

Syntheses and Properties of Cross-Linked Polymers From Functionalized Triglycerides

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ABSTRACT: A number of functionalized triglycerides were synthesized from glyceryl trioleate via epoxidation followed by reduction to give glyceryl tris(9-hydroxy)trioleate (a triol) or hydrolytic ring opening to obtain glyceryl tris(9,10-dihydroxy)trioleate (a hexaol). A selective monoepoxidation reaction of glyceryl trioleate was also carried out and the resulting monoepoxide was hydrolyzed to give glyceryl 9,10-dihydroxytrioleate (a diol). Glyceryl tris(9-hydroxy)trioleate was brominated followed by displacement with sodium azide and reduction to give glyceryl tris(9-amino)trioleate (a triamine) and glyceryl tris[9-(*N*-isopropylamino)]trioleate. These functionalized triglycerides were crosslinked with 1,4-phenylene diisocyanate. The crosslinked polymers exhibit thermoset characteristics. Thermal analysis results suggest

that the polymers are in amorphous states, and their thermal stability was significantly affected by crosslink degree. The crosslinked polymer derived from the diol retained 56% of its weight at 408°C, whereas the polymers derived from the aforementioned hexaol with higher crosslink degree retained only 36% of the original weight. Glass transition temperatures of these polymers range from -1.0°C to 10.2°C. The thermal stable polymer, **12**, derived from the aforementioned diol exhibits a linear viscoelastic character and can be used as thermoplastics. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 647–656, 2008

Key words: biopolymers; crosslinking; plant oil; triglycerides; thermal gravimetric analysis; differential scanning calorimetry; dynamic viscoelastic properties

INTRODUCTION

Polymers and polymeric composites are widely used in various industries including automotive, aerospace, marine, sport, military, biomedical, pharmaceutical, optoelectronic, adhesives, and coatings. These materials are lightweight and have low assembly cost, excellent mechanical properties, high corrosion resistance, and dimensional stability.¹ These materials are generally made of synthetic chemicals derived from petroleum.¹ As the applications increase, alternative sources of these materials are needed. One alternative source is the utilization of affordable materials from renewable sources, such as natural triglyceride oils, as the main component for polymers and composites.^{2–6} Besides food uses, plant oils are currently used as minor components in coatings, plasticizers, lubricants, agrochemicals,

and inks as toughening agents or to improve fracture resistance of thermoset polymers.^{2–6} The methods involve functionalized triglycerides as crosslinking agents to interpenetrate main polymer networks^{7–16} and transformation of hydroxylated triglycerides to the corresponding acrylic esters followed by polymerization with polystyrene.^{2–4} Polyurethanes have been prepared¹⁷ by ozonolysis of the alkenyl functions of trilinolein and high-unsaturated oils (canola and soybean oils) followed by reduction with sodium borohydride and polymerization with 4,4'-methylenebis(phenyl isocyanate). Our interest in biorenewable materials prompted us to investigate plant-oil-derived polymers. We report herein our studies of functionalizations of triolein (glyceryl trioleate), subsequent polymerization reactions with a crosslinking agent, 1,4-phenylene diisocyanate and evaluation of thermal transitions, thermal stability and dynamic mechanical behavior of the newly synthesized polymers.

RESULTS AND DISCUSSION

Syntheses of functionalized triglycerides

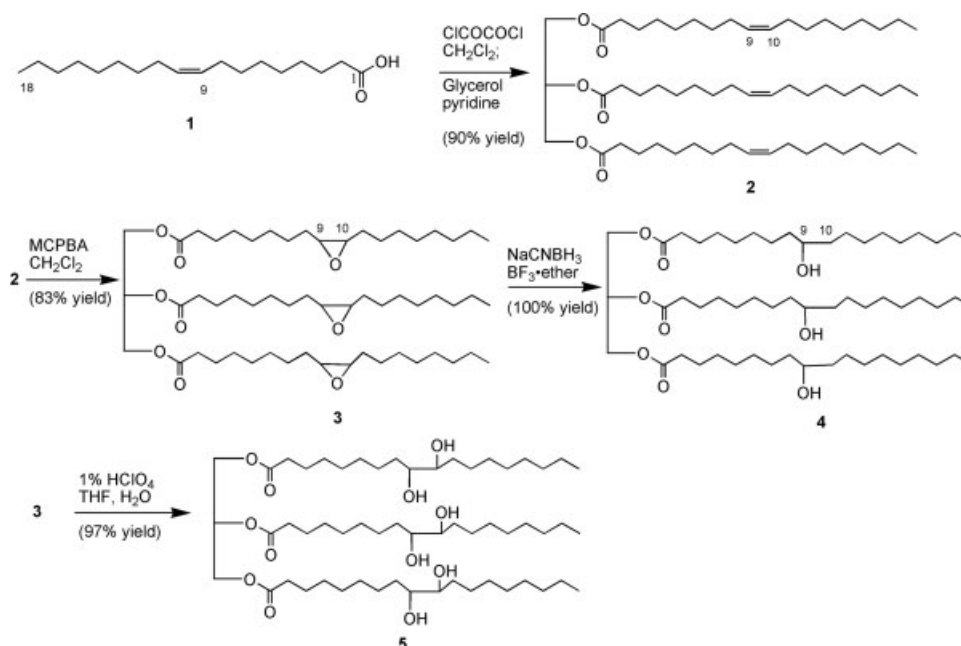
Our methodologies were to transform the alkenyl function of glyceryl trioleate to hydroxyl and amino functions followed by crosslinkage with 1,4-phenylene

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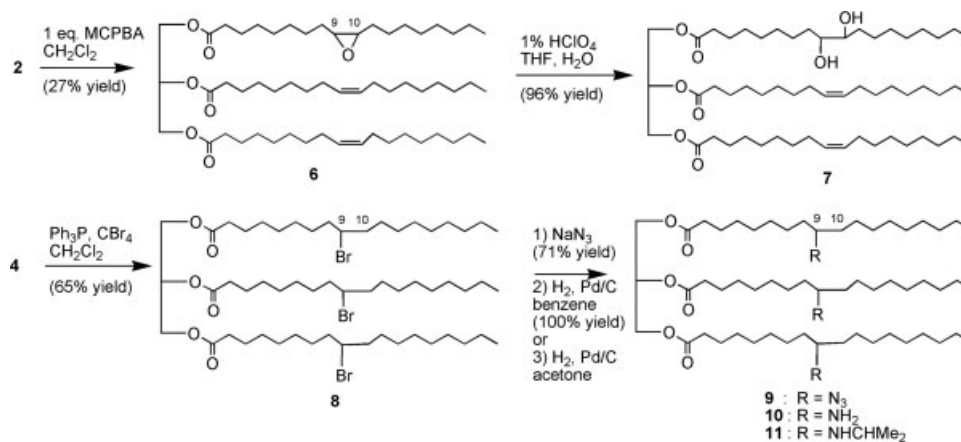
Contract grant sponsor: American Heart Association, Heartland Affiliate; contract grant number: 0750115Z.



