Supporting Information

# The renewable feedstock levoglucosenone as a building block for the development of bio-derived, functional acrylic polymers

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**Section S1: NMR data for LGO-OH**

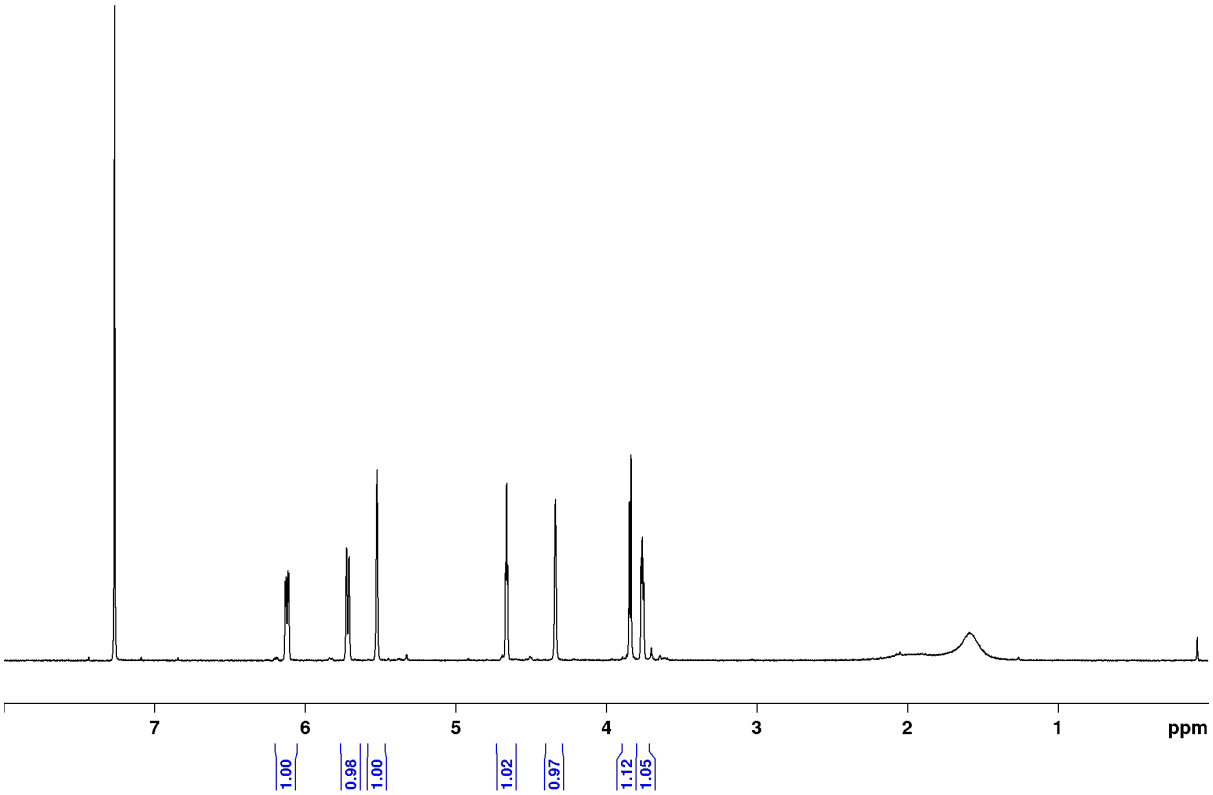



**Figure S1.** $^{1}$H NMR of LGO-OH ($CDCl_3$, 600 MHz).

**Section S2: NMR data for LGOA monomer**

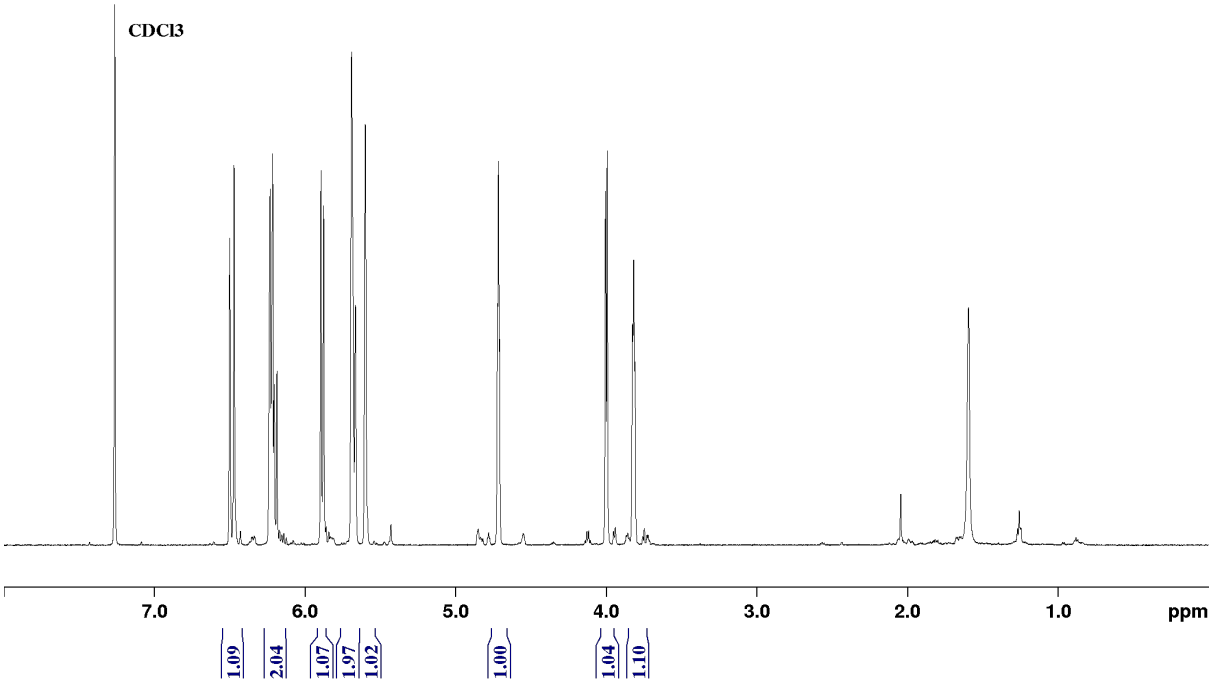



