Supporting Information

Supplement: Tailorable and Programmable Liquid Crystalline Elastomers Using a Two-Stage Thiol-Acrylate Reaction

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Detailed Synthesis Procedures and Rationale

Thiol Monomers

Initial polydomain main-chain LCE samples were synthesized via a thiol-acrylate Michael addition reaction. Two thiol monomers, pentaerythritol tetrakis (3-mercaptopropionate) (PETMP) and 2,2'-(ethylenedioxy) diethanethiol (EDDET), were purchased from Sigma Aldrich (St. Louis, MO, USA) and used in their as-received condition. These thiol monomers were selected for their use as a *tetra*-functional crosslinking monomer and *di*-functional flexible spacer between mesogens. It should be noted that a wide variety of multi-functional thiol monomers are commercially available. Shorter *di*-thiols were considered, such as 1,2-ethanedithiol, to increase the mesogen density upon synthesis; however, were ultimately not used in this study due to their high volatility, extreme odor, and exposure concerns. Thiol solutions were mixed with functional group ratios ranging from 0:1 to 1:0, with the most studied thiol solutions containing 13 mol% PETMP functional groups (i.e. 13% of the overall thiol groups belonged to PETMP). A listing of monomers used in this study can be seen in **Table S1**.

Diacrylate Mesogen

The diacrylate mesogen, 1,4-Bis-[4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylbenzene (RM257), was purchased from Wilshire Technologies (Princeton, NJ, USA) and also used in its as-received condition with no purification. Before being added to the thiol solution, RM257 was dissolved in 31 wt% of toluene at 80˚C to for 5 minutes. Prior studies have directly polymerized RM257 without the need of a solvent,[1] although they have typically done so at an elevated temperature (~100˚C) to melt the mesogen. We chose to dissolve the mesogen in toluene to perform the polymerizations at room temperature and reduce the viscosity of the overall solution for molding purposes. RM257 was then added to the thiol solutions to create a non-stoichiometric acrylate:thiol functional group ratio of 1.15:1 (i.e. an excess of 15% extra acrylate groups relative to thiol groups existed in all the solutions in this study).

Table S1: *Names and CAS registry numbers of monomers used in this study.*

Acronym	Commercial Name(s)	IUPAC Name	CAS Registry
RM257	1,4-Bis-[4-(3-acryloyloxy-propyloxy)benzoyloxy]-2-methylbenzene; 2-Methyl-1,4-phenylene bis(4-(3- (acryloyloxy)-propoxy)benzoate); RM257	3-[p-(4-{p-[3-(vinylcarbonyloxy)-propoxy]benzoyloxy}tolyloxycarbonyl) phenoxy]propyl acrylate	174063-87-7
EDDET	2,2'-(ethylenedioxy) diethanethiol	2-[2-(2-Mercaptoethoxy)ethoxy] ethanethiol	14970-87-7
PETMP	pentaerythritol tetrakis (3-mercaptopropionate)	3-(2-Mercaptopropionoxy)-2,2-bis[(2-mercaptopropionoxy)methyl]propyl 3-mercaptopropionate	7575-23-7

Catalyst and Initiator

Dipropyl amine (DPA) was selected as the Michael-addition catalyst for this system. It also should be noted that a wide variety of catalysts exist and Chan *et al.* previously published an excellent study on the effects of different catalysts on the reaction rates of thiol-Michael reactions.[2] Preliminary investigations into using DPA showed that the reaction time for the first-stage, Michael-addition reaction could be tailored by controlling the amount of DPA added to the system (**Figure S1a**). A value of 0.23 mol% DPA was added to the monomer solutions, which allowed for relatively rapid polymerization, while allowing enough time to transfer the solutions into molds. Lastly, DPA was diluted in toluene at a ratio of 1:100 to provide better control over the amount of DPA added to the solution as well as limit any localized reactions. For example, a drop of pure DPA would cause the monomer solution to immediately gel in the area where added.

The photoinitiator (2-hydroxyethoxy)-2-methylpropiophenone (HHMP) was selected for this system for its stability in the presence of light and at elevated temperatures (**Figure S1b**). A preliminary investigation into the stability of HHMP showed it remained unreacted in the presence of visible light at 75˚C over 30 hours. Ultimately, 0.5 wt% of the total monomer weight was added to the solution and mixed vigorously to ensure a homogenous mixture. Both catalyst and photoinitator were purchased from Sigma Aldrich and used in their as-received conditions.

