea
[3] Department of Electronics Engineering, Pusan National University, Pusan 46241, Korea
[4] Department of Chemistry & Biochemistry, University of Arizona, Tucson, Arizona

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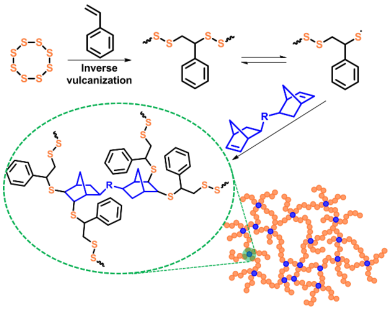
Abstract: Elemental sulfur (S_8) is an inexpensive chemical feedstock for polymeric materials but has the disadvantages of poor solubility in organic media and inferior physical properties in the elemental form. We report on the preparation of organosulfur chalcogenide hybrid inorganic/organic polymer (CHIPs) based on bifunctional norbornene comonomers using dynamic covalent polymerization (DCP). A poly(sulfur-*random*-styrene) (p(S-*r*-Sty)) resin was utilized to address the limited solubility/miscibility of norbornene-containing comonomers in liquid sulfur. This report demonstrated the ability to expand the scope of organic comonomers to prepare organosulfur CHIPs from elemenatal sulfur using a combination of inverse vulcanization and dynamic covalent polymerization.



Keywords: sulfur polymerization, dynamic covalent polymerization, inverse vulcanization, norbornenes, norbornyl comonomers.

1. Introduction

The elemental sulfur (S_8) as abundantly available by-product from the refining of oil and gas has drawn significant attention for value additions in the form utilization as a feedstock for polymeric materials.[1] However, the use of S_8 as a reagent for chemical synthesis and polymer chemistry is problematic due to the limited solubility and miscibility of elemental sulfur with the vast majority of organic chemical reagents/monomers, which arises from the highly crystalline nature of S_8. Furthermore, S_8 also intrinsically shows poor physical properties (*e.g.*, low mechanical strength, brittleness), which limits the processing of polymers with elemental sulfur *via* classical blending approaches.[2] However, S_8 is capable of chemical modification, since high temperature homolytic thermolysis of S-S bonds has long been known to undergo equilibrium polymerization leading to higher molar mass polymeric sulfur that readily depolymerizes back to monomer. Alternatively, Penzcek *et al.* were the first to report on anionic ring-opening polymerization of S_8 with thiiranes to prepare linear organopolysulfide based polymers. However, the lower rate constants of propagation (k_p) and the depolymerization of propagating polysulfides have historically complicated the use of sulfur for polymerization, which has further limited the scope of materials that have been investigated.

A major advance in this field was pioneered by Pyun *et al.* in a new process named "inverse vulcanization" where molten S_8 is directly used as the reaction medium and comonomer with vinylic comonomers to form organopolysulfides that were termed, organosulfur Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs).[3-10] This inverse vulcanization process has subsequently been extended to a wide variety of organic comonomers such as oleylamine,[11] allylics,[12] nitriles,[13] maleimide,[14] norbornenes,[10,15,16] benzoxazines,[17-19] and styrenics.[20,21] Macromolecular materials generated from the inverse vulcanization process possesses a high content of S-S bonds in the copolymer backbone, which imparts intriguing chemical activity, dynamic covalent bond reorganization, along with useful optical and electrochemical properties which have been used in applications such as mercury capture,[22] Li-S batteries,[23,24] IR-transparent lenses.[3]

While the inverse vulcanization has proven to be a viable polymerization method for making organosulfur CHIPs, the need for molten sulfur limits the scope of organic comonomers that can be used in these reactions since the vast majority of compounds are not miscible with liquid sulfur and may not survive the high temperatures ($T > 120$ °C) required for this process. To address this issue, Pyun *et al.* reported on the use of high sulfur content CHIPs resins based on poly(sulfur-*random*-styrene) (p(S-*r*-Sty)) to further react with a wide scope of organic comonomers, *via* a process termed, dynamic covalent polymerization (DCP), where the dynamic covalent S-S bonds in the low T_g CHIPs resin could be thermally activated to copolymerize with unsaturated comonomers.[25] The main advantage of using poly(S-*r*-Sty) resins for DCP is the enhanced miscibility with organic comonomers which greatly expands the

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***Corresponding Authors:** Jeffrey Pyun (jpyun@email.arizona.edu), Hyun-jong Paik (hpaik@pusan.ac.kr)

scope of organic comonomers for use in the preparation of CHIPs materials. The DCP process has been extended to (meth)acrylates[7] and vinyl ethers,[26] but still remains largely unexplored with new comonomer possibilities. We recently demonstrated that fused cyclic olefins derived from norbornadiene, which we termed, "NBD2" could be used as excellent organic comonomers for inverse vulcanization to afford highly crosslinked thermosets. Furthermore, the norbornenes and NBD2 were found to exhibit low long wave infrared absorbance as determined experimentally and using computational simulations.[15] However, the exploration of new bifunctional norbornenyl based comonomers has not been explored by inverse vulcanization or DCP.

Despite the recent work done for inverse vulcanization and DCP, there remains a need to afford methods to prepare thermoplastics of high molar mass and prepare materials with improved thermomechanical properties, particularly with T_g's greater than 100 °C.[10,27] Hence, there is a clear motivation to explore the synthesis of new comonomer motifs, particularly based on norbornenes that can be used to both improve thermomechanical properties and potentially impart useful optical properties to the final material.