**Figure S2.** $^{1}H$ NMR of LGOA ($CDCl_3$, 600 MHz).

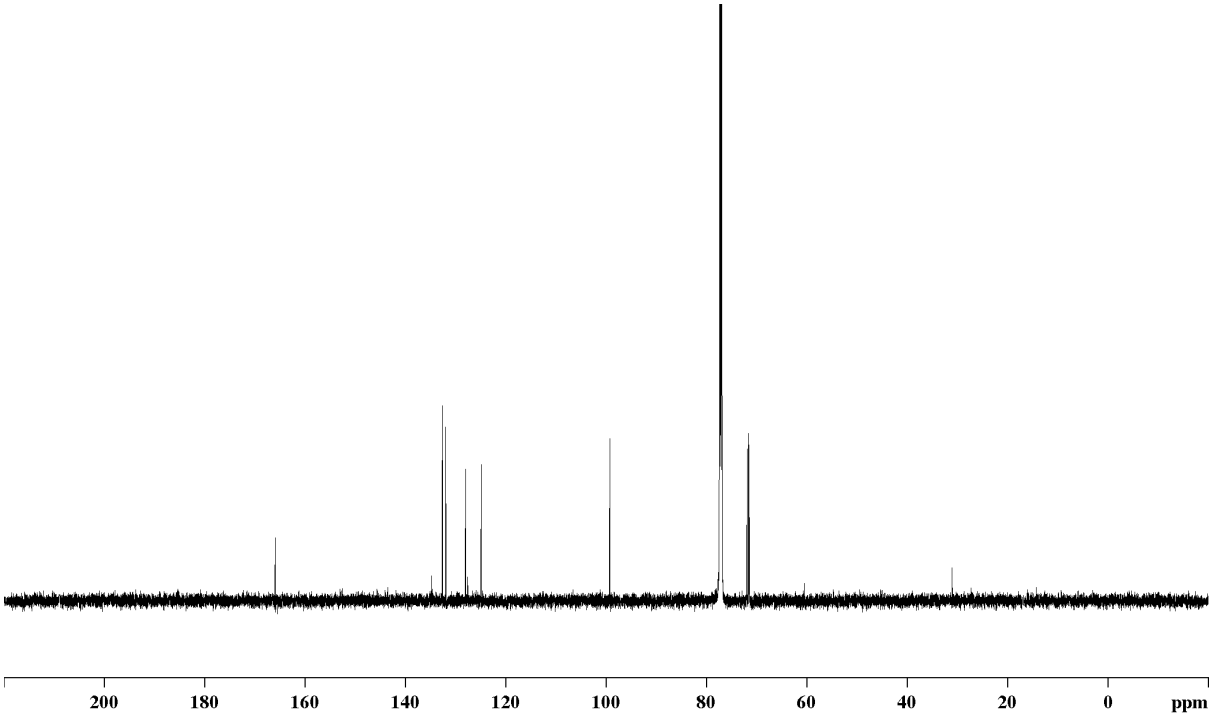



**Figure S3.** $^{13}C$ NMR of LGOA ($CDCl_3$, 150 MHz).

**COSY: LGO-acrylate**

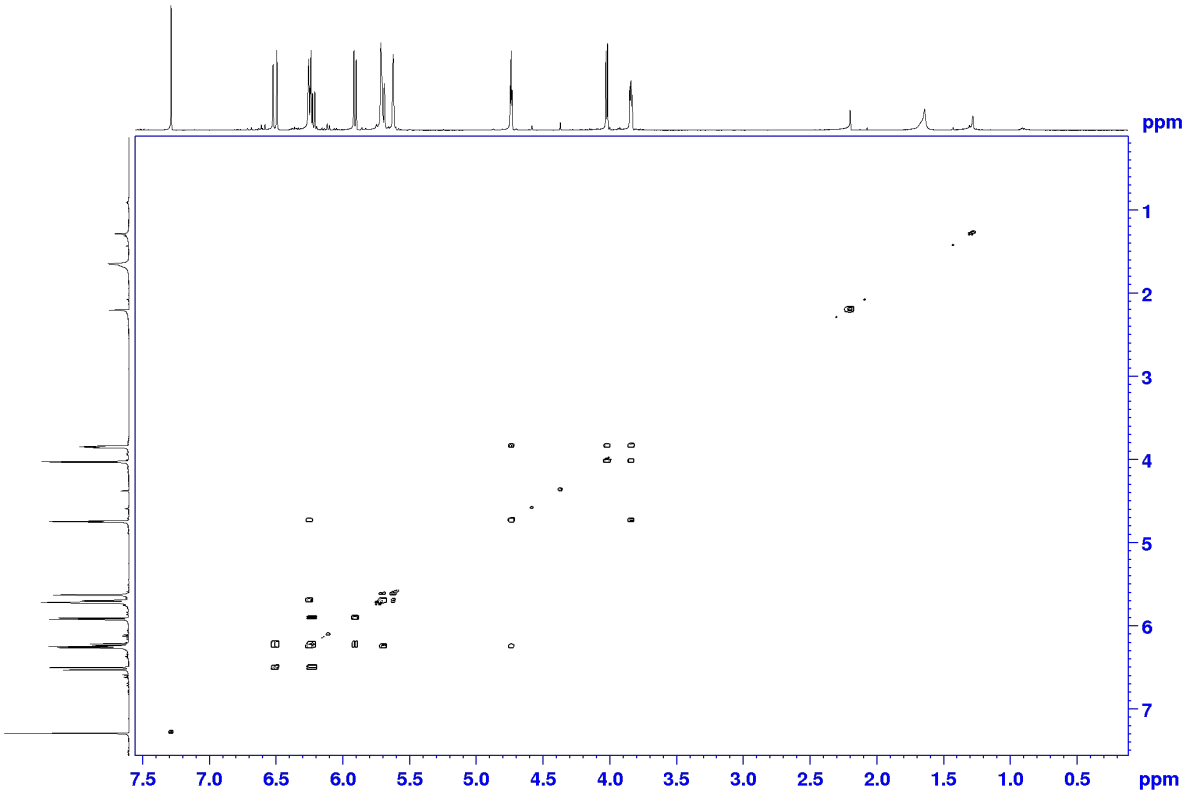



**Figure S4.** 2D COSY of LGOA ($CDCl_3$, 600 MHz).

**Section S3: NMR data for poly(LGOA)**

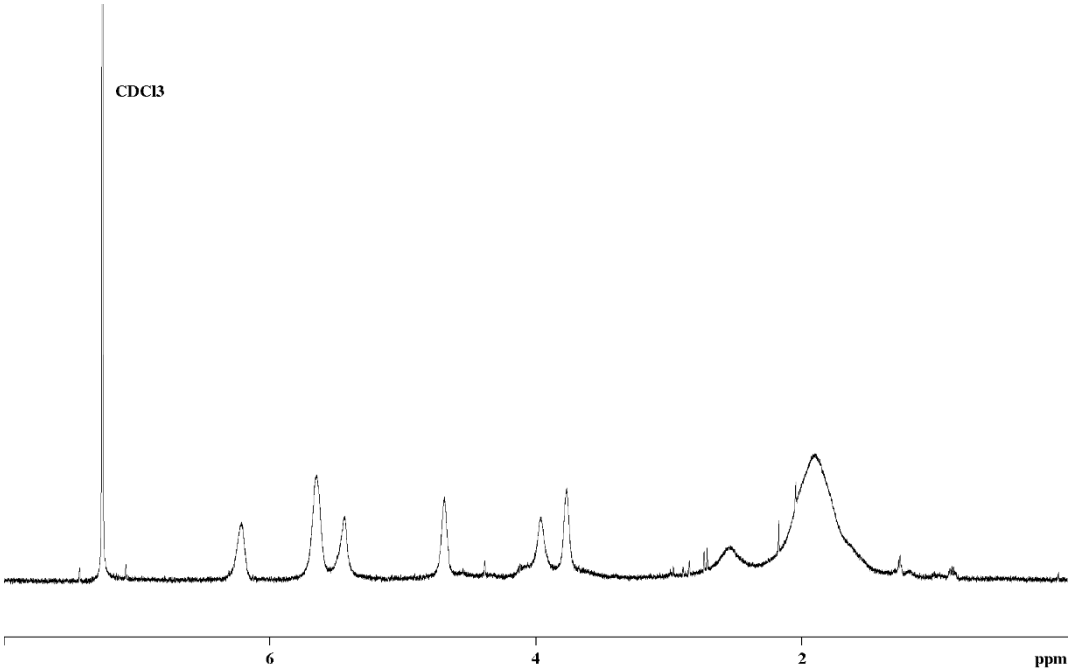



**Figure S5.** $^{1}H$ NMR of poly(LGOA) ($CDCl_3$, 600 MHz).

**Section S3: NMR data for poly(LGOA)**

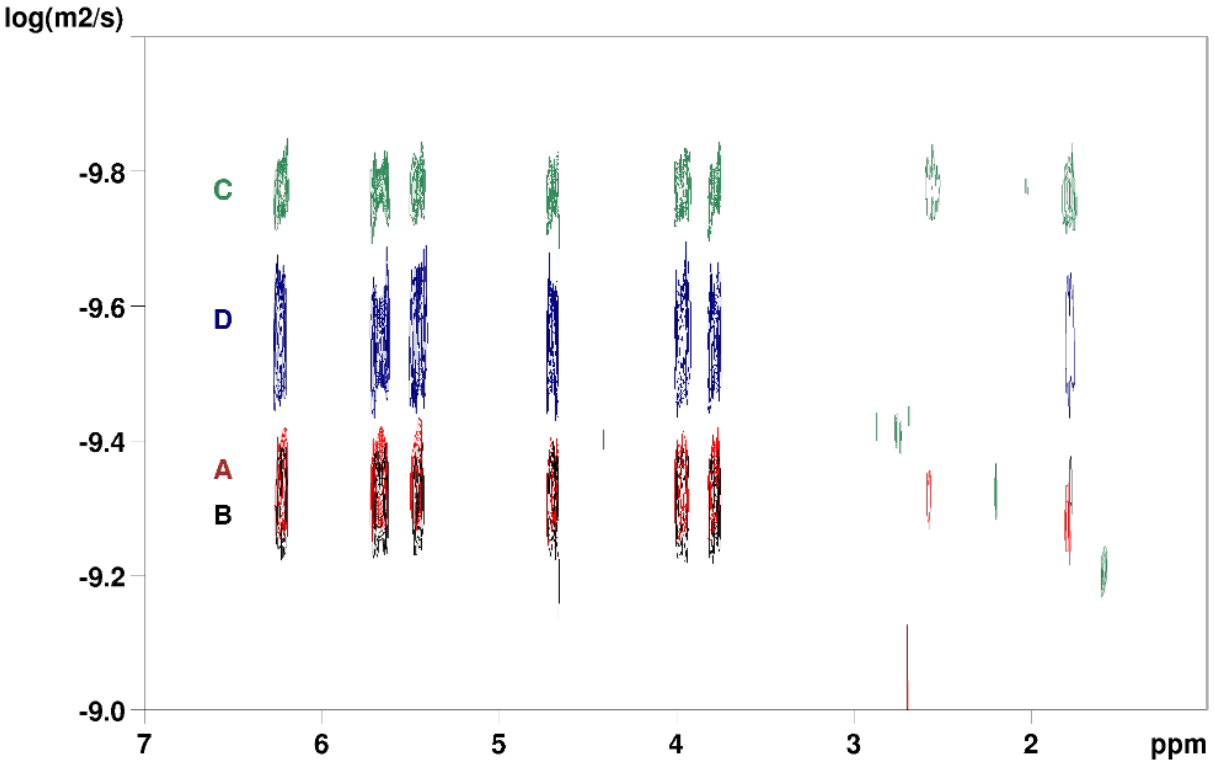



