

Photocrosslinked Norbornene–Thiol Copolymers: Synthesis, Mechanical Properties, and Cure Studies

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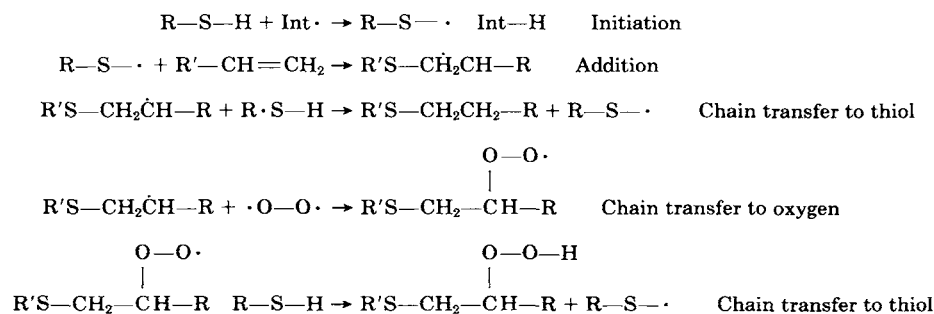
SYNOPSIS

A number of norbornene-functionalized resins were prepared and their photoinitiated crosslinking reaction with a multifunctional thiol was studied. Access to these novel resins can be gained by several synthetic routes. The most general of these routes is the $[4\pi + 2\pi]$ cycloaddition reaction (the Diels–Alder reaction) of the corresponding multifunctional acrylate ester with cyclopentadiene (CPD) monomer. The photocrosslinking reaction of these resins with multifunctional thiols such as pentaerythritol tetramercaptopropionate (PETMP) is quite rapid and sensitive to low UV dose as well as dose rate. FT-IR cure studies also indicated that the cure rate slows down dramatically as the conversion approaches the calculated gel points for the systems under study. Mechanical properties of cured thin films of these materials exhibited a wide range of tensile and dynamic mechanical properties, which depended on the structure of starting materials used in the preparation of the norbornene resin and the crosslinking thiol.

INTRODUCTION

The photoinitiated polymerization reaction between a multifunctional olefin and a multifunctional thiol (thiol-ene reaction) is a useful and versatile method for the preparation of ultraviolet (UV) curable adhesives, sealants, and coatings that find wide application in industry.¹ Because of the utility of this reaction, it has received a great deal of study. It is well established that the thiol-ene polymerization is a step growth process that propagates by chain

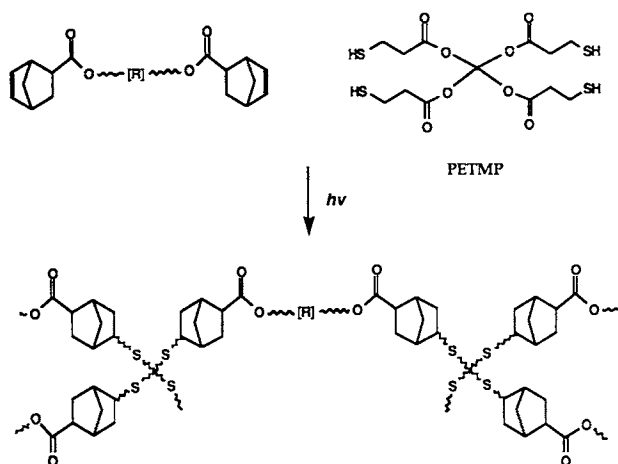
transfer and that the conversion kinetics can be predicted by the Carothers equation.^{2,3} Of the many unique features of this type of photopolymerization mechanism, the feature that has set this process apart from other UV-initiated processes is the observation that thiol-ene polymerizations are not inhibited by ambient oxygen or moisture.^{4,5} In fact, dissolved oxygen is actually incorporated into the polymer by a complex series of steps that have been described by Kharasch and co-workers⁶ and more recently by Szmant and his co-workers.^{7–10} This process is illustrated below.



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functionality such as allylic and butenyl, acrylic and methacrylic, and ketene acetal and vinylsiloxy as the "ene" components. The reasoning behind this was practical; model studies have shown that internal carbon-carbon double bonds as well as most cyclic olefins such as cyclohexene and cyclopentene react slowly, if at all with the propagating thiyl radicals.¹¹

Recently, work in our laboratories has indicated that certain types of strained cyclic internal olefins such as bicyclo[2.2.1]heptenyl derivatives (norbornene) will react readily with thiyl radical. When highly functionalized ($f \geq 2$) norbornene derivatives are reacted with multifunctional thiols such as pentaerythritol tetramercaptopropionate (PETMP, $f = 4$, illustrated below), a rapid and exothermic polymerization takes place. Model studies have indicated that norbornene derivatives can react up to 30 times as fast as allylic derivatives in competitive reaction schemes.¹²



Only preliminary results had ever been reported concerning the photoinitiated copolymerization of norbornene resins with crosslinking thiols.¹² Therefore, the purpose of this work was to prepare a wide variety of norbornene-functionalized hydrocarbon resins, to study the photopolymerization, to examine the mechanical and dynamic mechanical behavior of the derived polymers, and to determine the potential usefulness of these materials.

EXPERIMENTAL

Materials and Characterization

Most reagents and solvents were used as received without further purification except where noted. In

the cases where the norbornene resins were prepared directly from acrylate ester precursors, the acrylate esters used were commercially available products and were used as received. No attempts were made to purify these materials, which in some cases were mixtures mono-, di-, tri-, and tetraacrylates. All infrared spectra were recorded on a Nicolet MX-1 Fourier transform spectrometer. ^1H and ^{13}C -NMR experiments were carried out on a Varian EM 360 60 MHz NMR or a JEOL model FX 90Q 90MHz NMR except where noted. High-pressure liquid chromatography (HPLC) and gel permeation chromatography (GPC) were performed on a Perkin-Elmer Series 3B liquid chromatograph. GPC analysis was carried out with Polymer Laboratories PL gel columns (100, 500, 1000, and 10,000 Å pore size and 5 μm particle size) with methylene chloride or tetrahydrofuran as the mobile phase. Molecular weights were determined by comparison to polystyrene standards.

Curable compositions were prepared by mixing equivalent amounts of norbornene functional resins (n equivalents) with crosslinking thiol (n equivalents) and photoinitiator. Photoinitiator concentration in the reactive compositions was 0.12M (2% by weight of the reactive composition). The photoinitiator used throughout this study was Darocur 1173 (α -hydroxyisobutyrophenone) and was purchased from EM Industries, Elmsford, New York. The thiol used in this study [pentaerythritol tetra-(3-mercaptopropionate), PETMP] was purchased from Evans Chemetics, Lexington, Massachusetts, or from Argus Chemicals, Brooklyn, New York. Specimens for mechanical testing were cured under a Fusion System conveyerized dual lamp system (two H bulbs). Tensile properties were determined on an Instron Universal Testing Machine Model 4505 using 20-mil films according to a modified ASTM D-883 test. Dynamic mechanical tests were carried out on a Rheometrics Dynamic Analyzer RDA II with torsion rectangular geometry. Strain and frequency sweeps were carried out on duplicate samples to ensure that temperature sweeps were carried out in the linear response region. Multiple temperature sweeps were carried out to ensure that the T_g or moduli values did not change due to thermally induced crosslinking. T_g was taken as the maximum in the $\tan \delta$ curve and determined by Re-cap III version 2.3.1 software.