Herein, we report the synthesis of new difunctional norbornene comonomers containing (di)sulfide linkages for dynamic covalent polymerizations with CHIPs resins. New terpolymer and oligomer organopolysulfides were prepared by utilizing the poly(S-*r*-Sty) resin in the DCP process with the norbornene containing comonomers due to their good miscibility in poly(S-*r*-Sty) resin than liquid sulfur.

2. Experimental

2.1. Materials

Styrene (>99%) was purchased from Daejung. Tetrahydrofuran (THF, >99.9%) was purchased from SK-chemical. Benzophenone (>99%), methanesulfonyl chloride (>99.7%), sodium hydride (60% dispersion in mineral oil), tetrabromomethane (>99.9%), triphenylphosphine (>99.9%), sulfur (powder purified by refining) and sodium sulfide were purchased from Sigma-Aldrich. 5-norbornene-2-methanol (>98%, mixture of isomers) was purchased from Tokyo Chemical Industry. Pyridine (>99.5%), sodium hydroxide beads, calcium chloride (>99%) and n-Hexane (>95%) were purchased from Duksan.

2.2. Characterization

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were determined using size exclusion chromatography against polystyrene standards (SEC; Agilent, Santa Clara, CA, U.S.A.). The SEC was equipped with an Agilent 1100 pump, RID detector, and PSS SDV (5 μm, 10^5, 10^3, 10^2 Å 8.0 mm × 300.0 mm) columns. Tetrahydrofuran (THF) was used as a mobile phase at a flow rate of 1.0 mL/min and a column temperature of 313 K. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a 500 MHz Agilent Superconducting fourier-transform NMR (FT-NMR) spectrometer using $CDCl_3$ as a solvent. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer. Differential scanning calorimeter (DSC) analyses were performed with TA Instruments Q 100, which operated at 10 °C/min under nitrogen gas. Column chromatography was performed on a glass column packed with Merk's 230-400 mesh silica gel by eluting a mixture of hexane and ethyl acetate. Silica gel 60 F254 Merk TLC glass plate was used for thin layer chromatography (TLC) to confirm the samples using UV lamp or permanganate as a staining solution.

2.3. Synthesis of bicyclo[2.2.1]hept-5-en-2-ylmethyl methanesulfonate (N1)

To a solution of 5-norbornene-2-methanol (*mixture of endo, exo stereoisomers*) (5.00 g, 40.3 mmol) in dry CH_2Cl_2 (120 mL) was added pyridine (5.01 g, 64.4 mmol) and methanesulfonyl chloride (7.38 g, 64.4 mmol) at 0 °C. After warmed to room temperature, the resulting solution was stirred for 16 h. The reaction mixture was quenched with H_2O. After removing CH_2Cl_2 solvent under reduced pressure, the remaining solution was partitioned with saturated aq. Na_2CO_3 solution and Et_2O. The organic layer was separated, washed with aq. 1N HCl solution, dried over $MgSO_4$ and concentrated to give the desired product (8.1 g, 99%) as a yellowish oil. We confirmed chemical structure using ^{1}H NMR spectroscopy (Figure S1). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.54-0.59 (m, 0.6H), 1.16-1.22 (m, 0.4H), 1.29-1.34 (m, 1.4H), 1.41 (d, J = 8.7 Hz, 0.4H), 1.50 (dd, J = 8.5, 1.6 Hz, 0.6H), 1.81-1.92 (m, 1H), 2.46-2.55 (m, 0.6H), 2.80 (s, 0.4H), 2.87 (brs, 1H), 2.98 (brs, 0.6H), 3.01 (s, 1.8H, SO_3CH_3), 3.04 (s, 1.2H, SO_3CH_3), 3.81 (t, J = 9.6 Hz, 0.6H, $SOCH_2CH$), 4.01 (dd, J = 9.6, 6.4 Hz, 0.6H, $SOCH_2CH$), 4.12 (t, J = 9.4 Hz, 0.4H. $SOCH_2CH$), 4.30 (dd, J = 9.6, 6.4 Hz, 0.4H, $SOCH_2CH$), 5.99 (dd, J = 5.5, 2.7 Hz, 0.6H, $CH{=}CH$), 6.12 (s, 0.8H, $CH{=}CH$), 6.21 (dd, J = 5.7, 3.0 Hz, 0.6H, $CH{=}CH$). ^{13}C NMR spectral assignments are not included due to use of 5-norbornene-2-methanol (*mixture of endo, exo stereoisomers*).

2.4. Synthesis of S-(bicyclo[2.2.1]hept-5-en-2-ylmethyl) ethanethioate (N2)

To a solution of N1 (5.00 g, 24.7 mmol) in DMF (50 mL), potassium thioacetate (5.65 g, 49.5 mmol) was added. The resulting solution was warmed to 40 °C and stirred for 28 h. The reaction mixture was quenched with H_2O and extracted with Et_2O. The organic layer was separated, dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography with hexane/EtOAc (25/1) as eluent to give the desired product (4.5 g, 98%) as a yellowish oil. We confirmed chemical structure using ^{1}H NMR spectroscopy (Figure S2). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.57-0.62 (m, 0.6H), 1.16-1.21 (m, 0.4H), 1.24-1.30 (m, 1H), 1.33-1.38 (m, 1H), 1.44 (dd, J = 8.2, 1.8 Hz, 0.8H), 1.89-1.95 (m, 0.6H), 2.21-2.29 (m, 0.6H), 2.33 (s, 1.8H, $SOCH_3$), 2.35 (s, 1.2H, $SOCH_3$), 2.58-2.63 (m, 1H), 2.73 (dd, J = 12.8, 7.6 Hz, 0.6H), 2.80 (brs, 0.6H), 2.85 (brs, 1H), 2.90-3.03 (m, 0.8H), 5.95 (dd, J = 5.5, 2.7 Hz, 0.6H, $CH{=}CH$), 6.04-6.10 (m, 0.8H, $CH{=}CH$), 6.20 (dd, J = 5.5, 3.2 Hz, 0.6H, $CH{=}CH$). ^{13}C NMR spectral assignments are not included due to use of 5-norbornene-2-methanol (*mixture of endo, exo stereoisomers*).