**Figure S6.** DOSY NMR of poly(LGOA) ($CDCl_3$, 600 MHz) where A, B, C and D represent initial [monomer]:[RAFT] ratios of 50, 100, 200 and 300:1 respectively. Fractional conversion of monomer to polymer is provided in the main text.

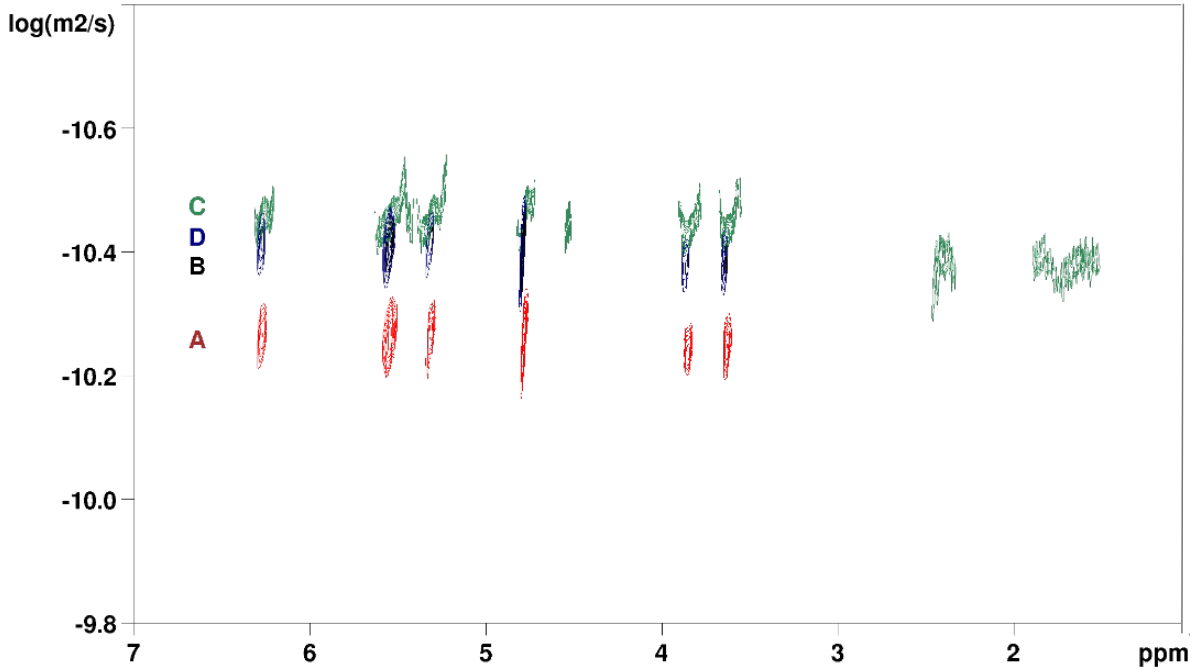



**Figure S7.** DOSY NMR of poly(LGOA) (DMSO-$d_6$, 600 MHz) where A, B, C and D represent initial [monomer]:[RAFT] ratios of 50, 100, 200 and 300:1 ratios respectively.