Photopolymerization Studies

Cure-photoresponse studies were carried out using a Blak Ray B-100 low-intensity long wavelength ul-

traviolet light (UV Products, Inc., Chicago, Illinois) with a 365-nm narrow-band interference filter (03 FIM 028, Melles Griot, Irvine, California). Incident light intensity was measured using a calibrated UV Powermeter and 365-nm detector (Optical Associates Inc., Milpitas, California) and was found to be 2.16 mW/cm^2 with the filter in place and 13.3 without the filter. Radiation doses were determined from the intensity measurements and exposure was controlled by means of a manually operated shutter. Polymerization of thin films was carried out on KBr discs. The rate of norbornene-thiol copolymerization was monitored by measuring the ratio of the absorbance of the cis-alkene group at 713 cm^{-1} (C—H out of plane bending vibration) after UV exposure to that of the unexposed film using the standard baseline technique. The hydrocarbon group absorbance at ca. 2860 cm^{-1} (C—H stretching vibration) was used as an internal standard. Acrylate reactions were monitored by using the alkene absorption at 1640 cm^{-1} (—C=C— stretching vibration). UV irradiation was carried out cumulatively with an approximately 3-min delay between successive exposures while the infrared spectrum was recorded. Care was taken to ensure that the spectra were recorded at the same location on the film after each exposure and that the film thickness remained constant during each set of measurements.

Synthesis of *endo, exo*-Norborn-2-ene-5-carbonyl Chloride, I

In a 1000-mL four-necked, round-bottomed flask equipped with a magnetic stirrer, an efficient condenser, a constant pressure addition funnel, and a thermometer connected to a Thermowatch temperature controller was stirred acryloyl chloride (271.8 g, 3.00 mol) under a nitrogen atmosphere. Freshly cracked and distilled cyclopentadiene monomer (198.2 g, 3.00 mol) was added at such a rate that the reaction temperature did not exceed $80\text{--}90^\circ\text{C}$ at any time during the addition. When the addition was completed, the reaction was stirred for an additional 3 h. Residual starting materials were removed using a water aspirator and the crude reaction mixture was then distilled *in vacuo* to give the purified product (420.1 g, 89% Th., bp $66\text{--}70^\circ\text{C}$ at 4 mmHg, lit.¹³ bp $70\text{--}72^\circ\text{C}$ at 8 mmHg).

Synthesis of *endo, exo*-Norborn-2-ene-5-methyl-5-carbonyl Chloride, II

In a 1000-mL four-necked, round-bottomed flask equipped with a magnetic stirrer, an efficient con-

denser, a constant pressure addition funnel, and a thermometer connected to a Thermowatch temperature controller was stirred freshly distilled methacryloyl chloride (250 g, 2.391 mol, Aldrich Chemical Co.) under a nitrogen atmosphere. Freshly cracked and distilled cyclopentadiene monomer (173.62 g, 2.63 mol) was added at such a rate that the reaction temperature did not exceed $80\text{--}90^\circ\text{C}$ at any time during the addition. When the addition was completed, the reaction was stirred for an additional 3 h. Residual starting materials were removed using a water aspirator and the crude reaction mixture was then distilled *in vacuo* to give the purified product (361.75 g, 89% Th., bp $74\text{--}76^\circ\text{C}$ at 4–7 mmHg, lit.¹⁴ bp 95°C at 12 mmHg).

Synthesis of *endo, exo*-Norborn-2-ene-5-methyl *endo, exo*-Norborn-2-ene-5-Carboxylate, III

Norbornenecarboxaldehyde (1000 g, 8.18 mol, Aldrich Chemical Co.) was added rapidly to aluminum isopropoxide (20.0 g) in a 2000-mL round-bottomed, three-necked flask equipped with a constant pressure addition funnel, a thermometer, and an efficient condenser under a nitrogen atmosphere. Provision was made for external cooling and a reaction temperature of 50°C was maintained by external cooling and moderating the rate of addition of the aldehyde. The reaction mixture was aged at 60°C for 2 h and then cooled. The reaction mixture was then diluted with 1000 mL of hexane, washed with water ($3 \times 400 \text{ mL}$) filtered to remove solid particulate matter, and concentrated on a rotary evaporator. The crude reaction mixture was then distilled *in vacuo* to give the purified product (776.94 g, 78% Th., bp $125\text{--}130^\circ\text{C}$ at 2.5–4.0 mmHg, lit.¹⁵ bp 117° at 0.2 mmHg).

Synthesis of *endo, exo*-Norborn-2-ene-5-isocyanate, IV

Note: Norborn-2-ene-5-carbonyl Azide, like all organic azides, is heat and shock sensitive and can decompose rapidly. Exercise all due caution in handling this material. Sodium azide (228.47 g, 3.51 mol in 250 mL deionized water) was added dropwise to a stirred solution of norborn-2-ene-5-carbonyl chloride (500 g, 3.19 mol) and tetra-(*n*-butyl)ammonium bromide (2.5 g, 0.0077 mol) in dichloromethane (1000 mL) in a 4-L beaker that had been cooled to $5\text{--}10^\circ\text{C}$ and maintained at this temperature throughout the reaction. After the addition was completed, the organic layer containing the carbonyl azide was separated and dried over anhydrous sodium sulfate and filtered. The filtered solution of

carbonyl azide was then added dropwise to a 2-L round-bottomed flask that was set up for distillation containing benzene (500 mL) maintained at 70°C. Dichloromethane was removed by distillation (overhead temperature 50–55°C) and collected. After the addition was completed the temperature of the reaction mixture was maintained at 70°C for 2 h. The reaction mixture was then concentrated on a rotary evaporator and distilled *in vacuo*. The purified product was collected as a fraction bp 60–65°C at 15 mmHg (lit.¹⁶ bp 70–74°C at 24 mmHg).

Synthesis of *endo*, *exo*-2-(Norborn-2-ene-5)-4,4-dimethyloxazolin-5-one Norbornene Azlactone (Naz), V

In a 1000-mL four-necked, round-bottomed flask equipped with magnetic stirring, an efficient condenser, a constant pressure addition funnel, and a thermometer was stirred 2-vinyl-4,4-dimethyloxazolin-5-one (501.66 g, 3.61 mol, SNPE Inc., Princeton, New Jersey) under a nitrogen atmosphere. The solution was thermostated at 40°C by means of a Thermowatch temperature controller and freshly cracked and distilled cyclopentadiene monomer (262.3 g, 3.97 mol) was added at such a rate that the reaction temperature slowly increased to 90–100°C over the course of the addition. When the addition was completed, the reaction mixture was aged at 95°C for 2 h and then concentrated on a rotary evaporator to remove excess cyclopentadiene monomer. The crude mixture was distilled *in vacuo* (bp 70–73°C at 0.2 mmHg) to yield the purified product (yield 689.7 g, 93% Th.) as a colorless liquid that rapidly solidified at room temperature. High-field NMR analysis (300 MHz) gave a spectra that was consistent with the expected product and indicated that the distillate was a mixture of *endo* and *exo* isomers of the desired product and was essentially pure. ¹H-NMR (CDCl₃,/TMS) δ = 1.2–1.5 (*m*, 10H), 1.85–2.38 (*m*, 1H), 2.9–3.2 (*m*, 2H), 5.75–6.20 (*m*, 2H). IR (neat) ν = 1815 (C=O anhydride), 1673 (C=N— imide), 709 cm⁻¹ (H—C=C—H).

Synthesis of Norborn-2-ene-5-methyl Chloroformate, VI

Norborn-2-ene-5-methanol (196.20 g, 1.58 mol, Aldrich Chemical Co.) was stirred in toluene (250 mL) in a 1000-mL three-necked, round-bottomed flask equipped with magnetic stirring, a dry ice condenser, a constant pressure addition funnel, and a thermometer. The reaction was carried out under a

nitrogen atmosphere, and the outlet of the bubble tube was vented into a dilute solution of sodium hydroxide. The solution was cooled to around 10°C, and a solution of phosgene (171.9 g, 1.738 mol) in toluene (250 mL) was added dropwise at such a rate that the reaction temperature did not exceed 25°C at any time. When the addition was completed, the reaction was warmed to room temperature and stirred for 16 h. Excess phosgene was removed by a subsurface nitrogen sparge at 30°C for 3 h. Excess solvent was removed on a rotary evaporator and the purified product was obtained by flash vacuum distillation (oil temperature 150°C, bp 75–80°C at 1.5 mmHg, lit.¹⁷ bp 105°C at 0.25 mmHg). Yield of the purified product was 113.3 g (38% Th.).

