Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPLEMENTARY INFORMATION

A composition-controlled cross-linking resin network through rapid visible-light photo-copolymerization

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Contents:

1. Chemical structure of monomers and initiators

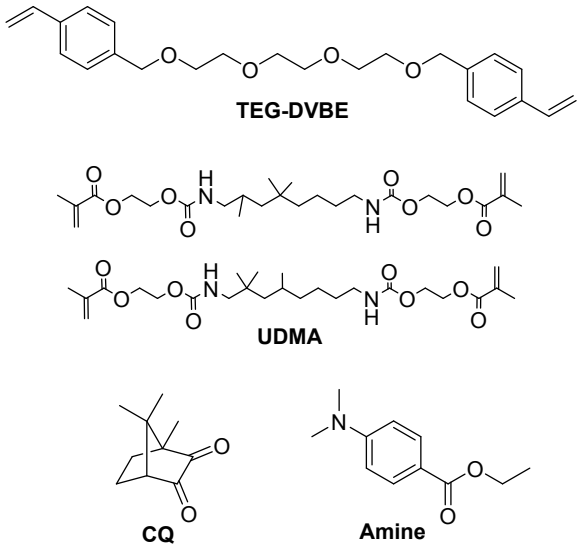

Figure S1. Chemical structure of monomers and initiators used in this paper.