2.5. Synthesis of bis((bicyclo[2.2.1]hept-5-en-2-ylmethyl)thio)methane (NC1)

To a solution of N2 (8.00 g, 43.4 mmol) in dry THF (180 mL), was added dropwise a solution of NaOH (5.21 g, 0.13 mol) in MeOH (60 mL) at room temperature. To a solution of N2 (8.00 g, 43.4 mmol) in dry THF (180 mL), a solution of NaOH (5.21 g, 0.13 mol) in MeOH (60 mL) was added dropwise at room temperature. After stirring for 5 min, dibromomethane (3.77 g, 21.7 mmol) was added dropwise to the solution. The resulting solution was stirred for 2 h. The reaction mixture was quenched with H_2O. After removing THF and MeOH solvent under reduced pressure, the remaining solution was partitioned with H_2O and Et_2O. The organic layer was separated, dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography with hexane/EtOAc (40/1) as eluent to give the desired product (5.8 g, 90%) as a colorless oil. We confirmed chemical structure using ^{1}H NMR spectroscopy (Figure S3). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.64 (dt, J = 11.5, 3.4 Hz, 1.3H), 1.22-1.31 (m, 2H), 1.35-1.40 (m, 2H), 1.44-1.46 (m, 1.4H), 1.59-1.64 (m, 0.7H), 1.91-1.97 (m, 1.3H), 2.24-2.33 (m, 1.3H), 2.37-2.48 (m, 2.7H), 2.69-2.74 (m, 2H), 2.81 (brs, 1.3H, SCH_2C), 2.84(brs, 0.7H, SCH_2C), 2.91(brs, 1.3H, SCH_2C), 3.65-3.69 (m, 2H, SCH_2S), 5.98 (dd, J = 5.7, 3.0 Hz, 1.3H, $CH{=}CH$), 6.07 (dd, J = 5.7, 3.0 Hz, 0.7H, $CH{=}CH$), 6.11 (dd, J = 5.5, 3.4 Hz, 0.7H, $CH{=}CH$), 6.19 (dd, J = 5.7, 3.0 Hz, 1.3H, $CH{=}CH$). ^{13}C NMR spectral assignments are not included due to use of 5-norbornene-2-methanol (*mixture of endo, exo stereoisomers*).

2.6. Synthesis 5-(bromomethyl)bicyclo[2.2.1]hept-2-ene (N3)

To a solution of 5-norbornene-2-methanol (4.00 g, 32.2 mmol) and tetrabromomethane (16.02 g, 48.3 mmol) in dry CH_2Cl_2 (80 mL), a solution of triphenylphosphine (25.35 g, 96.6 mmol) in dry CH_2Cl_2 (80 mL) was added dropwise at 0 °C. After warmed to room temperature, the resulting solution was stirred for 5 h. After removing CH_2Cl_2 solvent under reduced pressure, the residue was subjected to column chromatography with 100% hexane as eluent to give the desired product (5.8 g, 96%) as a yellowish oil. We confirmed chemical structure using ^{1}H NMR spectroscopy (Figure S4). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.58-0.63 (m, 0.6H), 1.20-1.33 (m, 1H), 1.39-1.44 (m, 0.8H), 1.49-1.52 (m, 1H), 1.85-1.90 (m, 0.4H), 1.93-1.99 (m, 0.6H), 2.49-2.58 (m, 0.6H), 2.80 (brs, 0.4H), 2.89 (brs, 1H), 3.01 (brs, 0.6H), 3.06 (t, J = 9.6 Hz, 0.6H, $BrCH_2$), 3.21-3.26 (m, 0.6H, $BrCH_2$), 3.39-3.49 (m, 0.8H, $BrCH_2$), 6.01 (dd, J = 5.5, 2.7 Hz, 0.6H, $CH{=}CH$), 6.09-6.14 (m, 0.8H, $CH{=}CH$), 6.23 (dd, J = 5.7, 3.0 Hz, 0.6H, $CH{=}CH$). ^{13}C NMR spectral assignments are not included due to use of 5-norbornene-2-methanol (*mixture of endo, exo stereoisomers*).