Synthesis of 1,6-Hexamethylene Di-(Norborn-2-ene-5-methyl) Carbonate, VII

Norborn-2-ene-5-methanol (314 g, 2.532 mol) and pyridine (217 g, 2.75 mol) were stirred in toluene (600 mL) under a nitrogen atmosphere in a 2000-mL four-necked, round-bottomed flask equipped with an efficient condenser, a thermometer, and a constant pressure addition funnel containing 1,6-hexamethylene bis-chloroformate (300 g, 1.235 mol).²³ The chloroformate was added at such a rate that the reaction temperature did not exceed 80°C at any time during the addition. When the addition was completed, the reaction mixture was aged at 70°C for 3 h then cooled to ambient. The reaction mixture was filtered through Celite diatomaceous earth, and the filtrate was concentrated on a rotary evaporator. The crude liquid was then passed through a 2-in. wiped film evaporator (Pope Scientific, Menomonee, Wisconsin) at 125°C and 0.5 mmHg. The yield of viscous oil was 473.1 g (92% Th.). IR (neat) ν = 2961 (C—H), 1744 (—O—CO—O—), 1400, 1326, 1253, 722 cm⁻¹ (H—C=C—H).

Synthesis of 1,6-Hexamethylene Di-(Norborn-2-ene-5-carbamate), VIII

Norborn-5-ene-2-methanol (145.04 g, 1.168 mol, Aldrich Chemical Co.) was stirred under a nitrogen atmosphere in toluene (200 mL) with diazabicycloundecane (DBU, 2.0 g) in a 1000-mL four-necked, round-bottomed flask equipped with mechanical stirring, a thermometer, and a constant pressure addition funnel containing hexamethylenediisocyanate (95.34 g, 0.567 mol). The diisocyanate was added dropwise, and the reaction temperature was allowed to rise to 70°C. When the addition was completed,

the reaction mixture was held at this temperature for 3 h and the progress of the reaction was monitored by infrared spectroscopy (ν NCO band at ca. 2271 cm^{-1}). When completed, the reaction mixture was cooled and the toluene was removed on a rotary evaporator. The product was recovered as a light yellow syrup that slowly crystallized on standing at room temperature. Yield of the crude product was 238.5 g (100% Th.). IR (neat) ν 3363 (N—H), 1631 (N—C=O), 716 cm^{-1} (H—C=C—H).

Synthesis of 1,6-Hexamethylene Di-(Norborn-2-ene-5-carboxamide), IX

Hexamethylenediamine (100 g, 0.861 mol) and pyridine (153.3 g, 1.94 mol) were stirred in toluene (750 mL) under a nitrogen atmosphere in a 2000-mL four-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer attached to a Thermowatch temperature controller, and a constant pressure addition funnel. Norborn-2-ene-5-carbonyl chloride (I, 276.09 g, 1.76 mol) was added dropwise at such a rate that the temperature slowly increased to 75°C over the course of the addition. After the addition was complete, the reaction mixture was stirred for 2 h and then methanol (5 g, 0.156 mol) was added to react with any excess acid chloride. Filtration to remove the pyridine hydrochloride salt followed by concentration of the filtrate on a rotary evaporator gave the crude product as a viscous oil that solidified on standing. The yield of crude product was 159.4 g (52% Th.). IR (neat) ν = 3292 (N—H), 1639 (N—C=O), 713 cm^{-1} (H—C=C—H).

Synthesis of 1,6-Hexanediol Di-(endo, exo-Norborn-2-ene-5-carboxylate) (HDDN), X

Hexanediol diacrylate (6054.5 g, 26.79 mol, Sartomer 238, Sartomer Company, Westchester, Pennsylvania) was stirred under a nitrogen atmosphere in a 12-L four-necked, round-bottomed flask equipped with mechanical stirring, a constant pressure addition funnel, an efficient condenser, and a thermometer connected to a Thermowatch temperature controller. Freshly cracked and distilled cyclopentadiene monomer (3541.6 g, 53.58 mol) was added at such a rate that the reaction temperature did not exceed 65°C at any time during the addition. The conversion of the acrylate was monitored by the disappearance of the characteristic IR vibration C=C stretching frequency at ca. 1640 cm^{-1} . The reaction was judged complete when this peak no longer changed on addition of more cyclopentadiene

monomer. The reaction mixture was then warmed to 90°C and aged at this temperature for 2 h. Excess cyclopentadiene was removed by vacuum distillation and the crude product was then stripped on a 2-in. wiped film evaporator (Pope Scientific Inc., Menomonee Falls, Wisconsin) at $50\text{--}60^\circ\text{C}$ and 0.2 mmHg. Yield of the resin was 9331.9 g (97% Th.). $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 1.15–2.3 (*m*, 17H), 2.8–3.4 (*m*, 5H), 4.0–4.3 (*m*, 4H), 5.9–6.35 (*m*, 4H). IR (neat) ν = 2972 (C—H), 2944 (C—H), 1733 (C=O), 711 cm^{-1} (H—C=C—H).

Synthesis of Bis-2,2-[4-(2-[Norborn-2-ene-5-carboxy]ethoxy)phenyl]propane, (Ethoxylated Bisphenol A Di-(Norborn-2-ene-5-carboxylate), (EBPA DN), XI

Ethoxylated bisphenol A diacrylate (700 g, 1.44 mol, 2.88 eq., determined by NMR, Sartomer 349, Sartomer Company, Westchester, Pennsylvania) was stirred in a 2000-mL, four-necked flask equipped as described above. Cyclopentadiene monomer (198 g, 3.0 mol) was added at such a rate as to keep the reaction temperature at about 90°C at the end of the addition. The extent of reaction was monitored by HPLC (acetonitrile–water, UV detector 254 nm) and IR by disappearance of the characteristic acrylate absorption band at 1644 cm^{-1} . When the reaction was complete, the reaction mixture was warmed to 120°C and excess cyclopentadiene monomer and dimer was removed by vacuum concentration. The norbornene-functionalized resin was recovered in quantitative yield; NMR spectroscopy was used to determine the absence of acrylic unsaturation and the equivalent weight of the resin (integration of bicyclic unsaturation versus ether methylene groups). $^1\text{H-NMR}$ (CDCl_3/TMS): δ = 1.0–2.3 (*m*, 12H), 2.7–3.3 (*m*, 6H), 3.5–4.6 (*m*, 12H), 5.7–6.3 (*m*, 4H), 6.7–7.35 (*q*, 8H). IR (neat) ν = 2968 (C—H), 1734 (C=O), 1236 (C—O), 713 cm^{-1} (H—C=C—H).

Synthesis of Trimethylolpropane Tri-(Norborn-2-ene-5-carboxylate) (TMPTN), XII

Trimethylolpropane triacrylate (338 g, 1.0 mol, CLI 4150, C/L Industries, Georgetown, Illinois) was stirred under nitrogen in a 1000-mL, four-necked, round-bottomed flask equipped with a Freidrichs condenser, a thermometer, a constant pressure addition funnel, and mechanical stirring at 40°C . Freshly cracked cyclopentadiene monomer (217 g, 3.3 mol) was added at such a rate that the temperature of the reaction slowly climbs to about 90°C

by the end of the addition. The reaction mixture was stirred at this temperature for 2 h. The extent of reaction was monitored by the decrease in the infrared absorption band at 1636 cm^{-1} . When the reaction was judged to be complete (no change in the infrared absorption), excess cyclopentadiene was removed by vacuum concentration of the resin. The yield of resin is 534 g (quantitative conversion). $^1\text{H-NMR}$ (CDCl_3/TMS) $\delta = 0.75\text{--}2.3$ (*m*, 22H), 2.5–3.3 (*m*, 6H), 3.7–4.2 (*d*, 6H), 5.75–6.25 (*m*, 6H). IR (neat) $\nu = 2973$ (C—H), 1736 (C=O), 1335, 1270, 1183, 1155, 1109, 1030, 711 cm^{-1} (H—C=C—H).