2. Additional figures for real-time Raman micro-spectroscopy

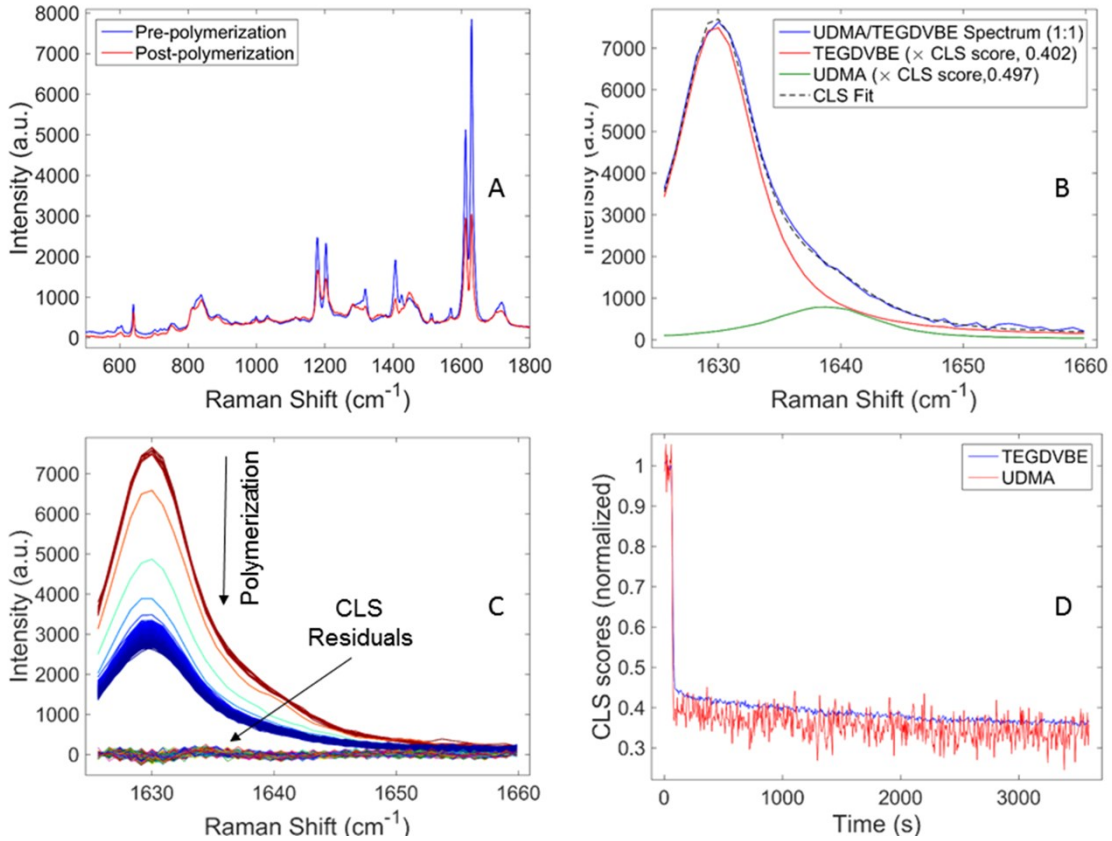

Figure S2. Example of CLS analysis of Raman spectra for estimating DC for the polymerization of a 1:1 TEG-DVBE/UDMA sample. Panel A shows Raman spectra of the 1:1 TEG-DVBE/UDMA monomer blend and copolymer. Panel B shows an example of the pure spectra fit using CLS to a sample Raman spectrum. Panel C shows Raman spectra, truncated to the spectral region used for CLS fitting, for a complete polymerization data together with the fit residuals. Panel D shows the corresponding normalized CLS score profiles for data set as a function of time.

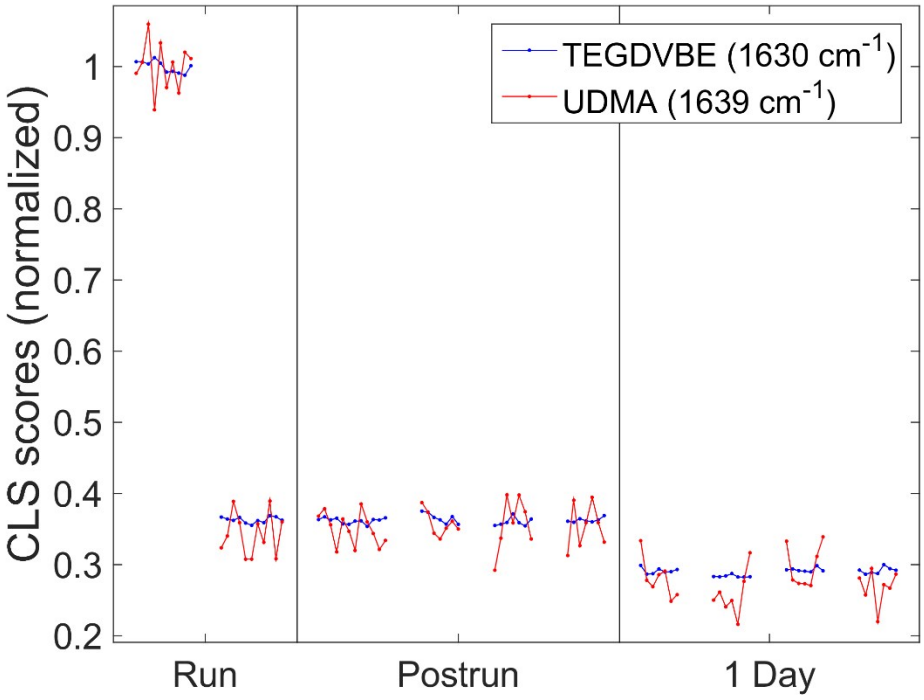

Figure S3. Additional CLS scores for the 1:1 TEG-DVBE/UDMA sample data presented in Figure 3B. The "Run" data correspond to specta collected prior to and 60 min after polymer photo-initiation. The "Postrun" data correspond to Raman spectra collected immediately following the 60 min continuous acquisition following photo-initiation. The spectra were acquired from 4 different locations (corresponding to the 4 line segments in the graph) within the reaction chamber to verify that the degree of conversion was consistent throughout the sample. The "1 Day" data were collected similarly approximately 24 hours after polymerization was initiated.

3. NMR spectra of monomer mixtures.

The mole ratio of monomers was determined by integrating the vinyl peak of TEG-DVBE at 6.71 ppm and the C=C double bond at 6.13 ppm.