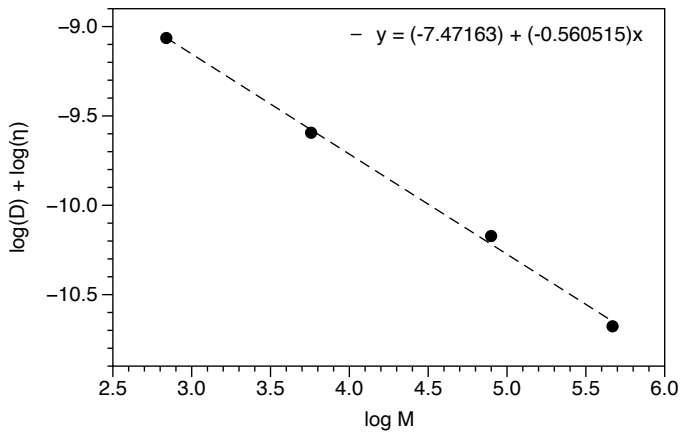



**Figure S8**. Viscosity-corrected DOSY NMR diffusion coefficient data of commercial PMMA standards (performed in $CDCl_3$, 600 MHz); the viscosity of CDCl3 at 298 K was 0.57 mPa s.

**Table S1**. Diffusion coefficient data of poly(LGOA) samples prepared via PET-RAFT polymerization and molar mass / hydrodynamic diameter data.

| **Sample** | **$\log_{10}(D_h)$ CDCl3 ($m^2\ s^{-1}$)** | **$M_{w,DOSY}$ (kDa)[a]** | **$r_{h,\ DOSY}$ (nm)[b]** | **$\log_{10}(D_h)$ DMSO-$d_6$ ($m^2\ s^{-1}$)** | **$M_{w,DOSY}$ (kDa)[a]** | **$r_{h,DOSY}$ (nm)[b]** |
|---|---|---|---|---|---|---|
| 50:1 | –9.337 | 5.8 | 0.83 | –10.257 | 27.9 | 2.00 |
| 100:1 | –9.304 | 5.1 | 0.77 | –10.409 | 52.0 | 2.85 |
| 200:1 | –9.647 | 20.7 | 1.69 | –10.455 | 62.8 | 3.17 |
| 300:1 | –9.552 | 14.0 | 1.37 | –10.404 | 50.9 | 2.82 |

[a]Average molar mass determined from calibration data in Figure S8 relative to PMMA standards; [b]calculated from the Stokes-Einstein equation.

**Section S4: FT-IR data for starting product, intermediates and polymer**

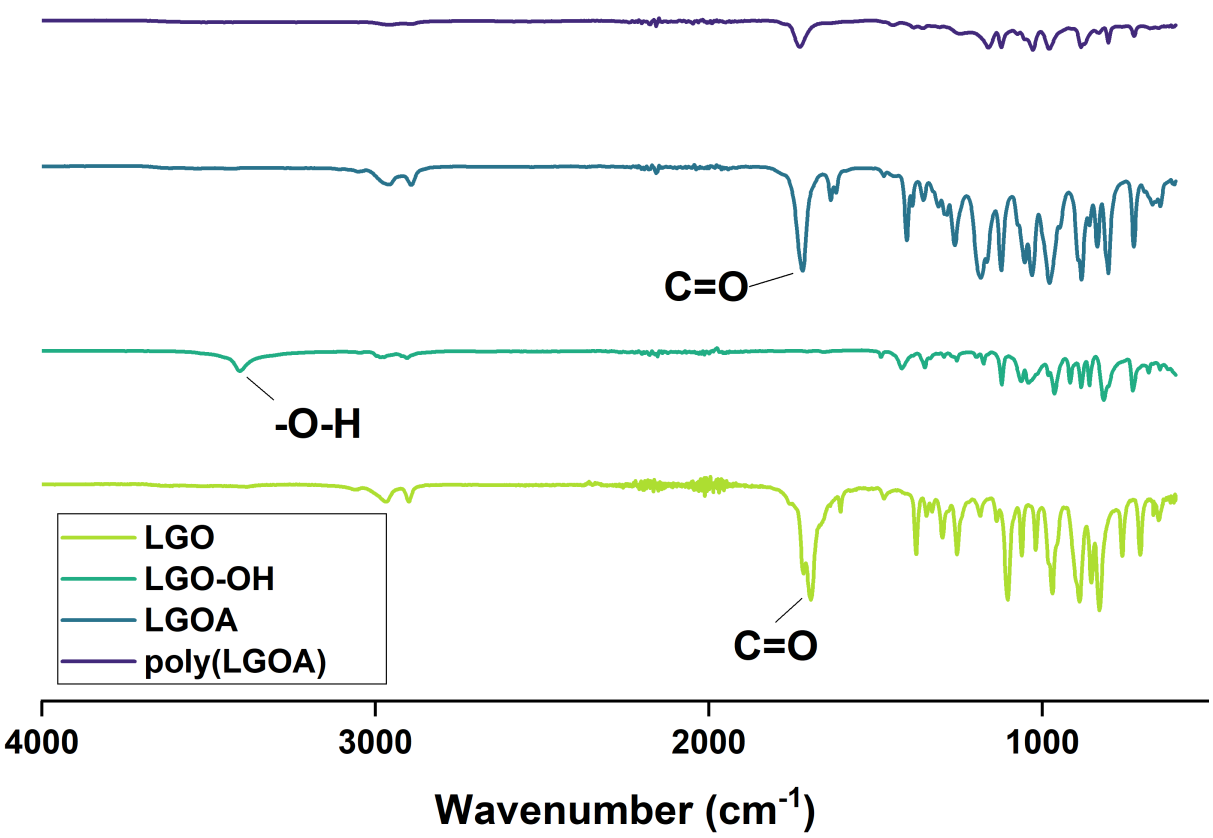



**Figure S9.** FT-IR spectra of LGO (bottom), LGO-OH (second from the bottom), LGOA (second from the top) and poly(LGOA) (top).