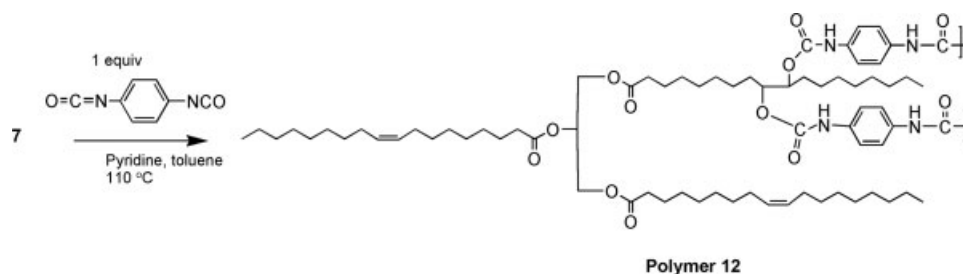
Scheme 1 Preparations of triglycerides 2, 4, and 5.

diisocyanate to produce polymers. To aid our spectroscopic analysis, we used pure glyceryl trioleate (2) derived from oleic acid (1) by the treatment with oxalyl chloride followed by esterification with glycerol and pyridine (90% overall yield) (Scheme 1). Epoxidation of compound 2 with >3 equivalents of *m*-chloroperbenzoic acid (MCPBA) in dichloromethane afforded triepoxide 3, which was reduced with sodium cyanoborohydride and boron trifluoride¹⁸ in THF providing triol 4. The regiochemistry of the hydroxyl functions of triol 4 has not been determined. From ¹H and ¹³C-NMR and sharp melting point (m.p. 70–71°C), it appears that a single compound is formed (without regioisomers). Acidic-ring opening of epoxide 3 with 1% perchloric acid in THF-H₂O gave hexaol 5.

To study the effect of functionalization of one of the three side chains of glycerol trioleate, we synthesize diol 7 in which two hydroxyl functions are on one side chain (Scheme 2). Hence, monoepoxidation of compound 2 with 1 equivalent of MCPBA in dichloromethane afforded monoepoxide 6 along with diepoxides and triepoxides and recovered starting material 2. Column chromatographic separation of the crude product gave pure monoepoxide 6, which ¹H and ¹³C-NMR spectra indicate a single isomer. The regiochemistry of the epoxy function of 6 is assumed. Hydrolytic ring opening of 6 with perchloric acid in THF and water provided diol 7 in 96% yield. Diol 7 possesses two hydroxyl functions on one of the CH₂OCO side chains and no hydroxyl function on the remaining side chains.



Scheme 2 Preparations of triglycerides 7, 10, and 11.



Scheme 3 Preparation of triglyceride polymer 12.

Triamines **10** and **11** were also synthesized for the production of polymers containing urethane functionality (Scheme 2). Bromination of triol **4** with 3 equivalents each of triphenylphosphine and carbon tetrabromide¹⁹ followed by displacement with sodium azide afforded triazido triglyceride **9**. Reduction of azide **9** with a catalytic amount of 10% Pd/C in benzene under 30 psi of H₂ gave triamine **10** in quantitative yield. A one-pot reductive amination of azide **9** was carried out by the treatment with H₂-10% Pd/C in acetone to give triisopropylamine **11** (quantitative yield). The azide function was first reduced to amine, which condensed with acetone (solvent) to form imine followed by hydrogenation affording amine **11**.

Syntheses of polymers

We used 1,4-phenylene diisocyanate (PDI)²⁰ as the sole crosslinking reagent for the construction of triglyceride polymers from various aforementioned functionalized triglycerides, and studied their physical properties. The para-orientations of two isocyanate groups of PDI provide an ideal reagent to construct rigid polymers. First, diol **7**, an oily material, was treated with 1 equiv of PDI and a catalytic amount of pyridine in refluxing toluene (Scheme 3). After removal of pyridine and toluene, a light brown solid polymer, **12**, was produced (yield is listed in Table I). Polymer **12** is a rubbery material and not soluble in most organic solvents including DMSO, DMF, chloroform, ethyl acetate, ethanol, etc. NMR spectral data of the polymer cannot be obtained because the material is insoluble in organic and inorganic solvents. FTIR and gel content were measured.

Second, crosslinked polymer **13** derived from triol **4** was synthesized by the treatment of compound **4** with 1.5 equivalents of PDI and a catalytic amount of pyridine under refluxing toluene (Scheme 4). Similarly, a rubbery solid was produced and is insoluble in most organic and inorganic solvents. The NMR spectrum of polymer **13** cannot be obtained, and its physical properties were measured (*vide infra*) including FTIR and gel content.

Third, hexaol **5** was treated with 3 equivalents of PDI to produce polymer **14** (Scheme 5). Three equiv-

alents of PDI are needed for six hydroxyl functions of **5** react. A highly crosslinked polymer, **14**, was obtained, and its physical properties are described in the following section including FTIR and gel content.

Formation of urethanes from triamines **10** and **11** with PDI was similarly carried out without pyridine (Schemes 6 and 7). The crosslinked polymers, **15** and **16**, are solid materials and insoluble in most organic and inorganic solvents. Similarly, their NMR spectral data cannot be obtained, however, FTIR and gel content were measured.

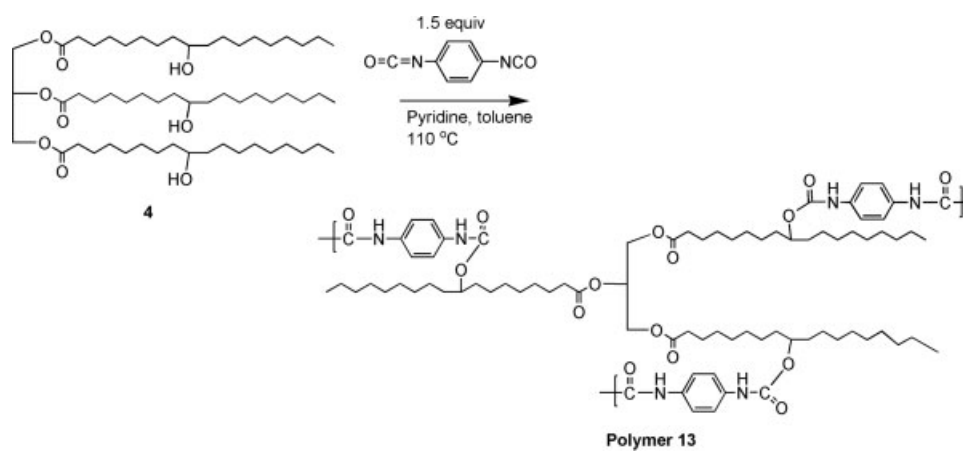
FTIR spectra of all polymers show aromatic C—H stretches ($\sim 3005\text{ cm}^{-1}$) and aromatic C=C stretches ($\sim 1605\text{ cm}^{-1}$). The carbonyl (C=O) stretches of the carbamate function (—OC=ONH—) of polymers **12–14** appear at $1736\text{--}1744\text{ cm}^{-1}$ (broad and strong), which overlap with the C=O stretch of the ester functions. The C=O stretches of the monomers show sharp and strong absorption bands at $\sim 1743\text{ cm}^{-1}$. The carbonyl stretches of the urea moiety (HN—C=ONH—) of polymers **15** and **16** appear at $1636\text{--}1645\text{ cm}^{-1}$ (strong), which allows the assignment of the urea function in the polymers. In turn, formations of the polymers through reactions of amines with isocyanate are supported.