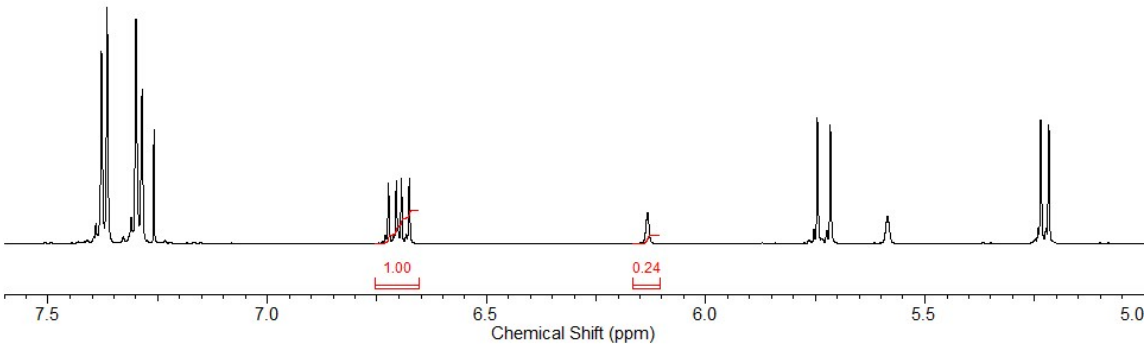

Figure S4. ^{1}H NMR spectrum of the mixture of UDMA and TEG-DVBE in 1:4 ratio in $CDCl_3$ at 298 K.

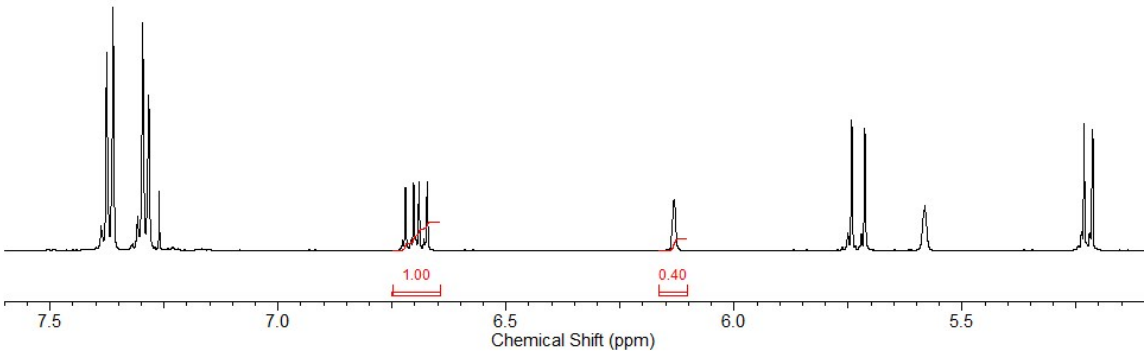

Figure S5. ^{1}H NMR spectrum of the mixture of UDMA and TEG-DVBE in 1:2.5 ratio in $CDCl_3$ at 298 K.

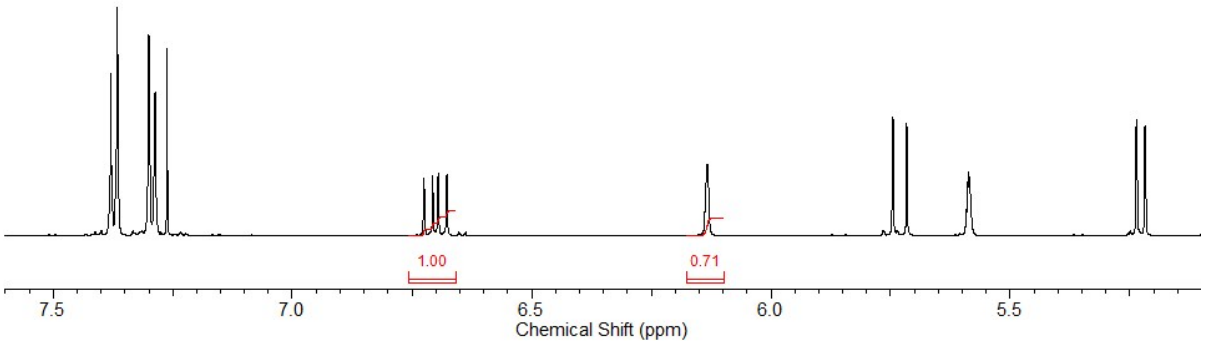

Figure S6. ^{1}H NMR spectrum of the mixture of UDMA and TEG-DVBE in 2:3 ratio in $CDCl_3$ at 298 K.