Synthesis of Pentaerythritol Tetra-(Norborn-2-ene-5-carboxylate) (PETN), XIII

Pentaerythritol tetraacrylate (2500 g, 7.89 mol, 16.59 equivalents of acrylate, Sartomer 295, Sartomer Company, Westchester, Pennsylvania) was stirred under a nitrogen atmosphere in a 5-L four-necked, round-bottomed flask equipped with mechanical stirring, a Freidrichs condenser, a constant pressure addition funnel, and a thermometer connected to a Thermowatch temperature controller. Freshly cracked and distilled cyclopentadiene monomer (1151.38 g, 17.48 mol) was added to the stirred reaction mixture at such a rate that the reaction temperature slowly climbed to 50°C during the course of the addition. External cooling was necessary at times. When the addition was completed, the reaction mixture was stirred at 50°C for 2 h and then excess cyclopentadiene was removed via vacuum distillation. The crude product was then stripped on a 2-in. wiped film evaporator (Pope Scientific Inc., Menomonee Falls, Wisconsin) at 50°C and 0.2 mmHg. Recovery of the product was quantitative. IR (neat) $\nu = 2974$ (C—H), 1738 (C=O), 1335, 1270, 1170, 1133, 1109, 1031, 711 cm^{-1} (H—C=C—H).

Synthesis of 2,2-bis-[4-(Norborn-2-ene-5-carboxy)cyclohexyl]propane Hydrogenated Bisphenol A Di-(Norborn-2-ene-5-carboxylate) (HBPA DN), XIV

Hydrogenated bisphenol A (441 g, 1.84 mol) was stirred in a 3-L four-necked, round-bottomed flask equipped with mechanical stirring, a constant pressure addition funnel, and a thermometer attached to a Thermowatch temperature controller, in dioxane (1750 mL) with triethylamine (394.64 g, 3.90 mol) and 4-dimethylaminopyridine (0.10 g) at 70°C under a nitrogen atmosphere. Norborn-2-ene-5-carbonyl chloride (I, 581.40 g, 3.71 mol) was added

dropwise, and the reaction temperature was not allowed to exceed 90°C at any time. When the addition was completed, the reaction mixture was stirred at 90°C for an additional 4 h then cooled to room temperature. Triethylamine hydrochloride was removed via filtration. The filtrate was then diluted with 2000 mL of dichloromethane and washed with 5% aqueous sodium hydroxide solution ($2 \times 300\text{ mL}$), 2M HCl ($2 \times 300\text{ mL}$), and finally deionized water ($3 \times 300\text{ mL}$). The solution was dried over anhydrous sodium sulfate, filtered, and concentrated on a rotary evaporator. The crude product was recrystallized from heptane and dried over night in a vacuum oven and had a melting point of $166\text{--}176^\circ\text{C}$. Yield of the purified product was 334 g (38% Th.). IR (KBr) $\nu = 2967$ (C—H), 2943 (C—H), 2864 (C—H), 1725 (C=O), 1346, 1334, 1270 (C—O), 1184, 1175, 1024, 711 cm^{-1} (H—C=C—H).

Synthesis of Bis-2,2-[4-(2-[Norborn-2-ene-6-carboxy-5-carboxy]ethoxy)phenyl]propane, XV

Ethoxylated bisphenol A (Dianol 22, 158.0 g, 0.50 mol, Akzo Chemie), nadic anhydride (168.9 g, 1.03 mol), pyridine (81.37 g, 1.03 mol), and 4-dimethylaminopyridine (12.2 g, 0.1 mol) were stirred in toluene (600 mL) under a nitrogen atmosphere in a 2000-mL four-necked, round-bottomed flask equipped with mechanical stirring, an efficient condenser, and a thermometer. The reaction mixture was warmed to 70°C for 3 h and then to 100°C for 6 h. The reaction was monitored using infrared spectroscopy (band at 1740 cm^{-1}). When the reaction was judged complete, the solution was cooled to room temperature, washed with 3M HCl ($1 \times 600\text{ mL}$) and the organic phase was separated. The solvent was removed on a rotary evaporator and replaced with dichloromethane (600 mL). The solution was then washed with deionized water ($5 \times 200\text{ mL}$), dried over anhydrous sodium sulfate, filtered, and then concentrated on a rotary evaporator to give the crude product as a glassy solid. The yield of product was 320 g (99% Th.). IR (neat) $\nu = 3416$ (—O—H), 2959 (C—H), 1741 (C=O), 1708 (C=O), 1510, 1252 (C—O), 1232 (C—O), 1181, 713 cm^{-1} (H—C=C—H).

Synthesis of Poly(tetramethylene oxide 650) Di-(Norborn-2-ene-5-)methyl Carbonate, XVI

Hydroxy-terminated poly(tetramethylene ether 650) (232.91 g, 0.719 eq. OH, BASF Corporation, Parsippany, New Jersey) and pyridine (64.3 g, 0.814 mol) was stirred in toluene (300 mL) under a nitrogen atmosphere in a 1000-mL four-necked,

round-bottomed flask equipped with mechanical stirring, a thermometer, and a constant pressure addition funnel containing norborn-2-ene-5-methyl chloroformate (150 g, 0.74 mol). The chloroformate was added dropwise at such a rate that the reaction temperature slowly climbed to 60°C during the addition. When the addition was completed, the reaction mixture was aged at 70°C for 3 h at which point methanol (5.0 g, 0.16 mol) was added to the reaction mixture. The reaction mixture was filtered through Celite diatomaceous earth, and the filtrate was concentrated on a rotary evaporator to remove solvent. The crude yellow oil was then passed through a 2-in. wiped film evaporator (Pope Scientific, Menomonee Falls, Wisconsin) at 125°C and 0.3 mmHg. The yield of product was 328 g (93% Th.). IR (neat) ν = 2943 (C—H), 2858 (C—H), 1744 (C=O), 1447, 1400, 1368, 1326, 1255, 1113, 985, 957, 721 cm^{-1} (H—C=C—H).

Synthesis of Poly(tetramethylene oxide 650) Di-(Norborn-2-ene-5-Carboxylate), XVII

Hydroxy-terminated poly(tetramethylene oxide 650, PolyTMO) (401.94 g, 1.241 eq. OH, BASF Corporation, Parsippany, New Jersey) and pyridine (111.06 g, 1.41 mol) was stirred in toluene (400 mL) under a nitrogen atmosphere in a 2000-mL four-necked, round-bottomed flask equipped with mechanical stirring, a thermometer, and a constant pressure addition funnel containing norborn-2-ene-5-carbonyl chloride (200 g, 1.278 mol). The acid chloride was added dropwise at such a rate that the reaction temperature slowly climbed to 70°C during the addition. When the addition was completed, the reaction mixture was aged at 70°C for 3 h at which point methanol (5.0 g, 0.16 mol) was added to the reaction mixture. The reaction mixture was filtered through Celite diatomaceous earth, and the filtrate was concentrated on a rotary evaporator to remove solvent. The crude oil was then passed through a 2-in. wiped film evaporator (Pope Scientific, Menomonee Falls, Wisconsin) at 125°C and 0.4 mmHg. The yield of product was 535 g (96.5% Th.). IR (neat) ν = 2942 (C—H), 2857 (C—H), 2796 (C—H), 1733 (C=O), 1366, 1336, 1270, 1251, 1237, 1185, 1175, 1156, 1111, 1067, 1029, 711 cm^{-1} (H—C=C—H).