2.7. Synthesis of 1,2-bis(bicyclo[2.2.1]hept-5-en-2-ylmethyl)disulfane (NC2)

A solution of sodium sulfide (2.57 g, 10.7 mmol) and sulfur (0.34 g, 10.7 mmol) in EtOH (10 mL) was heated to reflux and stirred for 30 min. After cooling to room temperature, N3 (4.00 g, 21.4 mmol) was added to the solution. The resulting solution was heated to reflux and stirred for 2 h. The reaction mixture was quenched with H_2O. After removing EtOH solvent under reduced pressure, the remaining solution was partitioned with H_2O and hexane. The organic layer was separated, dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography with 100% hexane as eluent to give the desired product (1.01 g, 34%) as colorless oil. We confirmed chemical structure using ^{1}H NMR spectroscopy (Figure S5). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.64 (dt, J = 11.5, 3.4 Hz, 1H), 1.22-1.33 (m, 3H), 1.35-1.40 (m, 2H), 1.43-1.47 (m, 1H), 1.73-1.80 (m, 1H), 1.91-1.97 (m, 1H), 2.38-2.46 (m, 1H), 2.48-2.56 (m, 2H), 2.72 (brs, 1H, SCH_2C), 2.79 (dd, J = 7.8, 3.7 Hz, 2H), 2.82 (brs, 1H, SCH_2C), 2.85 (brs, 1H, SCH_2C), 2.92(brs, 1H, SCH_2C), 5.97 (dd, J = 5.3, 3.0 Hz, 1H, $CH{=}CH$), 6.08 (dd, J = 5.8, 3.0 Hz, 1H, $CH{=}CH$), 6.12 (dd, J = 5.5, 2.7 Hz, 1H, $CH{=}CH$), 6.18 (dd, J = 5.7, 3.0 Hz, 1H, $CH{=}CH$). ^{13}C NMR spectral assignments are not included due to use of 5-norbornene-2-methanol (*mixture of endo, exo stereoisomers*).

2.8. Synthesis of bis(bicyclo[2.2.1]hept-5-en-2-ylmethyl)sulfane (NC3)

To a solution of *S*-(bicyclo[2.2.1]hept-5-en-2-ylmethyl) ethanethioate (0.70 g, 3.8 mmol) in dry THF (21 mL), a solution of NaOH (0.46 g, 11.4 mmol) in MeOH (7 mL) was added dropwise at room temperature. After stirring the solution for 5 min, a solution of bicyclo[2.2.1]hept-5-en-2-ylmethyl methanesulfonate (0.92 g, 4.6 mmol) in THF (1 mL) was added dropwise *via* cannula. The resulting solution was warmed to 50 °C and stirred for 48 h. The reaction mixture was quenched with H_2O. After removing THF and MeOH solvent under reduced pressure, the remaining solution was partitioned with H_2O and Et_2O. The organic layer was separated, dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography with hexane/EtOAc (100/1) as eluent to give the desired product (0.53 g, 56%) as a colorless oil. We confirmed chemical structure using ^{1}H NMR spectroscopy (Figure S6). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.61 (dd, J = 11.4, 2.7 Hz, 1H), 1.20-1.38 (m, 5H), 1.44 (d, J = 7.3 Hz, 1H), 1.57-1.65 (m, 1H), 1.90-1.95 (m, 1H), 2.25-2.33 (m, 3H), 2.59 (t, J = 8.95 Hz, 2H), 2.71 (brs, 1H, SCH_2C), 2.81 (d, J = 12.4 Hz, 2H, SCH_2C), 2.92 (brs, 1H, SCH_2C), 5.96-5.97 (m, 1H, $CH{=}CH$), 6.05-6.07(m, 1H, $CH{=}CH$), 6.10-6.13 (m, 1H, $CH{=}CH$), 6.16-6.18 (m, 1H, $CH{=}CH$). ^{13}C NMR spectral assignments are not included due to use of 5-norbornene-2-methanol (*mixture of endo, exo stereoisomers*).

2.9. Synthesis of 1,4-bis((bicyclo[2.2.1]hept-5-en-2-ylmethoxy)methyl)benzene (NC4)

To a solution of 5-norbornene-2-methanol (2.50 g, 20.0 mmol) in dry THF (30 mL), sodium hydride (NaH 60% dispersion in oil, 1.14 g, 28.5 mmol) was added at 0 °C. After stirring the solution for 20 min at 0 °C, a solution of α,α'-dichloro-*p*-xylene (1.47 g, 8.39 mmol) in THF (15 mL) was added dropwise via cannula. The resulting solution was heated to 50 °C and stirred for 20 h. The reaction mixture was cooled to room temperature and quenched with aq. 1N HCl solution. After removing THF under reduced pressure, the remaining solution was partitioned with

H_2O and Et_2O. The organic layer was separated, dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography with hexane/EtOAc (15/1) as eluent to give the desired product (2.4 g, 68%) as a white solid. We confirmed chemical structure using ^1H NMR spectroscopy (Figure S7). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.46-0.51 (m, 1.2H), 1.11 (dt, J = 11.4, 3.9 Hz, 0.8H), 1.22-1.34 (m, 3.6H), 1.43 (dq, J = 8.2, 2.0 Hz, 1.2H), 1.74 (dt, J = 8.9, 4.2 Hz, 0.8H), 1.82 (ddd, J = 11.7, 9.1, 3.9 Hz, 1.2H), 2.36-2.46 (m, 1.2H), 2.79 (d, J = 1.8 Hz, 2.8H), 2.95 (brs, 1.2H), 3.05 (t, J = 8.9 Hz, 1.2H, OCH_2CH), 3.19 (dd, J = 9.1, 6.4 Hz, 1.2H, OCH_2CH), 3.36 (t, J = 9.1 Hz, 0.8H. OCH_2CH), 3.52 (dd, J = 9.1, 5.9 Hz, 0.8H, OCH_2CH), 4.43-4.60 (m, 4H, OCH_2Ph), 5.88 (dd, J = 5.7, 3.0 Hz, 1.2H, CH=CH), 6.06 (dd, J = 5.7, 3.0 Hz, 0.8H, CH=CH), 6.09-6.12 (m, 2H, CH=CH), 7.31-7.35 (m, 4H, Ph). ^{13}C NMR spectral assignments are not included due to use of 5-norbornene-2-methanol (*mixture of endo, exo stereoisomers*).