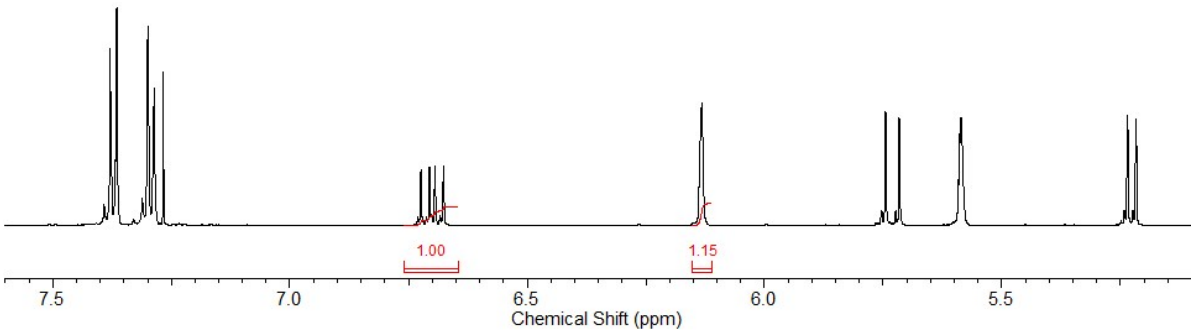

Figure S7. ^{1}H NMR spectrum of the mixture of UDMA and TEG-DVBE in 1:1.1 ratio in $CDCl_3$ at 298 K.

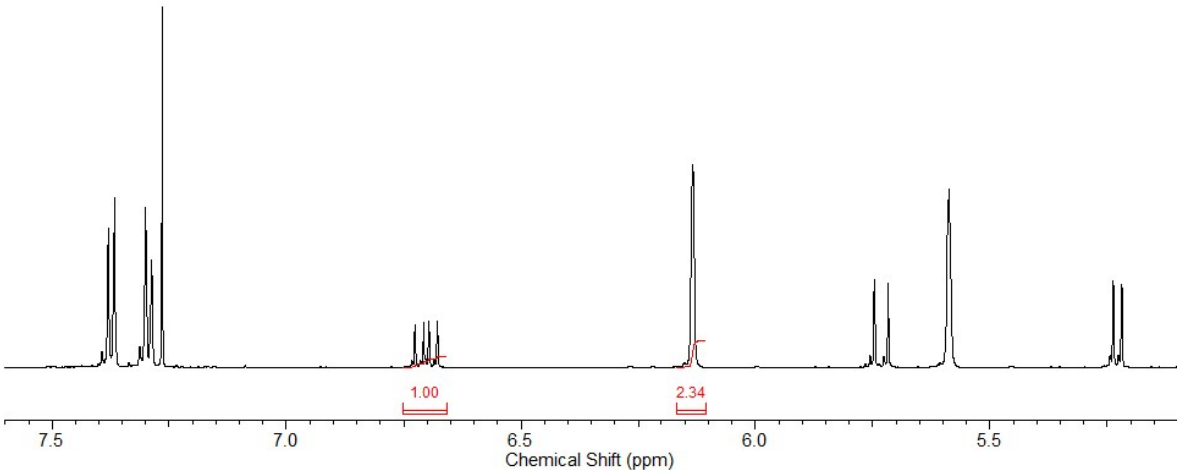

Figure S8. ^{1}H NMR spectrum of the mixture of UDMA and TEG-DVBE in 2.3:1 ratio in $CDCl_3$ at 298 K.