Synthesis of Poly(tetramethylene oxide 650) Di-(Norborn-2-ene-5-Carbamate), XVIII

Hydroxy-terminated poly(tetramethylene oxide 650) (174.74 g, 0.539 eq. OH, BASF Corporation, Parsippany, New Jersey) was stirred under a nitro-

gen atmosphere with diazabicycloundecane (0.5 g) in a 500-mL four-necked, round-bottomed flask equipped with mechanical stirring, a thermometer, and a constant pressure addition funnel containing norborn-2-ene-5-isocyanate (75 g, 0.556 mol). The addition of isocyanate was controlled at such a rate that the reaction temperature did not exceed 35°C during the addition period. The reaction mixture was then heated to 70°C and held at that temperature for 6 h. When infrared spectroscopic analysis showed no further change in the NCO band, the reaction mixture was cooled, and the crude oil was then passed through a 2-in. wiped film evaporator (Pope Scientific, Menomonee Falls, Wisconsin) at 125°C and 0.4 mmHg. The yield of crude oil was 243.3 g (98% Th.). IR (neat) ν = 3320 (N—H), 2941 (C—H), 2858 (C—H), 1720 (C=O), 1522, 1364, 1334, 1275, 1247, 1239, 1206, 1112, 1049, 722 cm^{-1} (H—C=C—H).

Synthesis of Poly(tetramethylene oxide 650) Di-[2-(Norborn-2-ene-5-Carboxamido)-2,2-Dimethylacetate], XIX

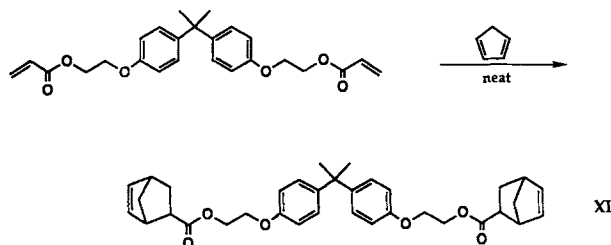
A mixture of 2-(norborn-2-ene-5)-4,4-dimethylloxazolin-5-one (130.36 g, 0.636 mol), hydroxy-terminated poly(tetramethylene oxide 650) (200 g, 0.617 eq. OH, BASF Corporation, Parsippany, New Jersey) and diazabicycloundecane (3.31 g) was stirred under a nitrogen atmosphere in a 1000-mL four-necked, round-bottomed flask equipped with mechanical stirring, and efficient condenser and a thermometer. The reaction mixture was heated to 100°C. After 8 h infrared spectroscopy indicated that the distinctive azlactone carbonyl band at 1817 cm^{-1} had completely disappeared. The crude product was then passed through a 2-in. wiped film evaporator (Pope Scientific, Menomonee Falls, Wisconsin) at 125°C and 0.4 mmHg. The yield of viscous oil was 314.8 g (96% Th.). IR (neat) ν = 2941 (C—H), 2859 (C—H), 1739 (C=O), 1526, 1363, 1280, 1155, 1113, 713 cm^{-1} (H—C=C—H).

RESULTS AND DISCUSSION

The Synthesis of Norbornene-Functionalized Resins and Monomers

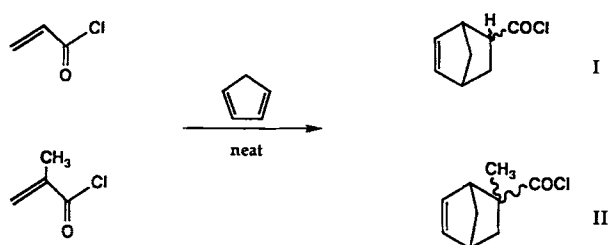
Synthetic access to norbornene-functionalized resins and monomers can be achieved by a number of general routes that give high yields of the desired products in excellent purity. The most general of these routes is based on the Diels–Alder reaction, which involves reacting cyclopentadiene monomer

with the corresponding multifunctional acrylate ester. This procedure, outlined below, is usually quite exothermic and generally gives the desired product in quantitative yields. The resulting products are a mixture of *endo* and *exo* isomers. The high yields and unambiguous product structure obtained in the Diels–Alder route is an important factor in its usefulness in preparing monomers and resins for use in this step growth polymerization scheme. It is well known that monomer purity and level of functionality can be a limiting factor in achieving a high degree of polymerization.³ This process is illustrated below for the reaction of ethoxylated bisphenol A diacrylate, which yields the corresponding norbornene ester resin (**XI**) in quantitative yield (see Experimental section).

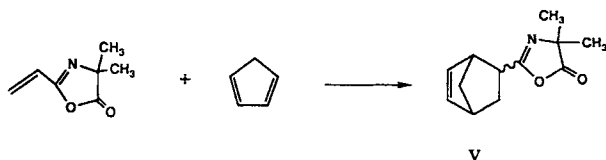


In general, neat acrylate esters react spontaneously with cyclopentadiene (CPD) monomer at room temperature, and solvent mediation of the reaction is usually not necessary if the acrylate component is liquid at the temperature at which the reaction is carried out (usually 30–120°C). Even esters with high degrees of steric crowding, such as pentaerythritol tetraacrylate and trimethylolpropane triacrylate, give quantitative conversions to the corresponding norbornene esters under moderate conditions.

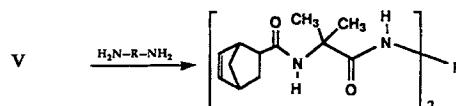
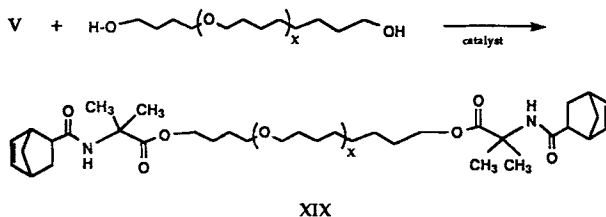
Methacrylate ester derivatives react only sluggishly with CPD, and Lewis acid catalysis¹⁸ is often necessary to activate the dieneophile component and achieve acceptable conversion. Newer methods of dieneophilic activation have been developed that avoid the use of these harsh Lewis acids, but involve the use of aqueous systems¹⁹ with low organic loading or specialized reagents.²⁰ Low reactivity of the dieneophile is also a problem observed in the reaction of acrylamide functional systems. To a certain extent, this problem can be circumvented by use of the acid chloride derived from acryloyl or methacryloyl chloride and CPD in a normal Schotten–Baumann esterification–amidation scheme (compounds **I** and **II**).



A new and interesting nonacid chloride route to norbornenecarboxamide derivatives involves the functionalization of either polyols or polyamines with 2-(norborn-2-ene-5)-4,4-dimethyloxazolin-5-one or norbornene azlactone (Naz) via a ring opening reaction of the azlactone function. Norbornene azlactone can be prepared directly from the reaction of CPD monomer with commercially available 2-vinyl-4,4-dimethyloxazolin-5-one.

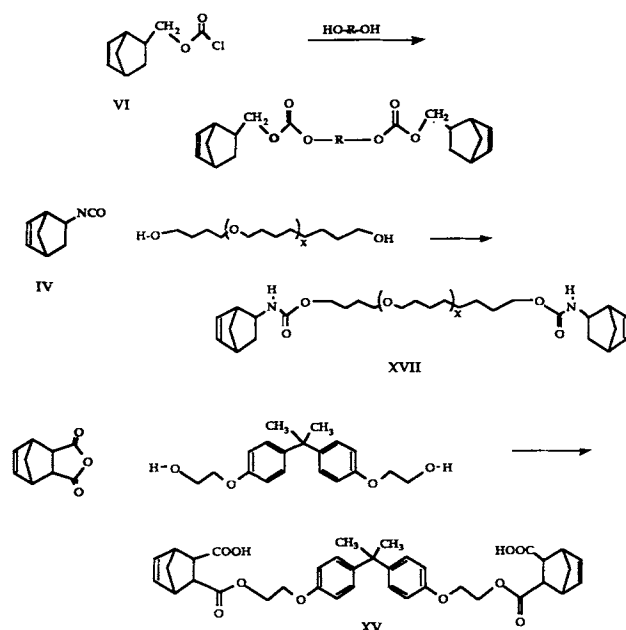


The ring opening chemistry of norbornene azlactone is analogous to that described for the 2-vinyl derivative,²¹ i.e., reactions with polyols such as tetramethylene oxides (polymegs) need to be catalyzed by a suitable amine such as 4-dimethylaminopyridine or DBU while polyether amines such as the Jeffamine series react with norbornene azlactone spontaneously.