Physical properties

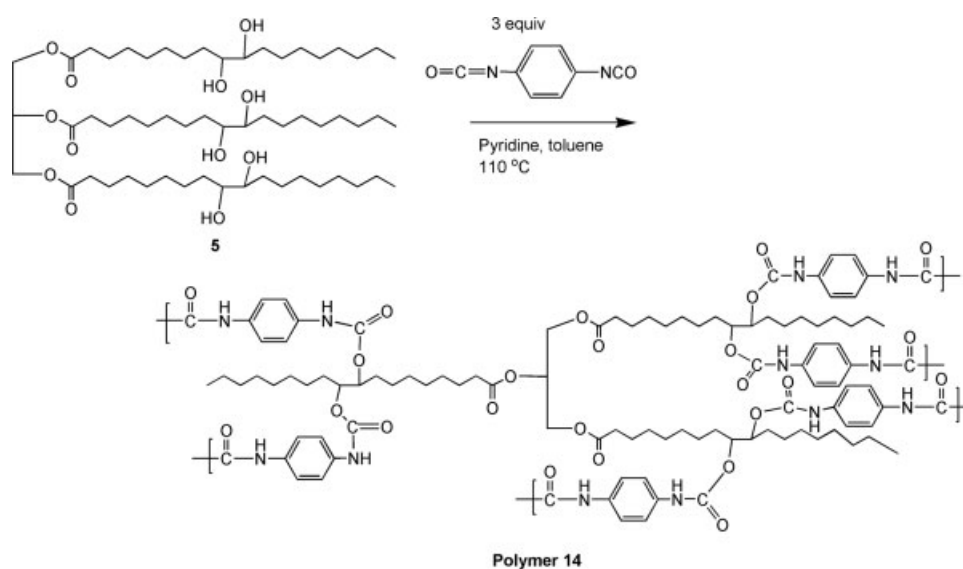
Since the bulks of the above crosslinked thermoset polymers are insoluble in organic and inorganic solvents, the average molecular weights can not be determined. We therefore studied gel contents, thermal and mechanical properties of these polymers including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) (providing

TABLE I
Yields and Gel Contents of Polymers 12-16

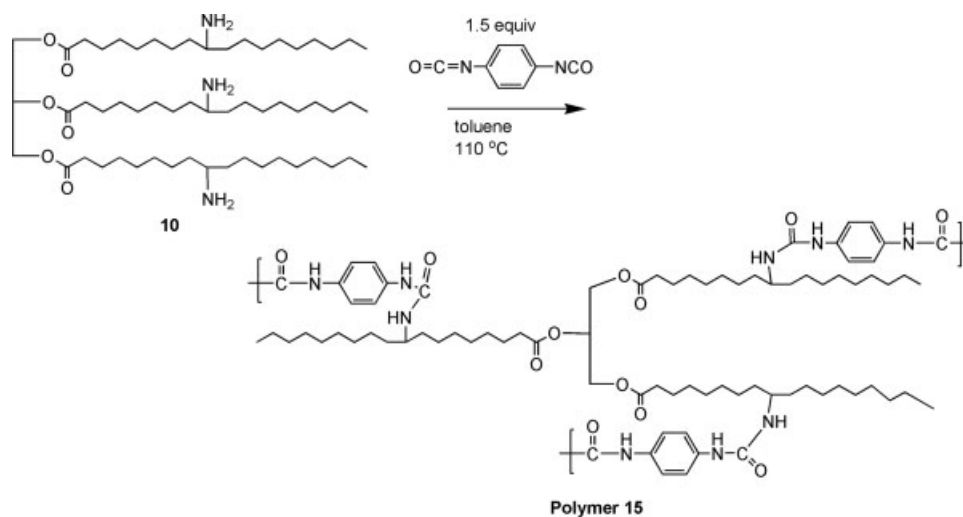
Polymer	Yield (%)	Gel content (%)
12	64	77
13	83	91
14	95	96
15	90	95
16	86	92



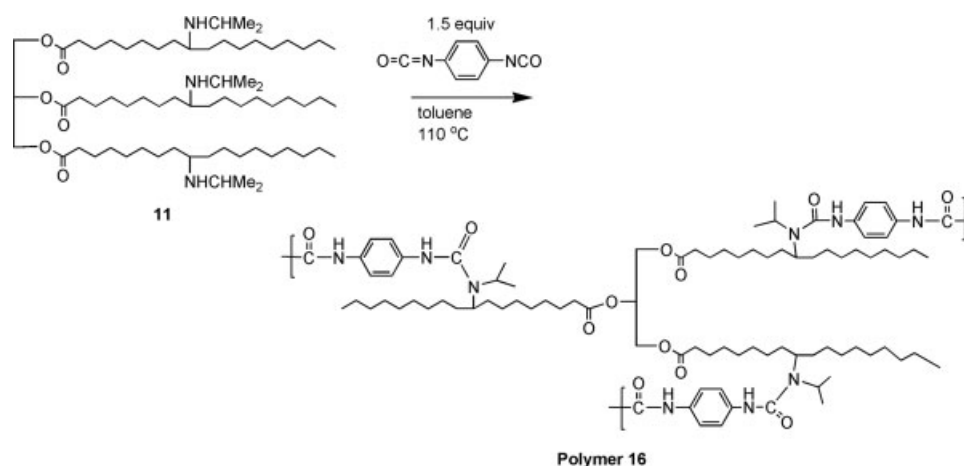
Scheme 4 Preparations of triglyceride polymer 13.



Scheme 5 Preparations of triglyceride polymer 14.