2.10. Synthesis of poly(S-*r*-Sty)

The poly(S-*r*-Sty) was synthesized according to reported procedure.[28] Sulfur (3.5 g, 13.6 mmol) was added into vial equipped with a magnetic stir bar and heated to 130 °C in oil bath until a yellow molten sulfur was formed. Styrene (1.5 g, 14.4 mmol) which made free of inhibitor by passing through basic alumina column was then added dropwise to the molten sulfur *via* syringe. The reaction mixture was stirred at 130 °C for 6 h until the complete disappearance of the vinyl peak of styrene in ^1H NMR spectra. The resulting copolymer was cooled to room temperature. The crude product was purified by silica gel column chromatography with hexane as eluting solvent to remove the residual sulfur (TLC, Rf=0.8). After the removal of sulfur, the column was eluted with THF to afford the pure copolymer (4.68 g yield).

2.11. General Procedure for the Synthesis of poly(S-*r*-Sty-*r*-Norbornene comonomer) (p(S-*r*-Sty-*r*-NC)) terpolymers

NC (50 mg) was added to p(S-*r*-Sty) (50 mg) and heated to 170 °C for 2 h until the complete disappearance of the vinyl peaks of the norbornene groups in ^1H NMR spectra. The resulting copolymer was cooled to room temperature.

3. Results and discussion

The general approach taken to prepare these novel organosulfur CHIPs materials, was the design of a series of new difunctional norbornene based monomers, beginning with 5-norbornene-2-methanol, and varying the linker motif to prepare difunctional norborneyl comonomers with thioether, disulfide, or benzylic ether units. These monomers were readily prepared using either one or two synthetic steps, all with respective isolated yields. We initially explored the direct inverse vulcanization of these comonomers with the liquid sulfur at elevated temperatures (T > 120 °C). Since not all of these compounds were miscible with molten sulfur, we used DCP process for the preparation of organosulfur CHIPs materials due to the better miscibility of organic comonomers in poly(S-*r*-Sty) than neat liquid sulfur[7] (Figure 1).

The norbornene comonomers **NC1-4** were prepared from commercially available 5-norbornene-2-methanol as shown in

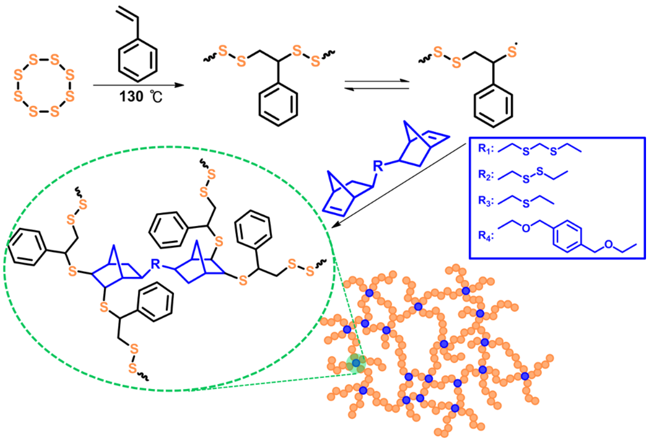
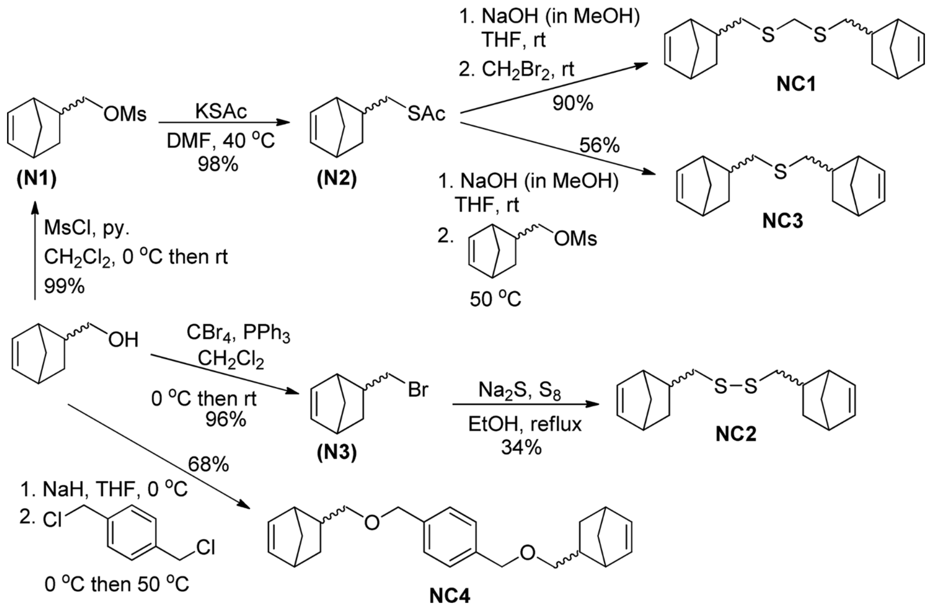


Figure 1. Dynamic covalent polymerization of p(S-*r*-Sty) with norbornenyl comonomers.



Scheme 1. Synthesis of norborneyl comonomers (NC1-4) used for DCP to prepare CHIPs terpolymers.