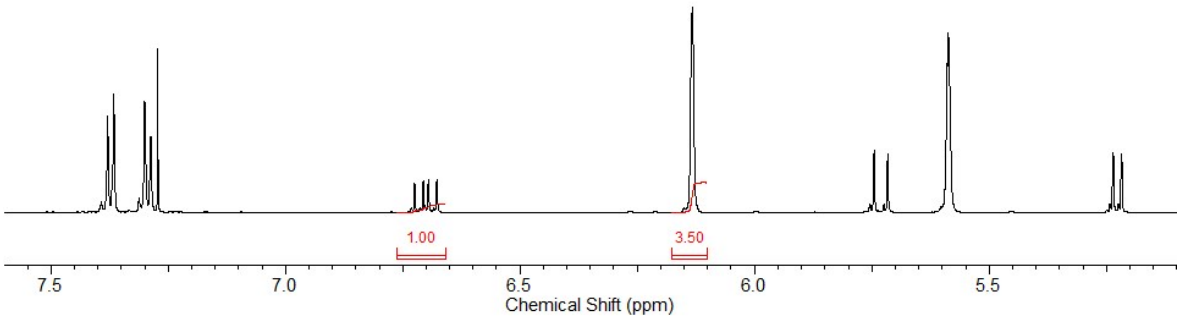

Figure S9. ^{1}H NMR spectrum of the mixture of UDMA and TEG-DVBE in 3.5:1 ratio in $CDCl_3$ at 298 K.

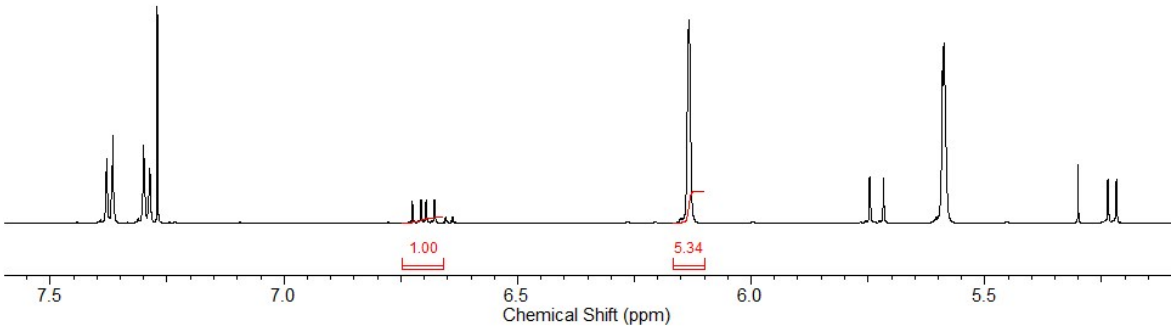

Figure S10. ^{1}H NMR spectrum of the mixture of UDMA and TEG-DVBE in 5.3:1 ratio in $CDCl_3$ at 298 K.

4. FTIR spectra of monomer mixtures before and after polymerization.

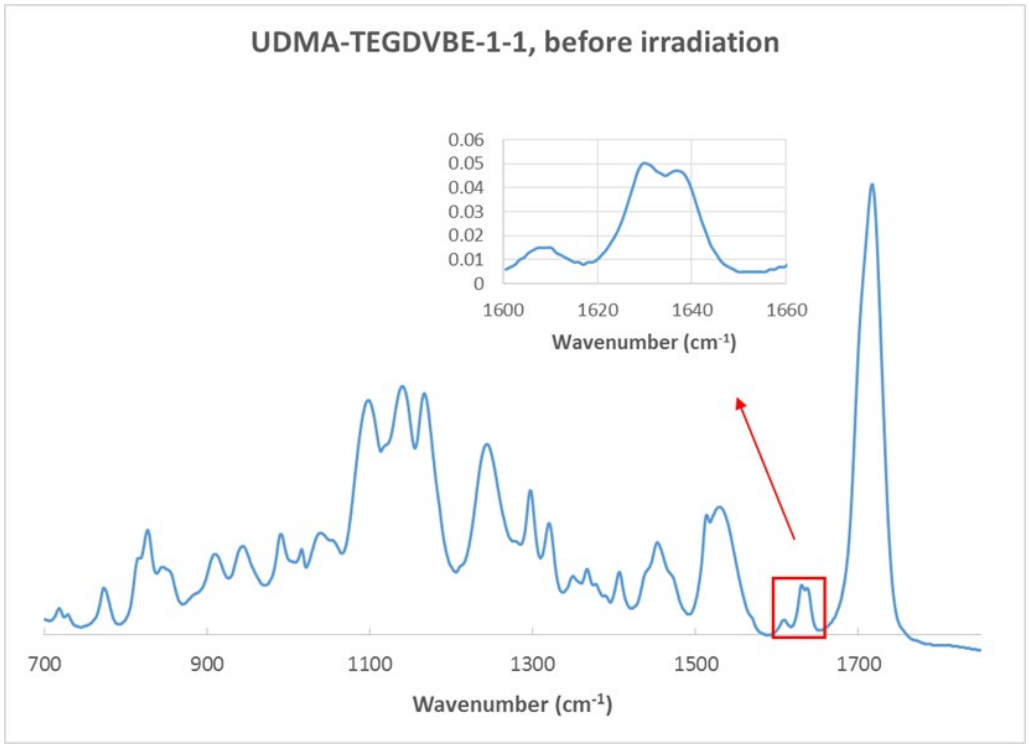

Figure S11. FTIR spectra of the mixture of UDMA and TEG-DVBE in 1:1 ratio before irradiation.