Scheme 6 Preparations of triglyceride polymer 15.



thermodegradation properties), and dynamic mechanical properties. These data provide useful information of the polymers for future material applications.

Gel content: the polymers were heated to reflux in chloroform for 3 h and filtered. The gel (insoluble fraction) and the filtrate (soluble polymer) were dried under vacuum, and weights of the residues were obtained. The gel content % is equaled to the weight of the gel divided by the weight of the initial polymer multiplied by 100%. Results of the gel contents are summarized in Table I.

Thermal characterization

Differential scanning calorimetry

Thermal behavior of two triglyceride monomers, compounds 4 and 5, were characterized as controls using DSC. The prominent endothermic peaks showed in the DSC thermograms (Fig. 1) demonstrated that they are highly crystalline monomers.

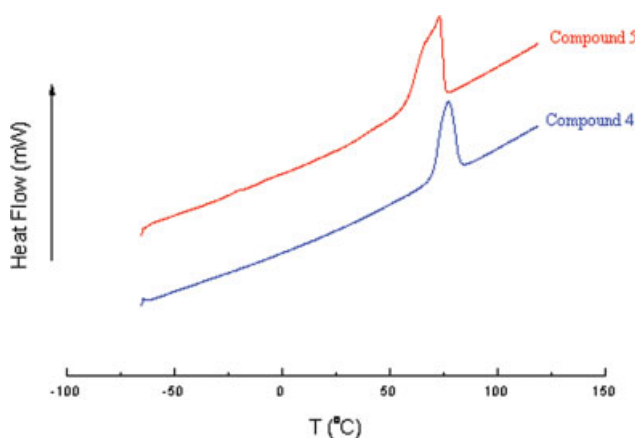


Figure 1 DSC thermograms of triglyceride monomers 4 and 5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

The crosslinked polymers did not show melting peaks, which indicate they could be in amorphous phase (Fig. 2; top panel).

Glass transition temperatures of the crosslinked polymers 12–16 were determined from the differential DSC thermograms and results are listed in Table II.

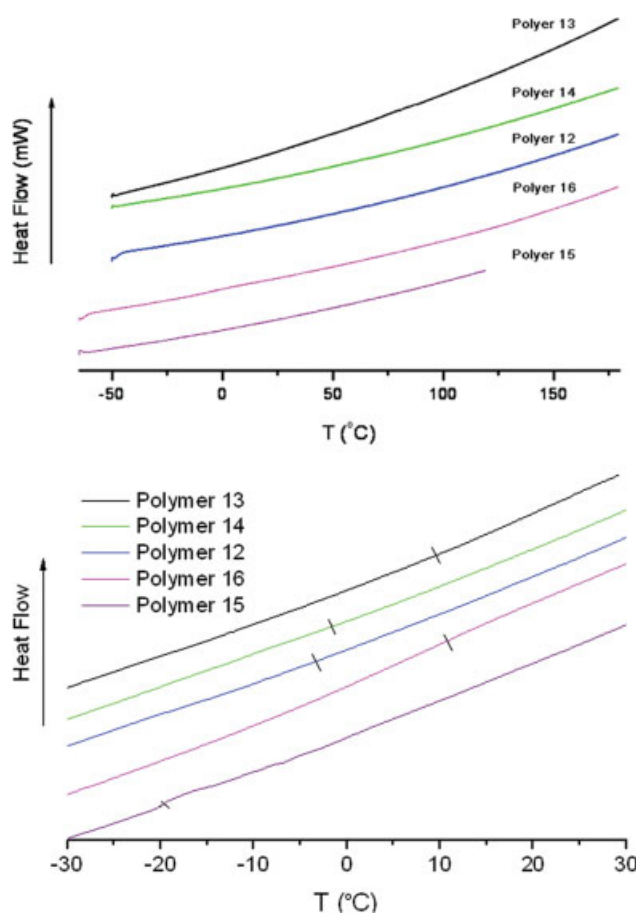


Figure 2 Top panel: DSC thermograms of triglyceride polymers 12–16. Bottom panel: zoom-in graphs from -30 to 30 °C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

TABLE II
Glass Transition Temperatures of the Triglyceride Polymers

Samples	Glass transition temperature (T_g , °C)
Polymer 12	-2.8
Polymer 13	10.0
Polymer 14	-1.0
Polymer 15	-20.7
Polymer 16	10.2

The glass transition temperatures of polymers 12–16 were determined from step transitions observed in DSC thermographs (Fig. 2, bottom panel). In the enlarged graphs (not shown), changes of the thermographs of the polymers showed step transitions, and the midpoints (Fig. 2, bottom panel; indicated with perpendicular small black lines) of the step transitions provided glass transition temperatures. Polymer 12, derived from diol 7, has the lowest glass transition temperature at -2.8°C . Since only one of the three alkyl chains of polymer 12 (Scheme 3) participated in the crosslinking, the movement of the two remaining noncrosslinked alkyl chains might internally plasticize the polymer.

Thermal stability

The thermal stability of all polymers was characterized by TGA. Polymer 12 (Fig. 3) appears as the most thermal stable polymer among all the investigated polymers as its thermal decomposition onset temperature was at 282.6°C . Although polymer 16 was susceptible to heat it started to decompose around 150°C . The steric repulsion created by the isopropyl substituent of the urea function in polymer 16 might contribute to the low thermal stability. Other cross-

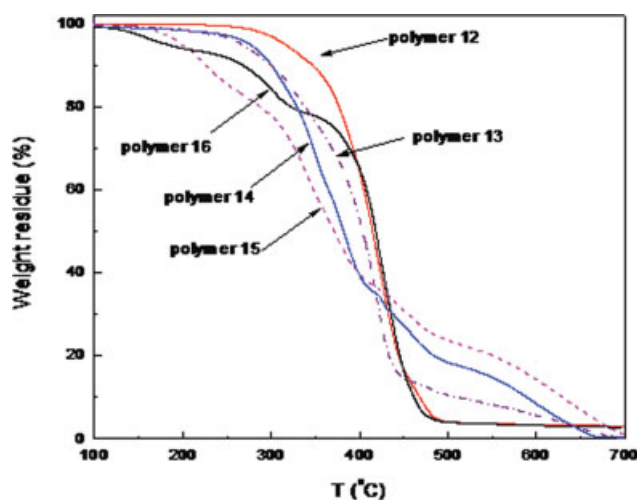


Figure 3 TGA thermograms of triglyceride polymers 12–16. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