Other small molecules [2.2.1]bicyclics such as norborn-2-ene-5-isocyanate (**IV**), and norborn-5-

ene-2-methyl chloroformate (VI), and nadic anhydride are also useful for the introduction of photocopolymerizable norbornene functionality onto active hydrogen compounds such as alcohols and amines. The general reactions of these reagents are well known and are illustrated below:



Dimerization of norborn-2-ene-5-carboxaldehyde with aluminum isopropoxide under Tishchenko reaction^{15,22} conditions readily affords the corresponding norborn-2-ene-5-methyl norborn-2-ene-5-carboxylate (III). This dimer exhibits a very high intrinsic reactivity probably due to its low equivalent weight.

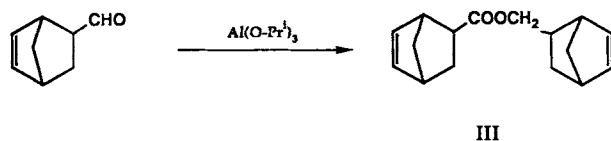


Table I summarizes the norbornene resins prepared, the chemical yield of the preparative method, and the range of functional groups that were prepared for the mechanical evaluation and photopolymerization studies.

Mechanical Properties of Norbornene-Thiol Copolymers

Mechanical and dynamic mechanical characterization of these resins has first focused on studying the

properties of thin films produced from the copolymerization of PETMP with the norbornene functional monomers. The thin films were studied as single-component mixtures of the norbornene resins and crosslinking thiol (PETMP, $f = 4$, held constant throughout the study) to characterize the behavior of different functional groups (ester, versus amide, urethane, etc.). The influence of the level of functionality in the norbornene resin ($f = 2$, versus 3, 4, etc.) was also studied as it will effect mechanical and thermal properties (such as T_g) since it will determine crosslink density. The properties of cured films of these materials are given in Table II.

T_g appears to correlate well with the level of functionality in the norbornene resins while the correlation of tensile moduli is somewhat sporadic. The highest T_g was obtained for a film of resin XIII (tetrafunctional pentaerythritol norbornene ester). However, this material was not as stiff as films prepared from some di- and trifunctional resins. For example, a crosslinked film of PETMP and resin XII, which is trifunctional, had the highest tensile moduli and the second highest T_g .

The interrelation of functional group structure and properties is shown by the results for the film containing resin IX (a difunctional norbornene amide). Here, it is assumed that restricted rotation around the amide linkage and hydrogen bonding between amides contribute to the high tensile modulus and tensile strength, as well as T_g .

This point is further illustrated by comparison of the rigid, hydrogen-bonding C_6 amide resin with systems having similar crosslink density where all bonding is assumed to be covalent, and contributions by more rigid resonance structures can be neglected (the C_6 ester or C_6 carbonate). The ester and carbonate are softer materials because their molecular structures do not incorporate stiffening units into the backbone. The resulting cured films exhibit much lower moduli and have high elongation to break.

The behavior of multicomponent mixtures was also of interest because several of the norbornene resins were attractive as reactive diluents for the higher molecular weight oligomeric species. Two component mixtures with increasing levels of functionality were also studied. Since films containing a single norbornene resin spanned such a wide range of properties, two new questions were raised. How much would properties be modified by blending and would phase separation occur in films that contained two norbornene resins? Four two-component blends were studied using 1 : 1 (w : w) mixtures of the resins. Three mixtures contained combinations of

Table I Norbornene-Functionalized Resins

Resin	Entry	N-Functional Group	f ^a	Yield %	Chemical Structure
1,6-Hexanediol di-(N-carbonate)	VII	Norbornenemethyl carbonate ester	2	92	Nor-CH ₂ O-COO-(CH ₂) ₆ -OCO-OCH ₂ Nor ^b
1,6-Hexanediol di-(N-carboxylate)	X	Norbornene ester	2	97	Nor-COO-(CH ₂) ₆ -OCO-Nor
1,6-Hexanediamine di-(N-carboxamide)	IX	Norbornene amide	2	52	Nor-CONH-(CH ₂) ₆ -NHCO-Nor
1,6-Hexanediamine di-(N-carbamate)	VIII	Norbornene urethane	2	100	Nor-CH ₂ O-CONH-(CH ₂) ₆ -NHCOOCH ₂ Nor
Ethoxylated bisphenol A di-(N-carboxylate)	XI	Norbornene ester	2	100	[Nor-COO-CH ₂ CH ₂ O-(4-Ph)] ₂ -C(CH ₃) ₂
Trimethylolpropane tri-(N-carboxylate)	XII	Norbornene ester	3	100	CH ₃ CH ₂ C-[CH ₂ O-CO-Nor] ₃
Pentaerythritol tetra-(N-carboxylate)	XIII	Norbornene ester	4	100	C-[CH ₂ O-CO-Nor] ₄
Norbornenemethyl norbornenecarboxylate	III	Norbornenemethyl norbornene ester	2	78	NorCOO-CH ₂ -Nor
Hydrogenated BPA di-(N-carboxylate)	XIV	Norbornene ester	2	38	[NorCOO-(C ₆ H ₁₀)] ₂ -C(CH ₃) ₂
Poly(TMO 650) di-(N-carbonate)	XVI	Norbornenemethyl carbonate ester	2	93	Nor-CH ₂ O-CO-O[(CH ₂) ₄ O] _n -O-CO-O-CH ₂ -Nor
Poly(TMO 650) di-(N-carboxylate)	XVII	Norbornene ester	2	96	Nor-COO-[(CH ₂) ₄ O] _n -OOC-Nor
Poly(TMO 650) di-(N-carbamate)	XVIII	Norbornene urethane	2	98	Nor-NHCOO-[(CH ₂) ₄ O] _n -OCONH-Nor
Poly(TMO 650) di-(N-az)	XIX	Norborneneamido dimethylacetate	2	96	Nor-CONH-C(CH ₃) ₂ -COO[(CH ₂) ₄ O] _n -CO-C(CH ₃) ₂ NHCO-Nor
Ethoxylated bisphenol A di-(N-carboxylate-acid)	XV	Norbornene ester carboxylic acid	2	99	[Nor-(COOH)COO-CH ₂ CH ₂ O-(4-Ph)] ₂ -C(CH ₃) ₂

^a f is the number of functional groups of the norbornene resin.^b Nor = Norborn-2-ene-5-yl, or bicyclo[2.2.1]hept-2-ene-5-yl.