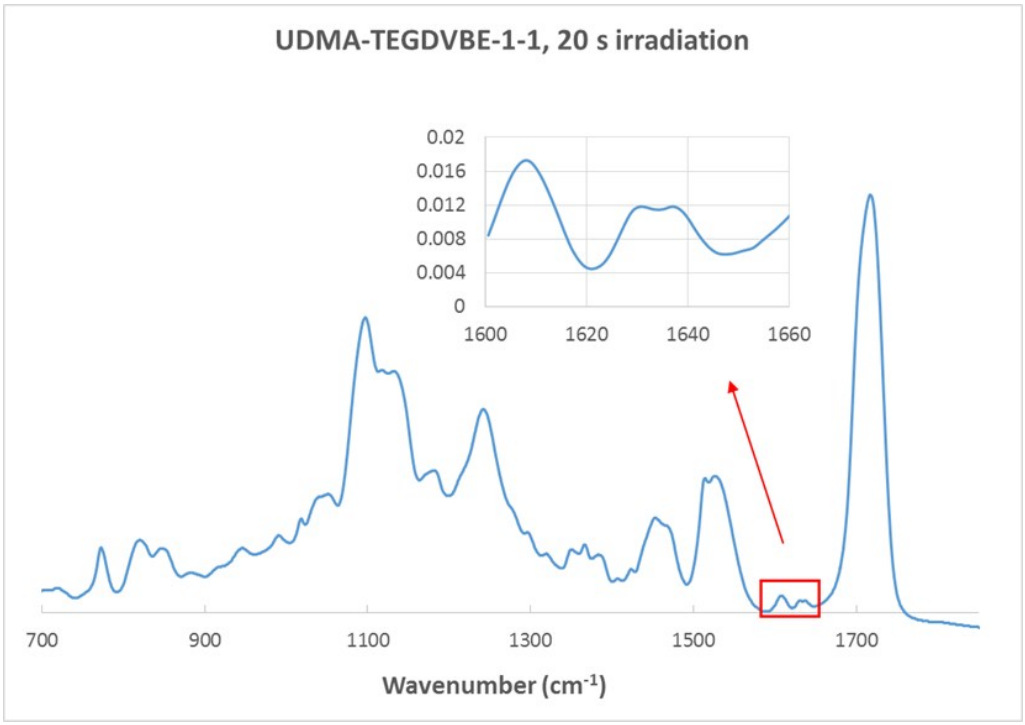

Figure S12. FTIR spectra of the mixture of UDMA and TEG-DVBE in 1:1 ratio collected right after 20 s irradiation.