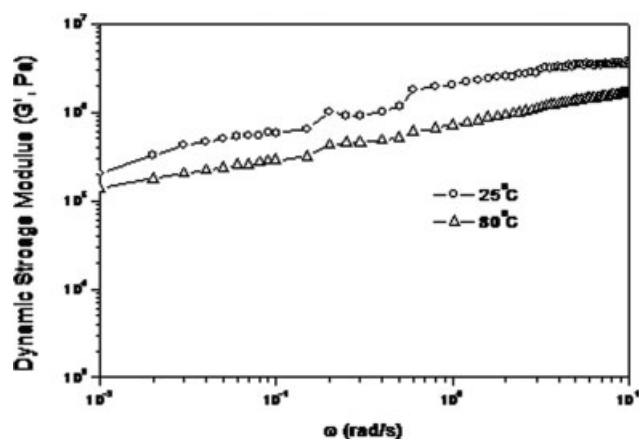


Figure 4 Dynamic mechanical properties of polymer 12.

linked polymers 13–15 showed their thermal stability between 282 and 150°C . For example, polymer 14 started significant weight loss at 217°C , and about 36% weight residue left at 408°C . Polymer 15 started to decompose at 173.6°C , and retained 35% of its original weight at 408°C . While in polymer 12, about 56% of original weight was retained at 408°C .

Viscoelastic characteristics

Dynamic viscoelastic properties are often used to measure the crosslinking degree of polymers.²¹ Dynamic storage modulus of polymer 12–14 were measured by varying frequencies at different temperatures and results are shown in Figures 4–6. Since polymers 15 and 16, derived from amines, showed thermal decompositions at relatively lower temperatures compared with that of polymer 12, their viscoelastic properties are not investigated. Polymer 12 exhibited a linear viscoelastic characteristic at low frequency (below 10 rad/s), which is similar to that of most thermoplastics. Hence, it likely can be used as a thermoplastic.²² Polymer 14 behaved as a rigid polymer as the modulus was

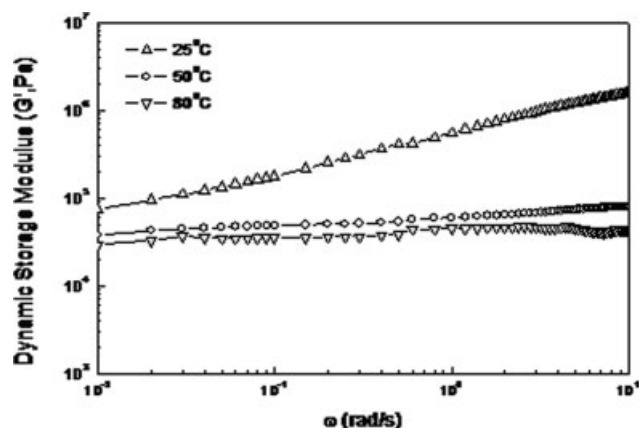


Figure 5 Dynamic mechanical properties of polymer 13.

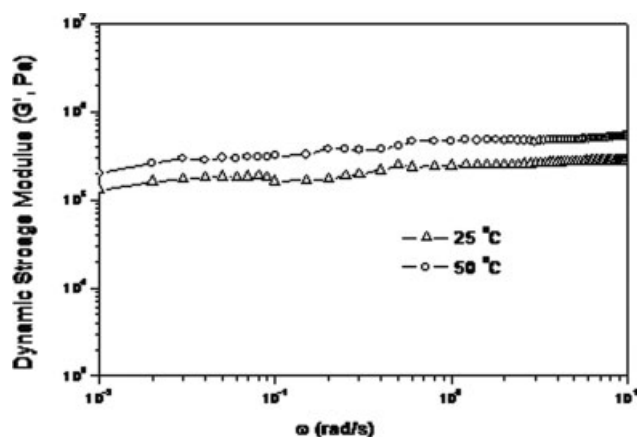


Figure 6 Dynamic mechanical properties of polymer 14.

independent of frequency and remained unchanged over the entire frequency range. The highly cross-linked structure of polymer 14 derived from a rigid 1,4-phenylene spacer between crosslinking points, which greatly restricts the chain response to frequency even at elevated temperatures (Fig. 6). At 25°C, polymer 13 exhibited similar relaxation behavior as that of polymer 12. Under elevated temperatures (50 and 80°C), no steady increase in dynamic storage modulus is found.

CONCLUSIONS

Glyceryl trioleate (2) were functionalized via triepoxidations and monoepoxidations followed hydrolytic ring opening and reduction to provide dihydroxylated, trihydroxylate, and hexahydroxylated triglycerides, which were crosslinked with PDI. The trihydroxylated triglyceride was converted to triamino and triisopropylamino glycerides separately followed by crosslinkages with PDI. Polymer 12, derived from dihydroxylated triglyceride, has the most potential in thermal and viscoelastic properties for future material development. Lower degree of crosslinking appears to provide elastic and rubbery materials and retain its original weight at high temperature ($\sim 408^\circ\text{C}$). This may result from a greater degree of self-assemblies of the unfunctionalized alkyl chains, and the viscoelastic results indicate a decrease of movements of the side chains. Similar polymers derived from soyabean oil will be prepared, and their properties will be reported in due course.

EXPERIMENTAL

Materials

Silica gel, grade 643 (200–425 mesh), was used for the flash column chromatographic separation. Tetrahydrofuran and diethyl ether were distilled over sodium and benzophenone before use. Methylene

chloride was distilled over CaH_2 and toluene and benzene were distilled over LiAlH_4 . Chemicals such as oleic acid and reagents were purchased either from Aldrich Chemical Company or Fisher Chemical Company, and were used without purification.

Instrumentation

Nuclear magnetic resonance spectra were obtained at 400 MHz for ^1H and 100 MHz for ^{13}C in deuteriochloroform, and reported in ppm. Infrared spectra are reported in wavenumbers (cm^{-1}). Mass spectra were taken from a Bruker Esquire 3000 Plus HPLC-UV-Electrospray Ionization Mass Spectrometer and a MALDI-TOF/TOF MS instrument, Ultraflex II (Bruker Daltonics) model. Melting points are uncorrected. FTIR spectra were obtained from a Nicolet Protege 460 FTIR spectrometer. KBr samples were prepared for all polymers for IR measurement.

Differential scanning calorimetry

Thermal transitions of diols, triols, hexaols, triamines, and their crosslinked polymers were determined using a DSC instrument (Perkin-Elmer Pyris 1, Norwalk, CT) measuring from -60 to 180°C at a scanning rate of $10^\circ\text{C}/\text{min}$ in an inert atmosphere of nitrogen with the nitrogen flow rate at $20 \text{ mL}/\text{min}$. All results were obtained from the second DSC run to remove any prior thermal history.

Thermogravimetric analysis

A thermal gravimetric analyzer (Perkin-Elmer Pyris1 TGA, Norwalk, CT) was used to determine the thermal degradation temperatures of the triglyceride polymers. The sample was heated from room temperature to 700°C at a ramp rate of $10^\circ\text{C}/\text{min}$ with nitrogen as the purge gas.