**Section S5**: E-factor calculations for the synthesis of LGOA

| Reaction | Reactants (g) | Final Product (g) | Amount of Waste (g) | E-Factor |
|---|---|---|---|---|
| Step 1: LGO reduction to LGO-OH | 43.62 | 0.703 | 42.72 | 60.8 |
| Step 2: Conversion of LGO-OH to LGOA | 106.4 | 0.215 | 105.7 | 151 |

**Section S6: Polymerization kinetics**

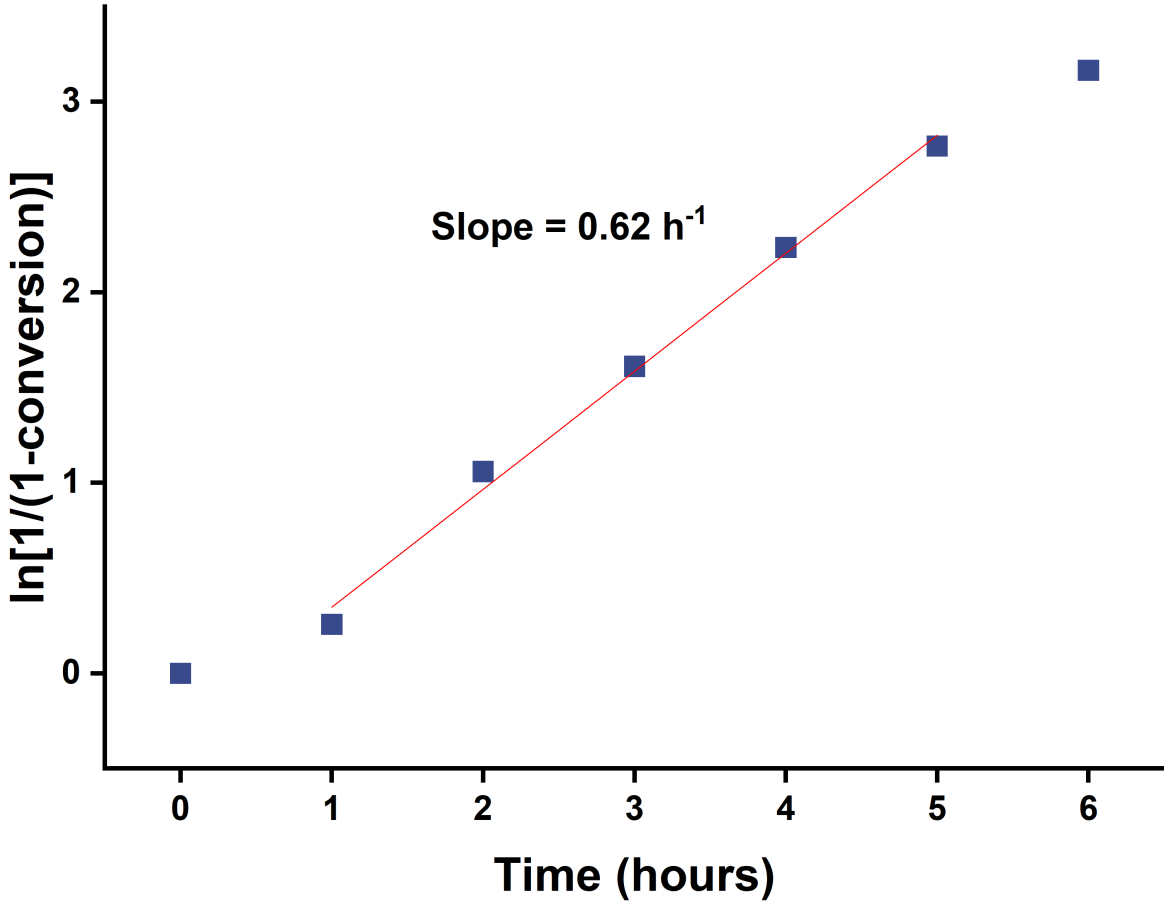



**Figure S10.** Conversion-time data shows linear relationship of ln(1/(1-conversion)) against time for the RAFT polymerisation of poly(LGOA). A pseudo- first order rate constant of 0.62 $h^{-1}$ was obtained from the linear fit of data in the 1-5 h time range.

**Table S2.** Calculations via $^{1}$H NMR analysis for the degree of consumption of the LGO C=C bond during free radical polymerisation.

| Time (h) | Av. Integration h(t) | h(0)-h(t) | Integration b,g(t) | b(t) | % Consumption of b |
|---|---|---|---|---|---|
| 0 | 0.256 | 0.000 | 0.568 | 0.312 | 0 |
| 6 | 0.012 | 0.244 | 0.288 | 0.276 | 11.5 |

**Table S3.** Calculations via $^{1}$H NMR analysis for the degree of consumption of the LGO C=C bond during PET-RAFT polymerisation.

| Time (h) | Av. Integration h(t) | h(0)-h(t) | Integration b,g(t) | b(t) | % Consumption of b |
|---|---|---|---|---|---|
| 0 | 5.5242 | 0.000 | 10.82 | 5.296 | 0 |
| 6 | 0.2256 | 5.299 | 4.7051 | 4.480 | 15.4 |

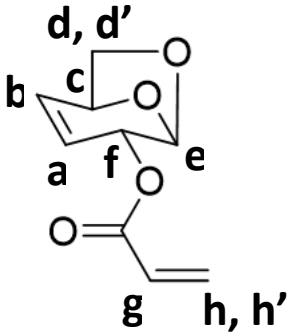



**Figure S11.** LGOA monomer with corresponding $^{1}$H NMR labels.

## Section S7. GPC Analysis of poly(LGOA)

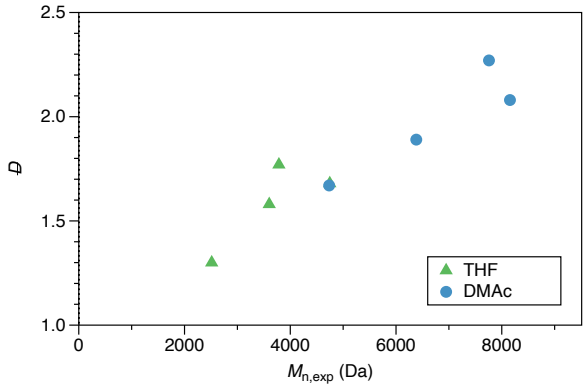



**Figure S12.** Variation of poly(LGOA) dispersity for samples analysed via both THF and DMAc GPC analysis using conventional calibration (accompanying data in Figure 3 of main manuscript).