Table II Tensile Properties and Glass Transition Temperatures for Thiol Crosslinked Films Containing a Single Norbornene Resin^a

N-Resin (with PETMP)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	T_g (°C)
XI (Aromatic ester $f = 2$)	1900 ± 300	40.0 ± 5.1	2.9 ± 0.5	36
XII (Alkyl ester $f = 3$)	2300 ± 50	61.0 ± 3.3	4.1 ± 0.6	67
XIII (Alkyl ester $f = 4$)	1550 ± 180	47.2 ± 6	4.9 ± 0.5	71
X (C ₆ ester $f = 2$)	810 ± 200	17.0 ± 1.5	105 ± 12	30
IX (C ₆ amide $f = 2$)	1720 ± 144	52.7 ± 1.9	4.15 ± 0.45	62
VIII (C ₆ urethane $f = 2$)	504 ± 72	15.3 ± 3.9	212 ± 16	36
VII (C ₆ carbonate $f = 2$)	127.8 ± 3.2	8.1 ± 1.3	106.0 ± 8.8	NA
III (Alkyl ester $f = 2$)	2115 ± 53	36.0 ± 7.64	6.18 ± 2.08	45

^a Crosslinking thiol was PTEMP [pentaerythritol tetra-(3-mercaptopropionate), $f = 4$] used at 1 : 1 equivalent level based on the equivalent weight of the norbornene resin. Photoinitiator was present in the reactive composition at 0.12M concentration (2% w/w).

the X, XI, and XII resins. A blend of III with XIV was also studied to evaluate the usefulness of III as a reactive diluent-solvent for the highly crystalline XIV. Cured films were prepared from these formulations and a stoichiometric equivalent of PETMP. Table III shows the properties of these cured materials.

These results show that blending X with XII produces a material with tensile properties that are close to the arithmetic average of the individual homopolymers. It is interesting to note, however, that elongation to break is essentially the same as that of the XII resin film (3.4% for the mixture of X and XII and 4.1% for XII). This result is somewhat difficult to reconcile since a significant modification of this property was expected in the mixture in light of the high elongation exhibited by X (> 100%). This is observed in both mixtures containing X.

The relationship of tensile properties and composition for these mixtures is quite complicated and considerable deviation from the arithmetic average for modulus and tensile strength is noted.

Modification of properties was also noted in the mixture containing III and XIV. The film made from the pure XIV resin was so brittle that extensive cracking and shattering made it difficult to obtain test specimens. Blending with III did not produce a material with significantly different tensile properties from the other blends tested. However, the elongation to break for the mixture over the single-component film of XIV shows the ability of III to modify the inherent brittle nature of XIV. This result indicates blends incorporating III could be useful for improving elongation in brittle systems. Alternatively, the tensile results indicate that a small amounts of XIV could be used to increase the stiff-

Table III Tensile Properties and Glass Transition Temperatures of Blended Norbornene Resin-PETMP Cured Films^a

N-Resin (with PETMP)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	T_g (°C)
X : XII (1 : 1)	1700 ± 40	44 ± 2.3	3.4 ± 0.4	46
X : XI (1 : 1)	2000 ± 50	39 ± 4.1	2.8 ± 0.4	35
XI : XII (1 : 1)	2600 ± 300	44 ± 16	2.2 ± 0.9	52
III : XIV (1 : 1)	2030 ± 74	55 ± 2	4.5 ± 0.3	64

^a Crosslinking thiol was PETMP [pentaerythritol tetra-(3-mercaptopropionate), $f = 4$] used at 1 : 1 equivalent level based on the combined equivalent weight of the norbornene resins used in the mixture. Photoinitiator was present in the reactive composition at 0.12M concentration (2% w/w).

Table IV Effect of Mixture Composition on Mechanical Properties for Blends of Norbornene Resins XI and XII Crosslinked with PETMP

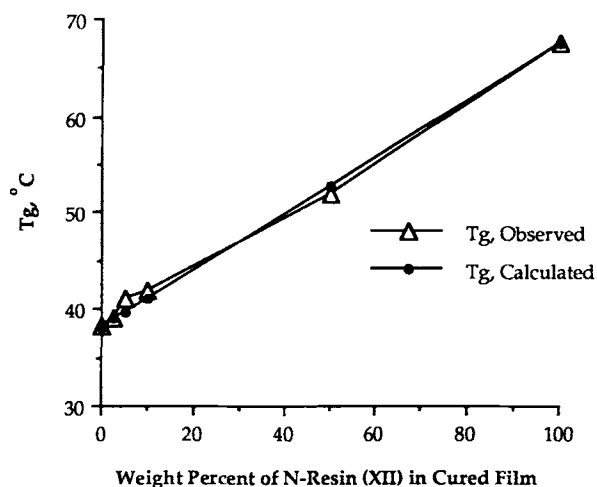
Resin ^a (w/w)	Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	T_g (°C)
XI (EBPA DN)	1434	30.35	3.83	38
XI : XII 39 : 1	1500	33.10	4.04	39
XI : XII 19 : 1	1603	33.58	3.85	41
XI : XII 9 : 1	1603	42.6	3.88	42
XI : XII 1 : 1	2600	44	2.20	52
XII (TMPTN)	2300	61	4.10	67

ness and decrease the elongation of softer, more elastomeric materials.

All norbornene blends studied were miscible at room temperature in the proportions studied. Temperature sweeps of the cured films obtained by dynamic mechanical analysis showed a single T_g for each blend; it is assumed that the oligomers were miscible and have formed a random copolymer.³² In addition all films were optically clear, another indication of miscibility.

Further mixture work focused on the effect of increasing the level of ene functionality on the glass transition and the mechanical properties. A simple mixture of a difunctional ene, **XI** (EBPA DN,) and a trifunctional ene, **XII** (TMPTN) was studied. These results are listed in Table IV.

These two ene components and the crosslinker

**Figure 1** Effect of blend composition on T_g for *N*-Resins XI and XII.

would be expected to form a random copolymer mixture. In this case we were interested in determining if the two component mixture obeyed the so-called *rule of mixtures*, which predicts the glass transition for random copolymers and was described by Fox and later by Wood.³² These results are presented in Figure I and indicate that this mixture of ene components shows a good correspondence with the predicted relationship, and therefore complete mixing can be assumed.

As observed earlier, the prediction of mechanical behavior for these mixtures is less straightforward than modeling T_g . Since norbornene functionality can be introduced into the molecule by a wide variety of synthetic reagents, a wide variety of norbornene-functionalized end groups (esters, carbonates, urethanes, amides, etc.) are accessible. It was of interest to probe, in a limited way, the effect of various functional groups as described above on a single oligomeric backbone (poly[TMO 650]).

Table V outlines the mechanical properties and glass transition temperatures of these materials. It is seen that in poly(TMO 650)-based systems, the identity of the end groups does not yield significant influence on final mechanical and thermal properties. Rather, the flexibility of the poly(TMO) 650 backbone exerts the major influence on the properties of the cured film regardless of the end group and produces a material that is rubbery at room temperature. When a long backbone is not built into the starting oligomer, end group functionality has a much greater influence on T_g and tensile properties. This is illustrated by comparing the properties of **IX** (the C_6 amide) with those of **XIX** [the poly(TMO 650) amide-acetate]. Hydrogen bonding between amide groups is possible in both systems.

Table V Tensile Properties and Glass Transition Temperatures of Various Norbornene-Functionalized Poly(TMO 650) Resins

<i>N</i> -Functionality (with PETMP)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	T_g (°C)
XVI (Norbornenemethyl carbonate ester)	4.70 ± 0.23	0.69 ± 0.05	17.3 ± 2.0	-39.0
XVII (Norbornene ester)	5.62 ± 1.03	0.81 ± 0.11	16.7	-39.0
XVIII (Norbornene urethane)	5.86 ± 0.28	1.17 ± 0.25	25.0 ± 6.6	-16.0
XIX (Norborneneamido dimethylacetate)	1.38 ± 0.28	0.53 ± 0.06	51.5 ± 7.7	-20.0

T_g varies by approximately 80°C. Tensile moduli differ by a factor of 1000; tensile strength of these two films differ by a factor of 100.

