Reprocessable and Recyclable Chain-Growth Polymer Networks
Based on Dynamic Hindered Urea Bonds

Mohammed A. Bin Rusayyis\textsuperscript{a}, and John M. Torkelson\textsuperscript{*,a,b}

\textsuperscript{a} Dept. of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA
\textsuperscript{b} Dept. of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, USA
\textsuperscript{*}Corresponding author. Email address: j-torkelson@northwestern.edu

Supporting Information

Table of Contents

1. Materials and Synthetic Procedures
2. Characterization and Molding Methods
3. Cross-linker Characterization Figures
4. Network Characterization and Molding Figures
5. References
1. Materials and Synthetic Procedures

Materials

All chemicals are commercially available and used as received unless otherwise noted. 2-Isocyanatoethyl methacrylate and \(N,N'-\)di-\(\text{tert-}\)butylethylenediamine were purchased from TCI America. Dichloromethane (DCM, Certified ACS) and methanol (99.9%) were supplied by Fisher. \(n\)-Hexyl methacrylate (HMA, 98%), azobisisobutyronitrile (AIBN, 98%), \(N,N'\)-dimethylacetamide (DMAc, anhydrous, 99.8%), toluene (99.9%) and chloroform-\(d\) (99.8 atom% D) were from Sigma-Aldrich. V-70 initiator was obtained from FUJIFILM Wako Chemicals. Hexyl methacrylate (HMA) monomer was de-inhibited using inhibitor remover (Sigma Aldrich, 311340) in the presence of calcium hydride (Sigma Aldrich, 90%). AIBN was recrystallized from methanol. DCM used in the synthesis of the cross-linker and DMAc were dried over 4Å molecular sieves for at least 48 h before use.

Synthesis of 5,8-di-\(\text{tert-}\)butyl-4,9-dioxo-3,5,8,10-tetraazadodecane-1,12-diyl bis(2-methylacrylate), (HUB Cross-linker)

2-Isocyanatoethyl methacrylate (2.01 g, 12.94 mmol) and pre-dried DCM (6 mL) were mixed in a 20-mL glass vial at room temperature. A solution of \(N,N'\)-di-\(\text{tert-}\)butylethylenediamine (1.12 g, 6.49 mmol) and pre-dried DCM (2 mL) was slowly added to the vial and the mixture was stirred at room temperature for 30 min. The solvent (DCM) was then removed to obtain the cross-linker as a white solid (3.05 g) (yield: 98%; melting point: 93 \(^\circ\)C). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.24 (t, \(J = 5.3\) Hz, 2H), 6.13 (s, 2H), 5.56 (s, 2H), 4.26 (t, \(J = 5.5\) Hz, 4H), 3.53 (q, \(J = 5.4\) Hz, 4H), 3.26 (s, 4H), 1.94 (s, 6H), 1.41 (s, 18H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 167.5, 159.3, 136.3, 125.6, 64.1, 54.8, 46.2, 40.0, 29.9, 18.3.

Synthesis of network

Reprocessable polymer networks containing dynamic hindered urea bonds were synthesized via free radical polymerization by reacting \(n\)-hexyl methacrylate with HUB Cross-linker, and V-70
initiator. In a typical synthesis, HUB Cross-linker (761.9 mg, 1.58 mmol) was dissolved in hexyl methacrylate (5.05 g, 29.66 mmol) in a 20-mL glass vial using DMAc (3.0 mL) as a solvent. The solution was stirred at room temperature until the cross-linker was completely dissolved after which V-70 initiator (95.0 mg, 0.31 mmol) was added and stirred to dissolve the initiator. The solution was then bubbled with nitrogen (N$_2$) gas at room temperature for 20 min, and then N$_2$ gas was allowed to continuously flow into the vial. The polymerization was proceeded at room temperature for 24 h after which it was quenched by exposing it to air. The obtained network was cut into small pieces, washed with DCM/methanol mixtures, and then dried in a vacuum oven at 50 °C for at least 24 h. Networks synthesized using AIBN were made in a similar way with the polymerization done at 70 °C.

2. Characterization and Molding Methods

NMR spectroscopy
$^1$H- and $^{13}$C-NMR spectroscopy were performed at room temperature using a Bruker Avance III 500 MHz NMR spectrometer. Deuterated chloroform (CDCl$_3$) was used as solvent, and the spectra were reported relative to tetramethysilane.

Fourier transform infrared (FTIR) spectroscopy
Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Bruker Tensor 37 FTIR spectrophotometer equipped with a diamond/ZnSe attachment. Sixteen scans were collected at room temperature over the 4000 to 600 cm$^{-1}$ range at 4 cm$^{-1}$ resolution.