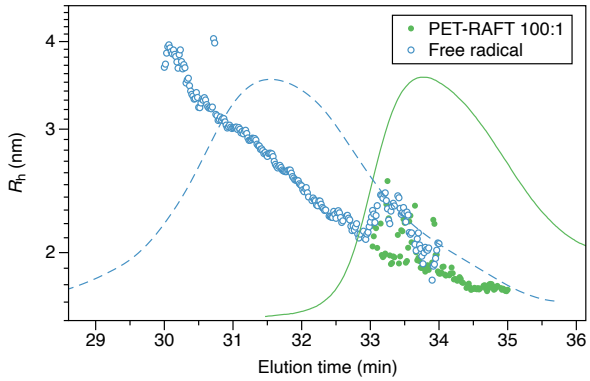



**Figure S13.** Variation of hydrodynamic radius of poly(LGOA) prepared via PET-RAFT polymerization (filled green circles) and free-radical polymerization (open blue circles) as a function of elution time, as determined by triple detection GPC. The refractive index chromatograms of both polymers are overlaid for reference.

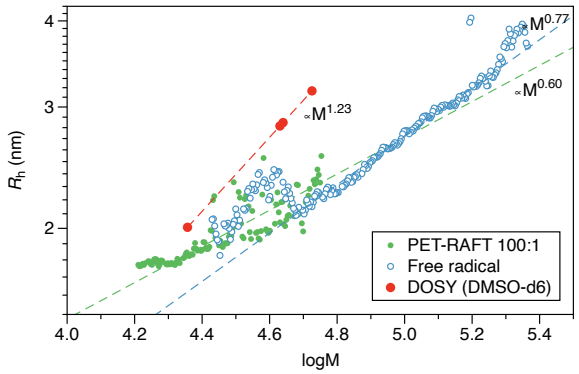
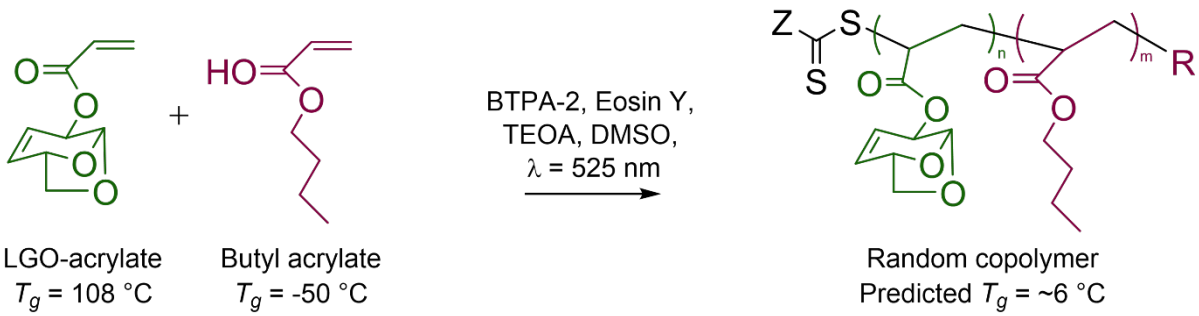



**Figure S14.** Variation of hydrodynamic radius of poly(LGOA) as a function of log (molar mass) for polymers prepared by PET-RAFT and free-radical polymerization, using absolute molar mass determination. The effective power law dependence of rh with M is shown; given the scatter in the data these trends are highly comparable. Hydrodynamic radius data of our samples as determined by DOSY NMR spectroscopy is provided for comparison (red circles; note these are based on molar mass relative to PMMA standards and performed in DMSO-$d_6$).

**Section S7: Copolymerization thermal data**




**Scheme S1.** Copolymerisation of LGOA and *n*-butyl acrylate to give a copolymer with a predicted $T_g$ of approximately 6 °C.

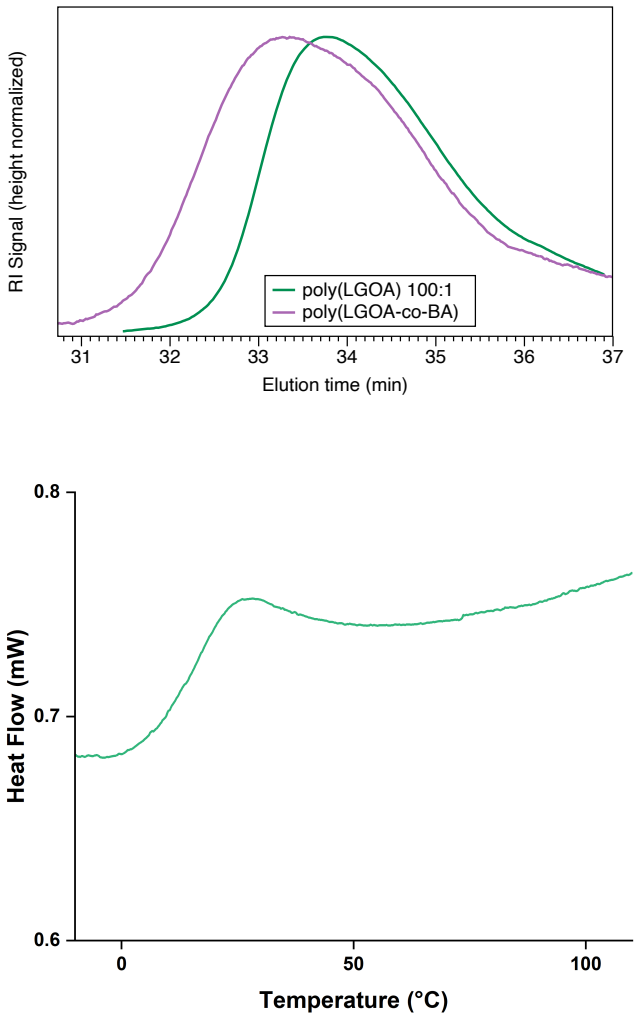



**Figure S15.** (Top panel) GPC chromatogram (THF GPC, conventional calibration) of LGOA-BA copolymer (purple curve); (Bottom panel) DSC curve with a $T_g$ of 9.1 °C for the 50:50 w/w copolymer of LGOA and BA prepared by PET-RAFT polymerization.