Scheme 1. The hydroxyl group was smoothly transformed to thioacetate group by mesylation followed by a substitution reaction of the resulting mesylate with potassium thioacetate in excellent yield. The comonomer **NC1** was synthesized by the sequential reactions of treatment with base and addition of dibromomethane for dithioacetal formation from the thioacetate precursor. With the same manner, the comonomer **NC3** was prepared by the sequential reactions of treatment with base and addition of the mesylate for sulfide formation. For the synthesis of the comonomer **NC2**, the 5-norbornene-2-methanol was converted to the corresponding bromide by Appel reaction, and then the bromide was reacted with sodium sulfide and sulfur to afford the desired **NC2** having disulfide linkage.[29] On the other hand, the comonomer **NC4** having ether linkage was synthesized directly from the alcohol by the sequential reactions of treatment with sodium hydride to produce the corresponding alkoxide and addition of *α,α'*-dichloro-*p*-xylene for substitution reaction of the alkoxide in reasonable yield.

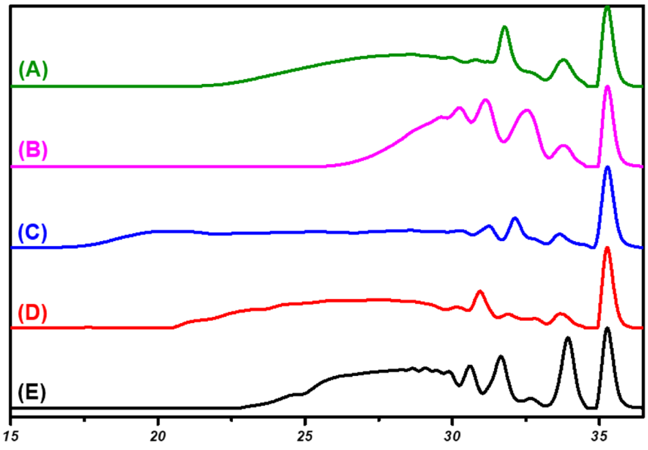


Figure 3. SEC analysis of (A) p(S-*r*-Sty-*r*-NC1), (B) p(S-*r*-Sty-*r*-NC2), (C) p(S-*r*-Sty-*r*-NC3), (D) p(S-*r*-Sty-*r*-NC4), and (E) p(S-*r*-Sty).

Poly(S-*r*-Sty) resin was readily synthesized by inverse vulcanization of molten S_8 (30 wt%) and styrene (70 wt%) at 130 °C for DCP with functional norbornene comonomers. ^{1}H NMR spectroscopy of the p(S-*r*-Sty) copolymer confirmed the formation of new carbon-sulfur (C-S) bonds as observed by the growth of a new set of multiple proton resonances between 3.00~5.00 ppm corresponding to the S-C-C-S peak and near quantitative conversion of styrene to the copolymer was confirmed by the disappearance of vinyl proton peaks at 5.18 and 5.61 ppm (Figure 2(E)). Poly(S-*r*-Sty) resin molar mass was determined by size exclusion chromatography with THF as the eluent (M_n = 260 g/mol; M_w/M_n = 5.15, Figure 3(E)). Then residual S_8 was removed by column chromatography to react the p(S-*r*-Sty) precursor with NC.

The synthesis of new organosulfur CHIPs terpolymers were achieved by individual DCP of p(S-*r*-Sty) (63-wt% S; 37-wt% Sty) with the four new NCs by maintaining 1:1 gravimetric feed ratio. At this condition, the NCs (50 wt% relative to total poly(S-*r*-Sty) were readily miscible and heated to 170 °C. This composition of p(S-*r*-Sty) was utilized since the resin was readily miscible with non-polar organic comonomers and possess a high content of