The structure of **VII** (the C₆ carbonate ester) is, except for backbone length, similar to that of **XVI** [the poly(TMO 650) carbonate]; although **VII** was soft and somewhat difficult to handle at room temperature, its tensile properties are an order of magnitude greater than the cured film containing oligomer **XVI**. Finally, the effect of polar functional groups on T_g in the same oligomeric series is reinforced. Comparison of T_g values of **XIX** (amide functional) and **XVIII** (urethane functionality) with **XVI** (carbonate ester) and **XVII** (carboxylate ester) show stiffening due to restricted rotation of the amide and urethane group and hydrogen bond formation. The T_g values for the former materials are higher than the latter by approximately 20–25°C. Clearly, the type of functionality in the end groups exerts an influence on the physical and mechanical properties of films in a homologous series. This effect can be magnified or attenuated by the backbone.

Photopolymerization Studies

Model studies on norbornene-thiol copolymer systems have indicated that these materials have a high intrinsic reactivity that is due to the release of a significant amount of ring strain energy in the [2.2.1]bicyclic system when the thiyl radical adds to the sp²-hybridized olefin carbons.¹² Earlier flash photolysis studies of the addition of phenylthio radicals to a series of cycloalkenes, cycloalkadienes, and bicycloalkenes showed that [2.2.1]bicyclic olefins have a high affinity to add thiyl radical and less of a propensity to undergo the reverse reaction.²⁴ The theoretical underpinnings of this enhanced reactivity have also been discussed.^{25–28} However, it is also

well established that regardless of the intrinsic reactivity of a polymer system, polymerization rates can drastically decrease as the polymerizing mixture approaches the gel point especially if the polymerization is carried out below $T_{g\text{ ultimate}}$ for the system.²⁹ Onset of gelation occurs at low conversions in acrylate photopolymerizations²⁹ and is difficult to predict due to the complex nature of the chain growth process and differences in monomer reactivity. In step growth processes such as thiol-ene polymerizations, the gel point (α) can be calculated based on the functionality of the comonomers,^{30,31} where α is the critical fractional conversion (gel point) and f_a and f_b are the average functionalities of the *a* and *b* comonomers, in this case the thiol and the ene, respectively:

$$\alpha = \sqrt{\frac{1}{(f_a - 1)(f_b - 1)}}$$

Gel point predictions were made for several of di-, tri-, and tetrafunctional norbornene resins for the photoinitiated copolymerization reaction with a standard crosslinking thiol, pentaerythritol tetramercaptopropionate (PETMP) and are listed in Table VI.

In order to confirm these predictions and to study the photoresponse of the norbornene resins, a UV cure study was designed. The method used FT-IR analysis of the samples at various UV doses to determine the effect of functionality on conversion (Table VII). A standard acrylate monomer, ethoxylated bisphenol A diacrylate was also studied, but at a higher dose (13.3 vs. 2.13 mJ/cm²). At the lower dose level, the acrylate was unreactive due to oxygen inhibition. Even this higher dose rate is probably not sufficient to completely overcome the effect of

Table VI Gel Point Calculations for Norbornene Functional Resins Crosslinked with a Tetrafunctional Thiol

<i>N</i> -Resin	Entry	Thiol	f_a	f_b	α
1,6-Hexanediol di-(<i>N</i> -carboxylate)	X	PETMP	4	2	0.57
Trimethylolpropane tri-(<i>N</i> -carboxylate)	XII	PETMP	4	3	0.40
Pentaerythritol tetra-(<i>N</i> -carboxylate)	XIII	PETMP	4	4	0.33
Ethoxylated bisphenol A di-(<i>N</i> -carboxylate)	XI	PETMP	4	1.98 ^a	0.65 ^a

^a Based on HPLC analysis of acrylate starting materials and derived norbornene-functionalized resin.

oxygen inhibition, and this is also apparent in the high UV dose required to reach the ultimate conversion level of 65%. When the norbornene systems were subjected to the higher dose rate, the polymerization was too fast to make measurements at the intermediate stages.

The results of the cure study confirm that, as expected, the two difunctional norbornene resins tend to cure to an overall higher fractional conversion (ca. 0.76 for HDDN and 0.65 for EBPA DN, in Table VI). The trifunctional resin in turn is more highly cured than tetrafunctional resin (0.60 for trifunctional TMP TN and 0.49 for tetrafunctional PETN). Plots of conversion versus UV dose for these systems are presented in Figure 2.

The general trend of reactivity and conversion is also reflected in the UV dose required to reach 50% conversion. This is a somewhat better indicator of reactivity as it allows us to differentiate the two difunctional norbornene resins from the tri- and tetrafunctional material. But even at 50% conversion it appears that the conversion of the tetrafunctional systems has already decelerated probably due to vitrification effects. Because this study was carried out at ambient temperature, it is important to note that the order of reactivity and conversion, HDDN

> EBPA DN > TMPTN > PETN is the reverse of the T_g trend.

CONCLUSIONS

Norbornene resins are a novel family of olefins that are extremely useful ene components in photoinitiated thiol-ene copolymerizations. The norbornene resins exhibit an enhanced reactivity toward thiols because of a high degree of strain that is inherent in the [2.2.1]bicyclic system. Norbornene resins and monomer are readily accessible by a number of routes including Diels–Alder cycloadditions of acrylate esters with cyclopentadiene monomer, reaction of norbornene functional acid chlorides and anhydrides, Tishchenko dimerization of norbornene functional aldehydes, and via a ring opening reaction of 2-(norborn-2-ene-5)-4,4-dimethyloxazolin-5-one.

Cure studies of the photoinitiated copolymerization with thiols indicate that this process is quite sensitive to low UV doses and that the polymerization slows down as the degree of conversion approaches the calculated gel point if the polymerization is carried out below $T_{g\text{ ultimate}}$. Photoinitiated copolymerizations with crosslinking thiols give ma-

Table VII Conversion and UV Dose Parameters

<i>N</i> -Resin (with PETMP)	Fractional Conversion	Total Dose (mJ/cm ²)	Dose to 50% (mJ/cm ²)	UV Intensity (mW/cm ²)
Ethoxylated bisphenol A di-(<i>N</i> -carboxylate) (EBPA DN)	0.65	600	65	2.13
1,6-Hexanediol di-(<i>N</i> -carboxylate) (HDDN)	0.76	380	30	2.13
Trimethylolpropane (tri-(<i>N</i> -carboxylate) (TMP TN)	0.60	300	85	2.13
Pentaerythritol tetra-(<i>N</i> -carboxylate) (PETN)	0.49	520	390	2.13
Ethoxylated bisphenol A diacrylate	0.65	8000	2800	13.3

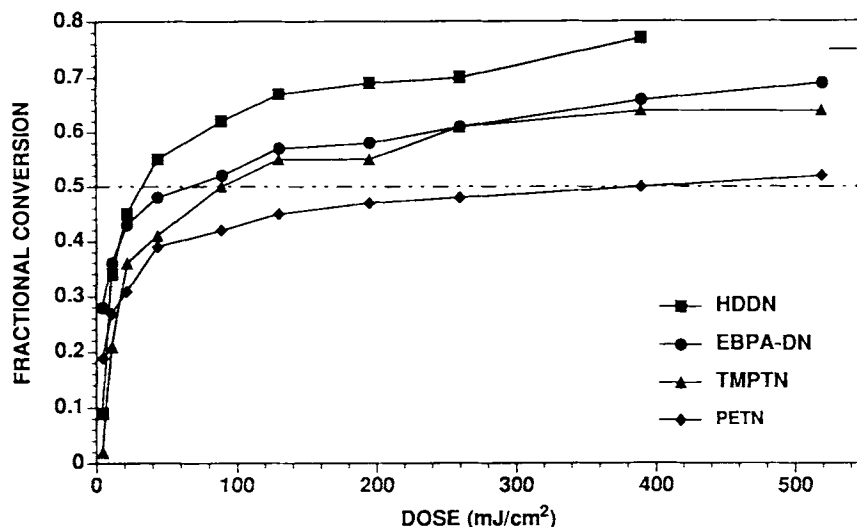


Figure 2 Fractional Conversion versus UV Dose in Norbornene-Thiol Copolymers.

materials that exhibit a wide range of static and dynamic mechanical properties.

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