Dynamic mechanical analysis

A parallel-plate geometry was used to evaluate the triglyceride polymers' dynamic mechanical behavior with a dynamic mechanical analyzer (DMA, Perkin-Elmer Pysis DMA7e, Norwalk, CT). The circular sample with 10-mm diameter and 1-mm thickness was mounted between the parallel plates and subsequently was compressed by the two plates. A strain sweep was initially performed to determine the linear viscoelastic region of the samples. A dynamic frequency sweep test was carried out with a 3% strain and 0.01–50 rad/s frequency range.

Glyceryl trioleate (2)

To a solution of 10.0 g (35.4 mmol) of oleic acid (1) in 50 mL of dichloromethane under argon was

added 6.74 g (53.1 mmol) of oxalyl chloride, and the solution was stirred at 25°C for 2 h. After removal of the excess of oxalyl chloride and solvent over a rotary evaporator, the oily residue, oleoyl chloride, was dried under vacuum and used in the next operation without purification. To a solution of 1.09 g (11.8 mmol) of glycerol and 5.72 mL (70.8 mmol) of pyridine in dichloromethane (20 mL) at 0°C under argon, was added a solution of the above oleoyl chloride in 50 mL of dichloromethane via cannula. The solution was stirred at 25°C for 2 h, diluted with 50 mL of dichloromethane, washed twice with water (50 mL each) and saturated aqueous sodium chloride (50 mL) solution, dried (MgSO₄), concentrated, and column chromatographed on silica gel using hexane : ethyl acetate (20 : 1) as eluant to give 9.40 g (90.2% yield) of compound 2, as an oil.²³ ¹H-NMR δ 5.34 (m, 6 H), 5.32 (m, 1 H), 4.09–4.34 (m, 4 H), 2.031 (t, *J* = 7.3 Hz, 6 H), 2.01 (m, 12 H), 1.61 (m, 6 H), 1.19–1.42 (m, 60 H), 0.88 (t, *J* = 5.9 Hz, 9 H); ¹³C-NMR δ 173.4, 173.0, 130.2, 129.9, 69.1, 62.3, 34.4, 34.2, 32.1, 30.0, 29.9, 29.8, 29.7, 29.5, 29.45, 29.4, 29.3, 29.29, 27.4, 27.37, 25.1, 25.0, 22.9, 14.3; HRMS *m/z* 907.7893 (907.7725, calcd for C₅₇H₁₀₄O₆Na⁺, M+Na⁺).

Glyceryl tris(9,10-epoxy)trioleate (3)

To a solution of 2.4 g (2.7 mmol) of glycerol triooleate (2) in 50 mL of dichloromethane under argon, was added 3.6 g (16.3 mmol) of *m*-chloroperbenzoic acid (MCPBA) at 0°C. After stirring the reaction mixture for 4 h, 30 mL of 10% NaHCO₃ was carefully added, the organic layer was separated, washed with water twice (30 mL each), and 30 mL of brine, dried (MgSO₄), and concentrated to give 2.1 g (83% yield) of triepoxide 3 as white solids.²⁴ ¹H-NMR δ 5.26 (m, 1 H), 4.12–4.32 (m, 4 H), 2.90 (broad s, 6 H), 2.32 (m, 6 H), 1.61 (t, *J* = 7 Hz, 6 H), 1.27–1.49 (m, 72 H), 0.88 (t, *J* = 6.6 Hz, 9 H); ¹³C-NMR δ 173.2, 173.0, 68.9, 62.1, 57.2, 34.2, 34.0, 31.9, 29.5, 29.4, 29.2, 29.0, 27.8, 26.6, 24.8, 22.7, 14.1; HRMS *m/z* 955.7618 (955.7573, calcd for C₅₇H₁₀₄O₉Na⁺, M+Na⁺).

Glyceryl tris(9-hydroxy)trioleate (4)

To a cold (0 °C) solution of 0.50 g (0.53 mmol) of triepoxide 3 in 20 mL of THF, were added 0.40 g (6.4 mmol) of sodium cyanoborohydride and 0.41 mL (3.2 mmol) of BF₃ · ether. After stirring at 25°C for 8 h, the reaction solution was diluted with 15 mL of water and extracted twice with ethyl acetate (20 mL each). The organic layers were combined and washed with water twice (20 mL each), and brine, dried (MgSO₄), concentrated to give 0.50 g (100% yield) of triol 4. m.p. 70–71°C; ¹H-NMR δ 5.24 - 5.28 (m, 1 H, CHOCO), 4.31–4.13 (m, 4 H, CH₂OCO), 4.1

(bs, 3 H, OH), 3.56 (bs, 3 H, CHO), 2.31 (m, 6 H), 1.27–1.61 (m, 84 H), 0.88 (t, *J* = 6.2 Hz, 9 H); ¹³C-NMR δ 173.3, 172.9, 72.6, 69.5, 62.7, 38.2, 38.1, 34.8, 34.7, 32.5, 30.4, 30.3, 30.2, 30.1, 30.06, 30.0, 29.9, 29.8, 29.7, 29.66, 26.3, 26.26, 25.5, 23.3, 14.7; FTIR (KBr) ν 3344 (broad, OH), 2925, 2850, 1740 (sharp s, C=O), 1467, 1215 (C—O), 1102 cm⁻¹. HRMS *m/z* 962.0140 (961.8048, calcd for C₅₇H₁₁₀O₉Na, M+Na⁺).

Glyceryl tris(9,10-dihydroxy)trioleate (5)

A solution of 0.80 g (0.86 mmol) of triepoxide 3 in 70 mL of 1% HClO₄ in THF/H₂O (3 : 2) was stirred at 25°C for 12 h, diluted with 100 mL of ethyl acetate, washed twice with water (50 mL each), and brine (50 mL), and concentrated to give 0.82 g (97% yield) of compound 5. m.p. 65–66°C; ¹H-NMR δ 5.24–5.28 (m, 1 H), 4.12–4.32 (m, 4 H), 3.58 (bs, 6 H), 2.32 (t, *J* = 7.33 Hz, 6 H), 1.27–1.66 (m, 78 H), 0.88 (t, *J* = 6.23 Hz, 9 H); ¹³C-NMR δ 173.3, 172.9, 74.5, 74.46, 68.9, 62.1, 34.2, 34.0, 33.7, 33.6, 31.9, 29.7, 29.6, 29.5, 29.45, 29.3, 29.2, 29.18, 29.0, 25.7, 25.6, 24.9, 24.8, 22.7, 14.1; FTIR (KBr) ν 3400 (broad, OH), 2918, 2849, 1741 (sharp s, C=O), 1466, 1241, 1168 cm⁻¹; HRMS *m/z* 1009.824 (1009.7890, calcd for C₅₇H₁₁₀O₁₂Na, M+Na⁺).