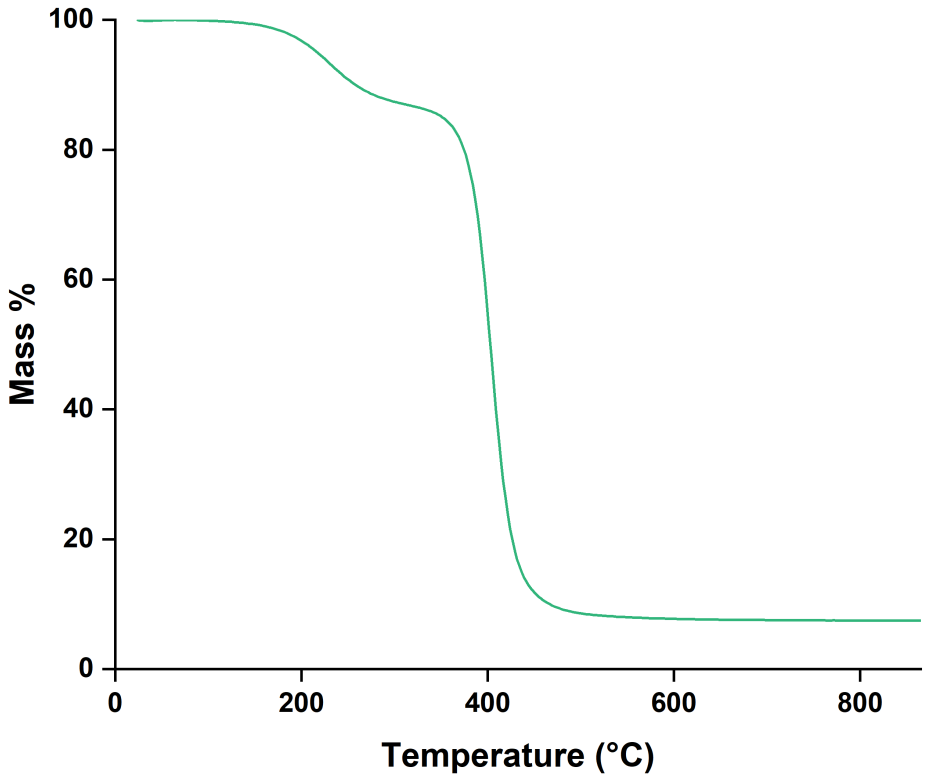



**Figure S16.** TGA thermogram of the 50:50 w/w LGOA/BA copolymer prepared by PET-RAFT polymerization. Note that the residual mass of 8.50% for the copolymer was approximately half that of the residual mass of poly(LGOA) (19.4% for a 100:1 [monomer]:[RAFT] ratio).

**Section S8: Calculation of % addition of monothiol to poly(LGOA)**

The % addition of the monothiol 1-dodecanethiol to poly(LGO)-acrylate was determined by comparing the total integration of the -$CH_3$ peak (0.90 ppm) to the remaining C=C proton peak (6.20 ppm) (Equation S6). The -$CH_3$ and C=C proton peaks were normalised by dividing through by 3 and 2 respectively.

$$\%Addition = \frac{\int_{0.9}/3}{\int_{0.9}/3 + \int_{6.2}/2} = \frac{18.6/3}{18.6/3 + 1/2} = 92.6 \quad \text{(S1)}$$

∴ The % addition of monothiol to polymer was 93%.

**Section S9: FTIR spectra of poly(LGOA) before and after PPM**

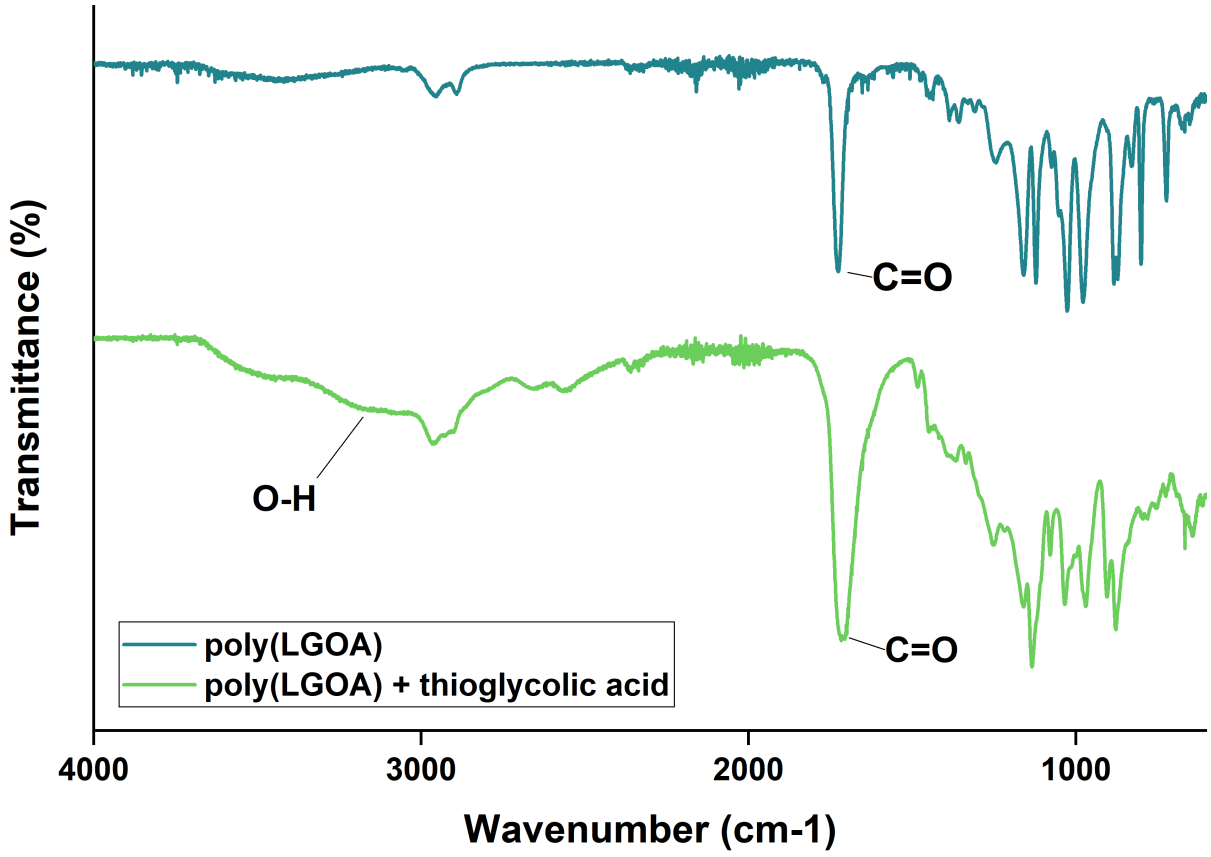
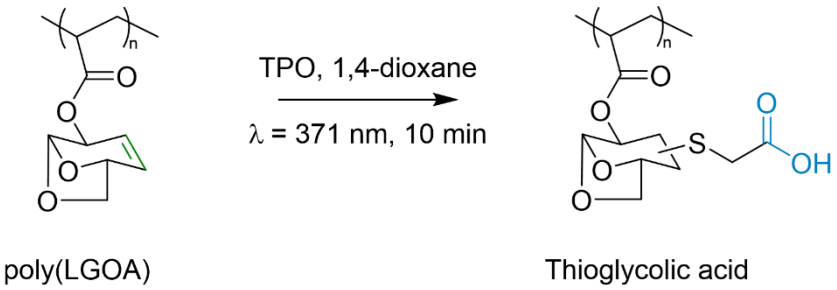



**Figure S17.** FTIR comparison of polymer before and after post-polymerisation modification with thioglycolic acid. The broad stretch between 2900-3300 $cm^{-1}$ highlights the presence of the O-H bond from the acid group.