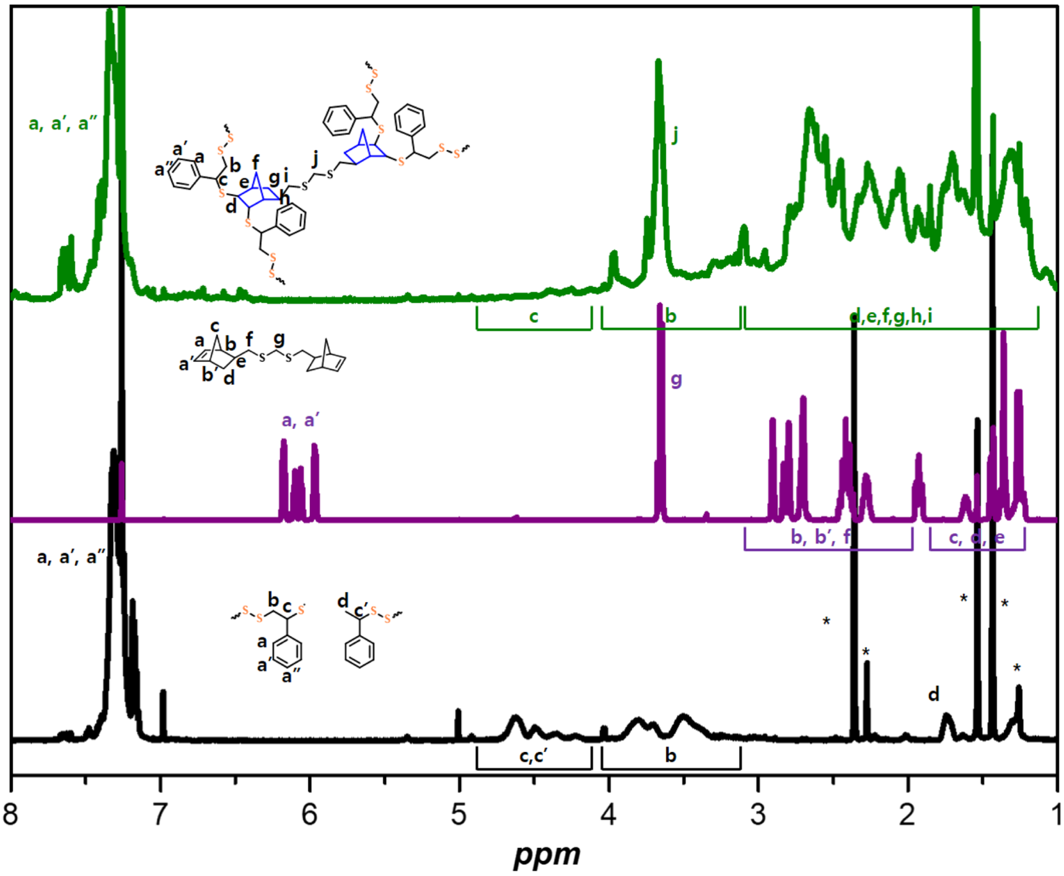


Figure 2. ^{1}H NMR spectra of p(S-*r*-Sty-*r*-NC1) (green line), NC1 (grey line), and p(S-*r*-Sty) (black line).

dynamic covalent fragments that enabled the generation of sulfur radicals by fragmentation of S-S bonds along the copolymer backbone. Sulfur radicals generated by fragmentation were then able to undergo thiol-ene additions to norbornenyl comonomers resulting in the formation of new organosulfur CHIPs terpolymers as characterized by ^{1}H NMR spectroscopy, FT-IR spectroscopy, SEC, elemental analysis and DSC. The successful incorporation of norbornene comonomers into the poly(S-*r*-Sty) backbone by DCP was confirmed by solution ^{1}H NMR spectrocoscopy. For example, almost 100% conversion of NC1 was confirmed by the consumption of protons from olefinic groups at 5.98~6.19 ppm in the ^{1}H NMR spectrum (Figure 2). The formation of new C-S bonds was evident by the appearance of methylene -CH$_2$- proton resonance from the dithioether spacer (with -S-CH$_2$-S- peak in NC1, Scheme 1), peak j, Figure 2). New proton resonances from C-S bonds from both the p(S-*r*-Sty) backbone and norbornene units appeared as broad, overlapped peaks from 3.00~4.80 ppm. While the ratio of sulfur and styrene is 7:3 for the synthesis of poly(S-*r*-Sty) (black), the ratio of them is 5:5 for the reaction of p(S-*r*-Sty) and NC (green). Therefore, the intensity of C methine proton (-S-S-CH$_2$-C**H**(C$_6$H$_6$)-S-S-) is decreased. In addition, DCP reaction of p(S-*r*-Sty) with NC generates other chiral centers, which makes further peak splitting and thus decreases the peak intensity. The other NC1 resonances from the cycloalkane backbone were observed as numerous overlapped peaks from 0.50 ppm~3.00 ppm (Figure 2). The presence of endo and exo-stereoisomers from the 5-norbornene-2-methanol mixture used in the DCP process further complicated the spectral region from d = 0.500-3.00 ppm.[30] Similar ^{1}H NMR spectra and evidence were observed for the DCP of poly(S-*r*-Sty) with NC2-4 to form new oragnosulfur CHIPs (Figure S8). We confirmed from the elemental analysis that the comonomer feed ratios of C% and S% were in good agreement with the final terpolymers after DCP (see Supporting Information, Table S1).

The molecular weight (MW) of the p(S-*r*-Sty-*r*-NC) terpolymer and the p(S-*r*-Sty) precursor could be compared using SEC (Figure 3). In the DCP process, S-S bonds are fragmented, so the molecular weight can be decreased. Thus, C-S bonding is produced by using thiol-ene reaction to increase MW. When p(S-*r*-Sty) was reacted with NC1, NC2, NC3, and NC4, M_n = 340, 240, 570, and 540 g/mol, M_w/M_n = 5.11, 2.00, 3.50, and 7.19, respectively (Figure 4(A)-(D)). In the case of NC1, NC3, and NC4, M_n increased. In the case of NC2, however, M_n decreased, which we attributed to the fragmentation of the organopolysulfide backbone due to the chain transfer process involving the dynamic S-S bonds of the NC2. In this study, the key question that was interrogated was whether the NC comonomer molecular architecture affected the molar mass of final terpolymers obtained from DCP. In general, terpolymers obtained from DCP of poly(S-*r*-Sty) resins were soluble, low T_g fluids of low molar mass. Poly(S-*r*-Sty) resins (M_n = 260 g/mol; M_w/M_n = 5.14) were initially used for DCP reactions with all NC comonomers with 1:1 feed ratios, respectively. However, we observed significant increases in molar mass for the DCP of poly(S-*r*-Sty) with NC3 (M_n = 570 g/mol; M_w/M_n = 3.50) as noted by the growth of higher molar mass species up to 59,600 g/mol. This finding suggested that dithioether (NC1) or disulfide linkages (NC2) molecular architectures were less efficient for the DCP process, while the benzyl ether motif (NC4) afforded modest enhancements of molar mass.