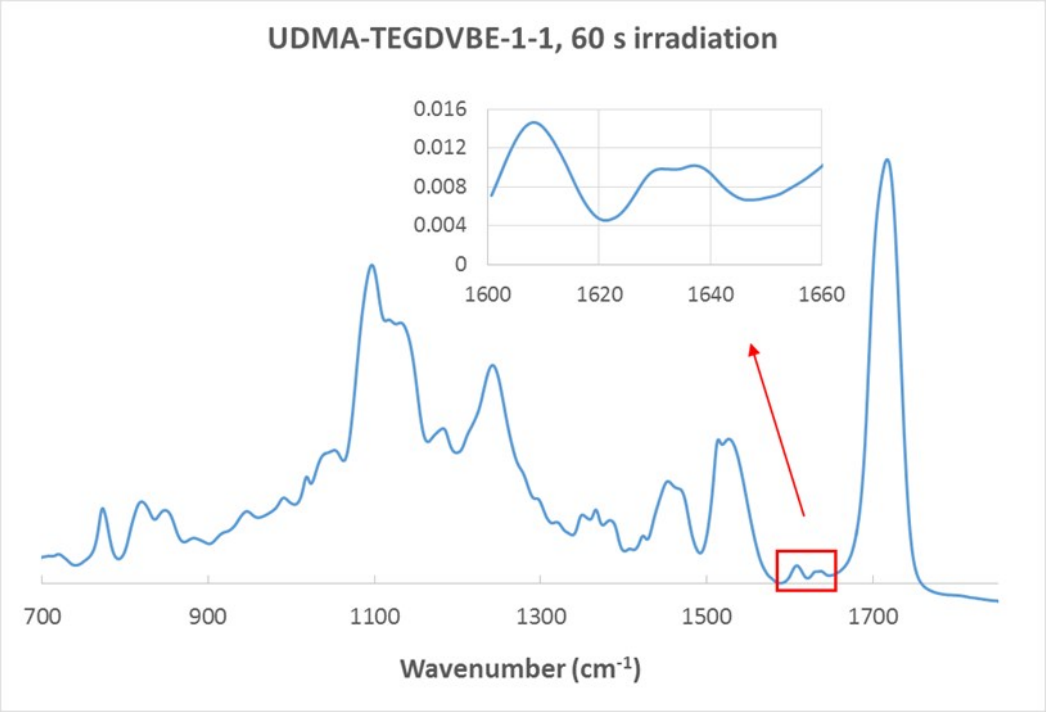

Figure S13. FTIR spectra of the mixture of UDMA and TEG-DVBE in 1:1 ratio collected right after 40 s irradiation.

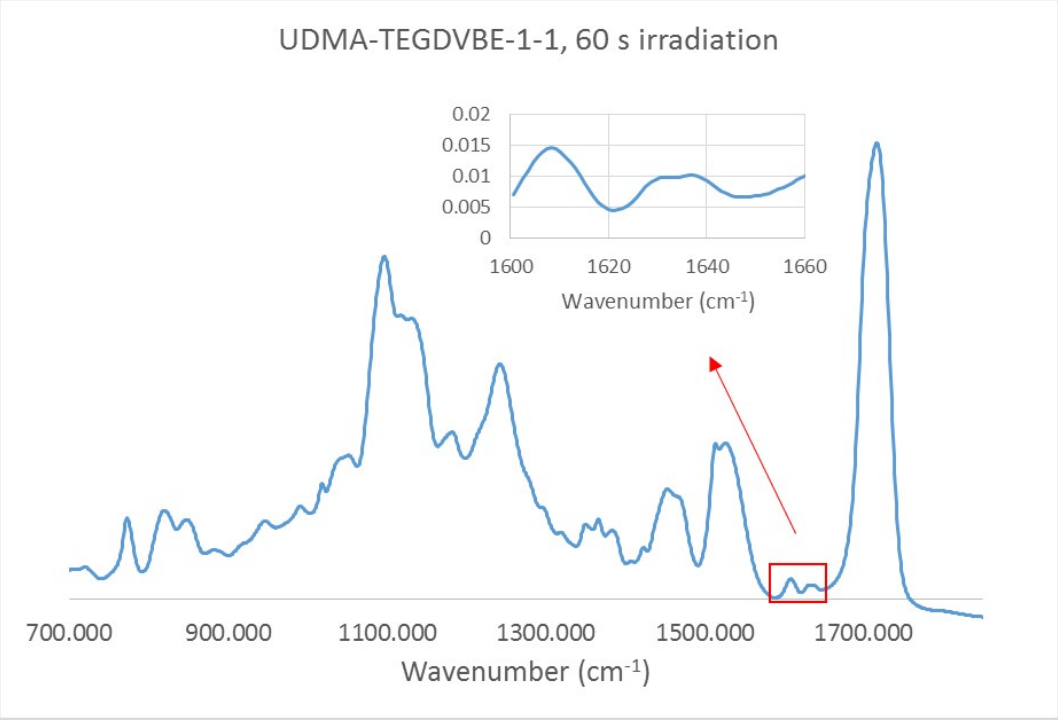

Figure S14. FTIR spectra of the mixture of UDMA and TEG-DVBE in 1:1 ratio collected right after 60 s irradiation.