Differential scanning calorimetry (DSC)
The melting temperature ($T_m$) of the synthesized cross-linker and the glass transition temperatures ($T_g$) of as-synthesized and molded networks were obtained by DSC using a Mettler Toledo DSC822e. The peak $T_m$ value of the cross-linker was determined from the endothermic peak of the first heating cycle (heating rate 10 °C min$^{-1}$). To determine the $T_g$s of the networks, network samples were annealed at −50 °C for 5 min followed by heating to 80 °C at a heating rate of 10 °C
min\(^{-1}\). The samples were then cooled again to \(-50\) °C (cooling rate \(-10\) °C min\(^{-1}\)) and then heated to \(80\) °C at a heating rate of \(10\) °C min\(^{-1}\). \(T_g\) values were obtained from the heating ramp of the second heating cycle using the \(1/2 \Delta C_p\) method.

**Swelling**

Swelling tests were performed by placing network samples in a 20-mL glass vial filled with toluene. The samples were allowed to swell for at least \(72\) h to reach equilibrium. Swollen samples were dried in a vacuum oven for at least \(48\) h to obtain gel fractions.

**Molding and reprocessing of networks**

(Re)processing of dried, as-synthesized networks was done by hot pressing small network pieces into \(\sim 1\) mm-thick sheets using a PHI press (Model 0230C-X1). Unless otherwise noted, the materials were (re)processed at \(80\) °C with a pressure of \(16\) MPa for \(1\) h.

**Dynamic mechanical analysis (DMA)**

DMA was performed using a TA Instruments RSA-G2 Solids Analyzer to characterize the thermo-mechanical performance of the network samples and evaluate recovery of cross-link density after each recycling step. In DMA experiments, tensile storage modulus (\(E'\)), tensile loss modulus (\(E''\)), and the damping ratio (\(\tan \delta = E''/E'\)) of the network samples were measured as functions of temperature under nitrogen atmosphere. The network rectangular specimens were heated from \(-55\) °C to \(150\) °C (or \(300\) °C) at a heating rate of \(3\) °C min\(^{-1}\). The tension-mode measurements were collected at a frequency of \(1\) Hz and \(0.03\)% oscillatory strain. Three measurements were performed for each sample, and the \(E'\) value at \(120\) °C was reported as the average rubbery plateau modulus with errors given by two standard deviations (Table 1).

**Stress relaxation**

Uniaxial stress relaxation measurements were performed on rectangular samples of the 1st mold network using a TA Instruments RSA-G2 Solids Analyzer. Samples were first annealed at the desired temperature for 10 min before a constant \(5\)% tensile strain was applied. The stress relaxation modulus was recorded until it had relaxed to \(20\)% of its initial value. Stress
relaxation data were fitted to the following Kohlrausch-Williams-Watts (KWW) stretched exponential decay function:\(^1\)

\[
\frac{E(t)}{E_0} = \exp \left[ -\left( \frac{t}{\tau^*} \right)^\beta \right]
\]

(1)

where \(E(t)/E_0\) is the normalized relaxation modulus at time \(t\), \(\tau^*\) is the characteristic relaxation time, and \(\beta\) (0 < \(\beta\) ≤ 1) is the stretching exponent that serves as a shape parameter characterizing the breadth of the relaxation distribution. The average relaxation time, \(<\tau>\), is given by\(^1\)

\[
<\tau> = \frac{\tau^* \Gamma(1/\beta)}{\beta}
\]

(2)

where \(\Gamma\) represents the gamma function.

3. Cross-linker Characterization Figures

\begin{figure}
\centering
\includegraphics[width=\textwidth]{HUB_Cross-linker.png}
\caption{\(^1\)H NMR spectrum of HUB Cross-linker.}
\end{figure}
Figure S2. $^{13}$C NMR spectrum of HUB Cross-linker.

Figure S3. FTIR Spectrum of HUB Cross-linker.
Figure S4. DSC thermogram of HUB Cross-linker.

Figure S5. Solubility of HUB Cross-linker in HMA (a) before and (b) after adding DMAc.
4. Network Characterization and Molding Figures

Figure S6. Heat flow curves of as-synthesized and molded network samples.

Figure S7. Stacked FTIR spectra of as-synthesized (original), 1st mold, 2nd mold, and 3rd mold HUB-based polymethacrylate network samples.
Figure S8. Pictures of 1st mold HUB-based polymethacrylate network samples (synthesized at room temperature using V-70 initiator). (a) Molded at 80 °C for 1 h; (b) molded at for 60 °C for 1 h; (c) molded at 40 °C for 1 h; (d) molded at 40 °C for 24 h; (e) molded at room temperature for 24 h.

Figure S9. High-temperature DMA response of 2nd mold and 3rd mold network samples.
Figure S10. Pictures of 1st mold HUB-based polymethacrylate network samples (synthesized at 70 °C using AIBN initiator). Samples were molded at 80 °C for (a) 30 min or (b) 60 min.

Figure S11. DMA curves of 1st mold HUB-based polymethacrylate network samples synthesized at 70 °C using AIBN and molded at 80 °C for 30 min or 1 h.

5. References