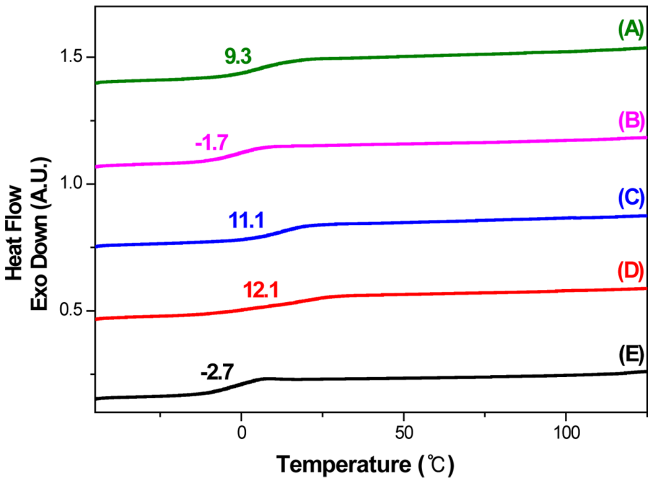
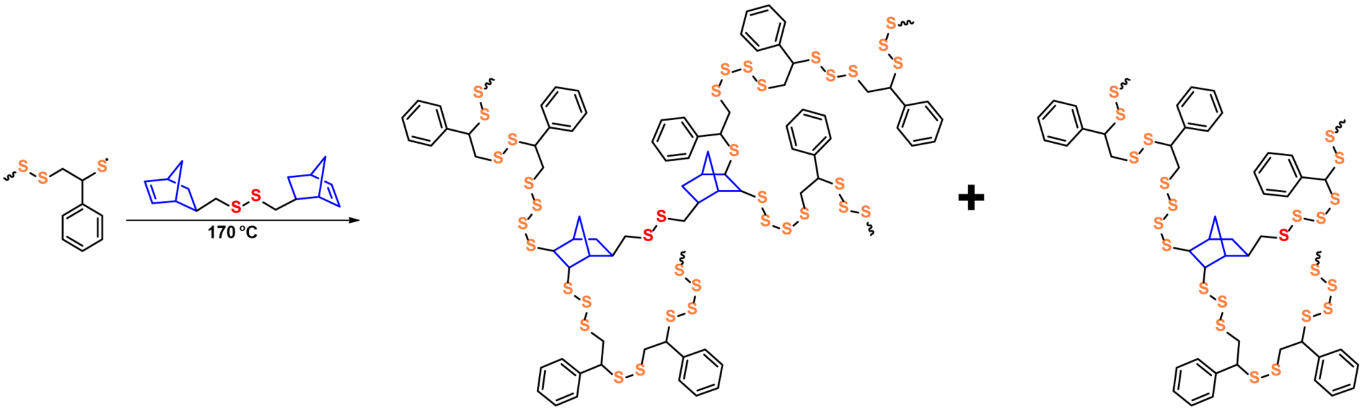


Figure 4. DSC analysis of (A) p(S-*r*-Sty-*r*-NC1), (B) p(S-*r*-Sty-*r*-NC2), (C) p(S-*r*-Sty-*r*-NC3), (D) p(S-*r*-Sty-*r*-NC4), and (E) p(S-*r*-Sty) in 3rd heating cycle.

DSC of terpolymers after the DCP process with poly(S-*r*-Sty) confirmed the incorporation of NC comonomer units, by the observation of new discrete T_g values in 3rd heating cycle. The poly(S-*r*-Sty) was initially observed to possess a lower T_g = -2.7 °C before DCP (Figure 4(E)). The T_g of the terpolymers synthesized using NC1, NC2, NC3, and NC4 were found to be 9.3, -1.7, 11.1, and



Scheme 2. Possible reaction routes for sulfur radical of NC2.

12.1 °C respectively (Figure 4(A)-(D)). The T_g values could be fairly closely correlated with the synthesized comonomer structures and SEC molar masses results. The terpolymers from NC2 exhibited a slightly increased T_g~-1.7 °C, which was attributed to the reduced molar mass from the chain transfer reactions involving the disulfide bond of the NC2 units. On the other hand, the terpolymer from the NC4 was observed with the largest enhancement of T_g due to the relatively rigid aromatic benzyl ether residue in the NC4. Since all of these terpolymers exhibited T_g below RT (molten state), these terpolymers were not suitable as transmissive materials for use in midwave, or long wavelength infrared applications. But these low T_g materials can be explored as novel lubricating fluids or precursors for elastomeric materials. In addition, the DSC results were in agreement with the results of elemental analysis. In the elemental analysis, the higher is the C%, the higher the T_g becomes. The p(S-*r*-Sty-*r*-NC4) terpolymer with the benzyl ether groups in the NC units exhibited highest T_g among the polymers (Table S1).

4. Conclusion

In this work, we demonstrated the synthesis of four kinds of sulfur terpolymers from the dynamic covalent polymerization of p(S-*r*-Sty) with NCs. NCs with different molecular architectures including ether, thioether, or disulfide linkages were synthesized and used in the DCP with p(S-*r*-Sty) for the first time to prepare new functional organosulfur CHIPs. These findings demonstrate the effect of bifunctional comonomer on the copolymerizations with the sulfur resin and point to the need for enhanced screening methods to optimize structure-reactivity design parameters for future studies.

Supporting information: Information is available regarding the ^{1}H NMR spectra, elemental analysis, DSC, and SEC of 4NC and CHIPs. The materials are available *via* the Internet at http://www.springer.com/13233.

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