Glyceryl triooleate 9,10-monoepoxide (6)

To a solution of 2.0 g (2.26 mmol) of glycerol triooleate (2) in 50 mL of dichloromethane under argon, was added 0.51 g (2.26 mmol) of MCPBA (77%) at 0°C. After stirring the reaction mixture for 4 h, 30 mL of 10% NaHCO₃ was added, the organic layer was separated, washed twice with water (30 mL each), and 30 mL of brine, dried (MgSO₄), concentrated, and column chromatographed on silica gel using hexane : ethyl acetate (30 : 1) as eluant to give 0.53 g (27% yield) of monoepoxide 6, as an oil. ¹H-NMR δ 5.33–5.36 (m, 4 H), 5.25–5.28 (m, 1 H), 4.12–4.32 (m, 4 H), 2.90 (m, 2 H), 2.31 (m, 6 H), 1.99–2.03 (m, 8 H), 1.21–1.62 (m, 70 H), 0.83–0.90 (m, 9 H); ¹³C-NMR δ 173.3, 172.8, 130.0, 129.7, 68.9, 62.1, 57.2, 57.15, 34.2, 34.0, 31.9, 31.87, 29.8, 29.7, 29.5, 29.3, 29.2, 29.1, 29.0, 27.9, 27.2, 27.19, 26.6, 24.9, 24.8, 22.7, 14.1; HRMS *m/z* 923.7783 (923.7674, calcd for C₅₇H₁₀₄O₇Na⁺, M+Na⁺).

Glyceryl 9,10-dihydroxytrioleate (7)

To a solution of 20 mL of 1% HClO₄ in THF/H₂O (3 : 2), was added 1.0 g (1.11 mmol) of epoxide 6. After stirring for 12 h, the reaction solution was diluted with 50 mL of ethyl acetate, washed twice with water (30 mL each), and 30 mL of brine, and concentrated to give 0.98 g (96% yield) of diol 7. ¹H-NMR δ 5.32–5.37 (m, 4 H), 5.20–5.30 (m, 1 H),

4.10–4.34 (m, 4 H), 3.37–3.43 (m, 2 H), 2.32 (t, $J = 5.9$ Hz, 6 H), 1.96–2.26 (m, 8 H), 1.27–1.68 (m, 70 H), 0.88 (t, $J = 6.7$ Hz, 9 H); $^{13}\text{C-NMR}$ δ 173.4, 173.0, 130.2, 129.9, 74.7, 69.2, 62.3, 34.4, 34.2, 33.9, 33.87, 32.1, 32.07, 30.0, 29.9, 29.8, 29.7, 29.65, 29.5, 29.49, 29.45, 29.4, 29.3, 29.1, 27.4, 27.38, 25.9, 25.8, 25.1, 25.0, 22.9, 14.2; FTIR (KBr) ν 3466 (broad, OH), 2925, 2854, 1745 (sharp s, C=O of ester), 1464, 1164 (C–O) cm^{-1} ; HRMS m/z 941.7580 (941.7780, calcd for $\text{C}_{57}\text{H}_{106}\text{O}_8\text{Na}^+$, $\text{M}+\text{Na}^+$).

Glyceryl tris(9-bromo)trioleate (8)

To a cold (0°C) solution of 0.58 g (0.62 mmol) of triol **4** and 0.98 g (3.7 mmol) of triphenylphosphine in 40 mL of dichloromethane under argon, was added 1.24 g (3.71 mmol) of carbon tetrabromide. After stirring at 0°C for 2 h, the mixture was concentrated and column chromatographed on silica gel using hexane : ethyl ether (4:1) as eluant to give 0.46 g (65% yield) of compound **8**. $^1\text{H-NMR}$ δ 5.24 (m, 1 H), 4.12–4.32 (m, 4 H), 4.02 (m, 3 H), 2.32 (t, $J = 7.7$ Hz, 6 H), 1.77–1.84 (m, 12 H), 1.27–1.64 (m, 72 H), 0.88 (t, $J = 6.6$ Hz, 9 H); $^{13}\text{C-NMR}$ δ 173.4, 173.39, 173.0, 69.2, 62.3, 59.1, 59.05, 39.5, 39.4, 39.37, 34.4, 34.39, 34.2, 32.1, 32.07, 29.8, 29.7, 29.68, 29.5, 29.45, 29.4, 29.38, 29.35, 29.33, 29.3, 29.2, 29.2, 29.12, 29.1, 27.8, 27.78, 27.75, 25.1, 25.0, 22.9, 22.87, 14.3; HRMS m/z 907.8130 (907.7725, calcd for $\text{C}_{57}\text{H}_{107}\text{Br}_3\text{O}_6\text{Na-3HBr}^+$).

Glyceryl tris(9-azido)trioleate (9)

A solution of 0.12 g (0.11 mmol) of tribromide **8** and 42 mg (0.66 mmol) of sodium azide in 15 mL of DMF was heated to reflux for 4 h, diluted with 15 mL of water, and extracted twice with ethyl acetate (30 mL each). The combined organic layer was washed with water, brine, dried (MgSO_4), concentrated, and column chromatographed on silica gel using hexane : ethyl ether (4 : 1) as eluant to give 77 mg (71% yield) of compound **9**. $^1\text{H-NMR}$ δ 5.24 (m, 1 H), 4.10–4.32 (m, 4 H), 3.19 (m, 3 H), 2.29 (t, $J = 7.3$ Hz, 6 H), 1.27–1.64 (m, 84 H), 0.88 (t, $J = 6.6$ Hz, 9 H); $^{13}\text{C-NMR}$ δ 173.3, 172.9, 69.1, 63.3, 62.3, 34.6, 34.3, 34.2, 32.04, 32.01, 29.7, 29.6, 29.55, 29.5, 29.45, 29.41, 29.4, 29.3, 29.2, 29.15, 26.3, 25.0, 22.8, 14.2; IR (neat) ν 1743.74 (C=O), 2096.73 (N_3); HRMS m/z 1036.8147 (1036.8242, calcd. for $\text{C}_{57}\text{H}_{107}\text{N}_9\text{O}_6\text{Na}^+$).