**Scheme S2.** PPM of poly(LGOA) with thioglycolic acid.

**Section S10: Crosslinking density determination using Flory-Rehner analysis**

$$\chi = \beta + \frac{V_s}{RT}(\sigma_t - \sigma_s)^2 \quad \text{(S2)}$$

$\chi$ is the polymer-solvent interaction parameter (Flory-Huggins interaction ($\chi$) parameter) $\beta$ = 0.34 is the lattice constant, R is the gas constant, T(K) is the absolute temperature, $\sigma_t$ and $\sigma_s$ represent the solubility parameters of the polymer and solvent respectively.

$$\phi = \left[1 + \frac{d_p}{d_s}\left(\frac{m_{wet}}{m_{dry}} - 1\right)\right]^{-1} \quad \text{(S3)}$$

$\phi$ is the volume fraction of the equilibrium swollen polymer, $d_p$and $d_s$ represent the polymer and solvent densities respectively, $m_{wet}$ and $m_{wet}$ are the masses of the polymer network pre and post swelling. Note that the polymer density was estimated to be approximately 1 gm/cm$^3$.

$$M_c = -d_p V_s \left(\phi^{\frac{1}{3}} - \frac{\phi}{2}\right) \times \frac{1}{\ln(1-\phi)+\phi+\chi\phi^2} \quad \text{(S4)}$$

$M_c$ is the average molecular weight of the polymer between the crosslinks, $V_s$ is the molar volume of solvent.

$$q_{eff} = \frac{M_{monomer}}{M_c} \quad \text{(S5)}$$

$M_{monomer} = 182.17\ gmol^{-1}$ defined as the molar mass of an LGOA repeat unit and $q_{eff}$ represents the effective crosslinking density. Determination of the solubility parameter of poly(LGO)-acrylate, $\chi$ can be calculated from Hansen solubility parameters. As poly(LGOA)is a novel polymer, the determination of $\chi$ involves estimating the polymer solubility parameter via a group-contribution method.[1] This prediction method is exclusively based on the various bond types and functional groups present within the given molecule.

The total solubility parameter $\sigma_t$ measured in units of $MPa^{\frac{1}{2}}$ is made up of partial/Hansen solubility parameters $\sigma_d$, $\sigma_p$ and $\sigma_{hb}$,

$$\sigma_t = \sqrt{\sigma_d^2 + \sigma_p^2 + \sigma_{hb}^2} \quad \text{(S6)}$$

where $\sigma_d$ is the dispersion Hansen solubility parameter, $\sigma_p$ is the polar Hansen solubility parameter, $\sigma_{hb}$ is the hydrogen-bonding Hansen solubility parameter. This technique involves the grouping of bond types and functional groups, then summing the dispersion, polar and hydrogen bonding contributions (S6-8).

$$\sigma_d = \left(\sum_i N_i C_i + W \sum_j M_j D + 17.3231\right) MPa^{\frac{1}{2}} \quad \text{(S7)}$$

$$\sigma_p = \left(\sum_i N_i C_i + W \sum_j M_j D + 7.3548\right) MPa^{\frac{1}{2}} \quad \text{(S8)}$$

$$\sigma_{hb} = \left(\sum_i N_i C_i + W \sum_j M_j D + 7.9793\right) MPa^{\frac{1}{2}} \quad \text{(S9)}$$

Note: Estimations may vary based on the way in which the functionalities of the monomer are grouped. Only first order contributions were considered in the calculations.

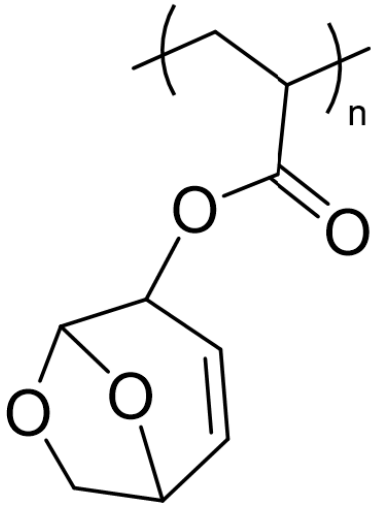



**Figure S18.** Representation of the poly(LGOA) repeating unit.

**Table S4.** First-order group contributions to the dispersion, polar partial and hydrogen-bonding partial solubility parameters for the identified functional groups of the poly(LGOA) repeating units.

| Group | $\sigma_d$ | $\sigma_p$ | $\sigma_{hb}$ | # of Groups |
|---|---|---|---|---|
| COO (ester) | 0.2039 | 3.4637 | 1.1389 | 1 |
| -CH=CH- (double bond) | 0.00048 | -0.2984 | -0.04 | 1 |
| $CH_2O$ (cyclic) | 0.2753 | 0.1994 | -0.161 | 1 |
| CHO (ether) | 0.8833 | 1.6853 | 0.447 | 1 |
| -CH< | 0.645 | 0.6491 | -0.2018 | 3 |
| $-CH_2$ | -0.0269 | -0.3045 | -0.4119 | 1 |
| | | | | |
| **Total** | **20.60** | **14.05** | **8.35** | |

Predicted total solubility parameter:

$$\sigma_t = \sqrt{20.6^2 + 14.05^2 + 8.35^2} = 26.3\ MPa^{\frac{1}{2}}$$

Hansen Solubility Parameter data for various solvents used in this work and their distance $R_a$ in the Hansen parameter space are provided below.

**Table S5.** Distance in the Hansen Solubility Parameter space of poly(LGOA) with various solvents.

| Group | $\sigma_d$ | $\sigma_p$ | $\sigma_{hb}$ | $R_a$[1] |
|---|---|---|---|---|
| DMSO | 18.4 | 16.4 | 10.2 | 5.3 |
| DMAc | 16.8 | 11.05 | 11.3 | 8.4 |
| DMF | 17.4 | 13.7 | 11.3 | 7.0 |
| THF | 16.8 | 5.7 | 8.0 | 11.3 |

| | | | | |
|---|---|---|---|---|
| chloroform | 18.2 | 6.2 | 6.3 | 9.4 |

[1] $Ra$ is defined as $\sqrt{4\Delta\sigma_d^2 + \Delta\sigma_p^2 + \Delta\sigma_{hb}^2}$ where $\Delta\sigma_i$ is the difference between each term in the expanded solubility parameter expression (dispersive, polar and hydrogen bonding respectively).

$S$ = Swelling ratio.

$$S = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad \text{(S10)}$$

**Table S6.** Equilibrium swelling ratios and effective crosslink densities of crosslinked polymers prepared from linear poly(LGOA) and the tetrathiol PETMP via thiol-ene click chemistry.

| **Solvent** | $\boldsymbol{S}$ | $\boldsymbol{q_{eff}}$ |
|---|---|---|
| DMF | 0.909 | 0.404 |
| DMSO | 1.27 | 0.408 |

**References**


1. E. Stefanis and C. Panayiotou, *International Journal of Thermophysics*, 2008, **29**, 568-585.