Glyceryl tris(9-amino)trioleate (10)

To a solution of 0.44 g (0.43 mmol) of azide **9** in 3 mL of benzene under argon, was added 40 mg of 10% Pd/C. The mixture was maintained under 30 psi atmosphere of hydrogen on a hydrogenator for 12 h, filtered, and the filtrate was concentrated to

give 0.39 g (100% yield) of compound **10**. FTIR (KBr) ν 3392 (broad, NH), 2924, 2853, 1743 (s, C=O), 1471, 1163 cm^{-1} ; $^1\text{H-NMR}$ δ 5.27 (m, 1 H), 4.10–4.34 (m, 4 H), 2.67 (m, 3 H), 2.31 (t, $J = 7.3$ Hz, 6 H), 1.20–1.70 (m, 84 H), 0.88 (t, $J = 6.4$ Hz, 9 H); $^{13}\text{C-NMR}$ δ 173.4, 173.0, 69.0, 62.3, 51.4, 38.4, 34.4, 34.2, 32.1, 30.0, 29.9, 29.8, 29.6, 29.5, 29.3, 26.4, 25.0, 22.8, 14.3; HRMS m/z 958.8931 (958.8527, calcd for $\text{C}_{57}\text{H}_{113}\text{N}_3\text{O}_6\text{Na}^+$).

Glyceryl tris[9-(N-isopropylamino)]trioleate (11)

To a solution of 0.31 g (0.31 mmol) of azide **9** in 5 mL of acetone under argon, was added 15 mg of 10% Pd/C. The mixture was maintained under 30 psi atmosphere of hydrogen for 12 h at 25°C , filtered, and the filtrate was concentrated to give 0.33 g (100% yield) of compound **11**. FTIR (KBr) ν 3350 (broad, NH), 2926, 2854, 1746 (sharp s, C=O), 1464, 1378, 1167 cm^{-1} ; $^1\text{H-NMR}$ δ 5.24 (m, 1 H), 4.10–4.32 (m, 4 H), 3.19 (m, 3 H), 2.88 (m, 3 H), 2.31 (t, $J = 7.7$ Hz, 6 H), 1.27–1.64 (m, 84 H), 0.96 (d, $J = 14.6$ Hz, 18 H), 0.88 (t, $J = 6.6$ Hz, 9 H); $^{13}\text{C-NMR}$ δ 173.5, 173.1, 69.1, 62.3, 54.7, 45.9, 34.9, 34.3, 32.1, 30.2, 30.1, 29.9, 29.85, 29.6, 29.3, 26.0, 25.1, 23.8, 22.9, 14.3. HRMS m/z 1084.9760 (1084.9936, calcd for $\text{C}_{66}\text{H}_{131}\text{N}_3\text{O}_6\text{Na}^+$).

Crosslinked polymer 12

To a solution of 0.90 g (1.01 mmol) of diol **7** and 0.16 g (1.01 mmol) of 1,4-phenylene diisocyanate (PDI) in 15 mL of toluene under argon, was added 15 mg of pyridine. After stirring at 80°C for 12 h, the reaction solution was filtered. The solid was immersed in 20 mL of dichloromethane and the mixture was allowed to sit for 12 h. The insoluble material was filtered and dried under vacuum to give 0.68 g (64% yield) of crosslinked polymer **12** as a rubbery solid. The gel content of polymer **12** was measured (*vide infra*). Polymer **12** is insoluble in most organic and inorganic solvents. FTIR (KBr) ν 3319 (broad, NH), 3004 (Ar C–H), 2925, 2854, 1738 (broad s, C=O), 1605 (Ar C=C), 1549, 1514, 1377, 1210 cm^{-1} .

Crosslinked polymer 13

A solution of 0.30 g (0.32 mmol) of triol **4**, 79 mg (0.49 mmol) of PDI and 15 mg of pyridine in 15 mL of toluene was heated to reflux for 4 h. The solvent and pyridine was removed by filtration. The solid was immersed in 10 mL of dichloromethane for 12 h and filtered. The insoluble material was filtered and dried under vacuum to give 0.31 g (83% yield) of polymer **13**, which is insoluble in most organic and inorganic solvents. The gel content of polymer **13** was measured (*vide infra*). FTIR (KBr) ν 3330 (broad, NH), 3005 (Ar C–H), 2923, 2853, 1744 (broad s,

C=O of ester and carbamate), 1608 (Ar C=C), 1520, 1466, 1408, 1310, 1214 (C—O) cm^{-1} .

Crosslinked polymer 14

A solution of 0.35 g (0.36 mmol) of hexaol **5**, 0.17 g (1.06 mmol) of PDI, and 15 mg of pyridine in 15 mL of toluene was heated to reflux for 4 h. The solvent and pyridine were removed by filtration, and the resulting solid was immersed in 10 mL of dichloromethane and allowed to sit for 12 h. The insoluble material was collected by filtration and dried under vacuum to give 0.49 g (95% yield) of polymer **14**, as a brown solid. Polymer **14** is insoluble in most organic and inorganic solvents and the gel content is measured (*vide infra*). FTIR (KBr) ν 3367 (broad, NH), 3004 (Ar C—H), 2925, 2853, 1736 (broad s, C=O of ester and carbamate), 1608 (Ar C=C), 1513, 1409, 1309, 1214 cm^{-1} .

Crosslinked polymer 15

A solution of 0.15 mg (0.16 mmol) of triamine **10** and 40 mg (0.24 mmol) of PDI in 10 mL of toluene was heated to reflux for 4 h. After cooling to 25°C, the reaction mixture was filtered, and the solid was immersed in 10 mL of dichloromethane for 12 h. The insoluble solid was collected by filtration and dried under vacuum to give 0.17 mg (90% yield) of polymer **15** as a brown solid. FTIR (KBr) ν 3430 (broad, NH), 3020 (w, =CH Ar), 2925, 2853, 1747 (s, C=O ester), 1645 (s, C=O urea), 1604 (C—C Ar), 1509, 1401, 1301, 1228, 1170 cm^{-1} .

Crosslinked polymer 16

A solution of 0.32 g (0.34 mmol) of trisisopropylamine **11** and 82 mg (0.51 mmol) of PDI in 15 mL of toluene was heated to reflux for 4 h. The solvent was removed by filtration, and the solid was immersed in 10 mL of dichloromethane for 12 h. The insoluble solid was collected by filtration and dried under vacuum to give 0.35 g (86% yield) of polymer **16** as a brown solid. FTIR (KBr) ν 3429 (broad s, NH), 2926, 2853, 1746 (s, C—O ester), 1636 (s, C=O urea), 1514, 1465, 1330, 1224, 1149 cm^{-1} .

Measurement of gel content

Following the reported procedure,^{25,26} polymer (0.2 g) and 10 mL of chloroform were refluxed for 3 h. The

mixture was filtered, weights of the insoluble solid (gel fraction) and soluble polymer fraction (obtained by removing chloroform under vacuum) were measured, and gel content was calculated by dividing gel fraction with the initial polymer weight. Results are summarized in Table I.

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