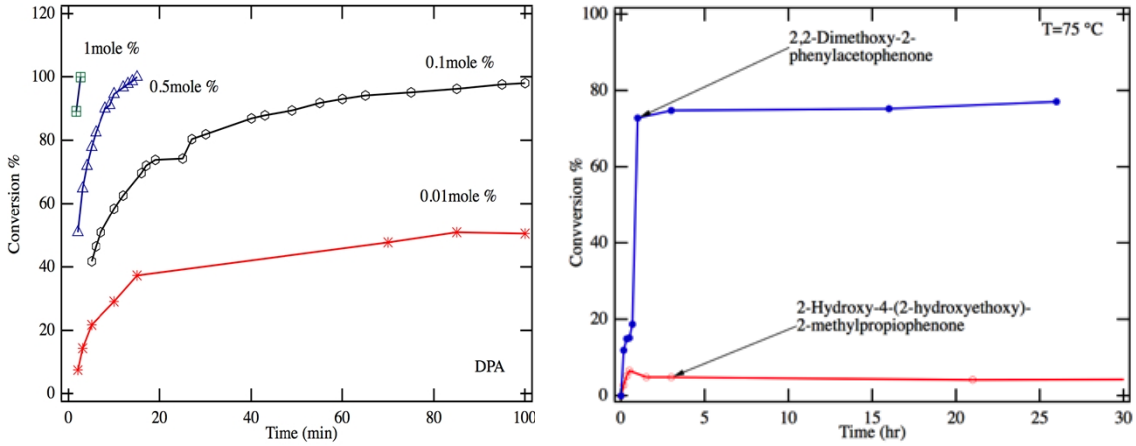

Figure S1: *Conversion vs. time for a representative thiol-acrylate (non-LCE) system using an equimolor ratio of EDDET and bisphenol-a-ethoxylate diacrylate using (a) a DPA catalyst and (b) two different photoinitiators at an elevated temperature. FTIR experiments were performed using a Nicolet 6700. The acrylate peak absorbance was measured at 6150 cm^{-1}. Spectra measurements were taken with different intervals of time and the peak areas for the acrylate were measured at constant baseline between 6103.6-6201.9 cm^{-1} wavenumber. Acrylate conversion is given by* $p = \left(1 - \frac{A_i}{A_f}\right)$*, where* A_i *and* A_f *are the initial and*

LCE Formulation

For clarity, the weights and calculations to create the most used LCE formulation in this study are shown in **Table S2**. This system comprises of 13 mol% PETMP crosslinker functional groups and an excess of 15% acrylate functional groups. This formulation was used for data in Figure 3 through 5.

Table S2: *Composition of LCE system used for thisi study. Mol-func is defined as the moles of a substance multiplied by its functionality to tailor the system in terms of functional groups present.*

Name	Weight (g)	MW (g/mol)	Functionality (f)	Purity (%)	Mol-Func (mmol-f)
RM257	1.000	588.6	2	97.3	3.306
EDDET	0.240	182.3	2	95	2.501
PETMP	0.048	488.7	4	95	0.374
Toluene	0.310	92.1	--	--	--
HHMP	0.006	224.3	--	--	--
DPA*	0.144	101.2	1	--	0.031

**Diluted 1:100 in toluene*

Preparation of Samples

After the monomer solution was created and mixed in a glass vial, it was placed in a vacuum chamber to remove any air bubbles caused by the mixing process. This process took less than 1 minute. Afterwards, the solution was poured into either rectangular or dog-bone shaped Teflon molds and allowed to cure overnight. It should be noted that the thiol-acrylate Michael addition reaction is not sensitive to oxygen or mold geometry. As a result, the manufacturing of these samples is highly scalable. This process was used to create thin films, ASTM Type IV and V dog-bone samples (**Figure S2**), and cylindrical samples measuring 4 mm in diameter. For thermomechanical testing in this study, rectangular samples were synthesized measuring approximately 9 x 60 x 2 mm^3.

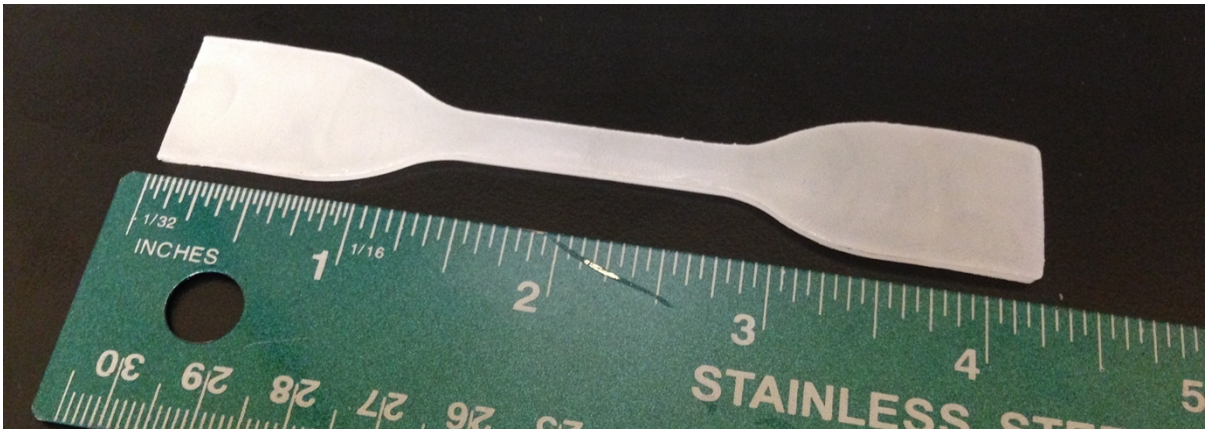

Figure S2: *An ASTM Type IV dog-bone sample was molded to demonstrate the ability to manufacture large LCE samples.*

Additional Experiments and Results

Thermal Analysis

Dynamic mechanical analysis (DMA) was performed using a TA Instruments Q800 machine (New Castle, DE, USA). Rectangular polydomain LCE samples measuring approximately 25 x 8 x 2 mm^3 were tested in tensile mode, with the active length measuring approximately 10 mm. Samples were cycled at 0.2% strain at 1 Hz and heated from -50 to 125°C at a rate of 3°C/min.

The glass transition temperature (T_g) was defined as the maximum of the tangent delta (tan ∂) curve. Differential scanning calorimetry (DSC) was also performed using a TA Instruments Q2000 machine. Samples with a mass of approximately 10 mg were loaded into a standard aluminum DSC pan. The samples were heated rapidly to 125°C at 10°C /min, held isothermally for 3 min, and cooled slowly to -80°C at rate of 2°C /min to reset any thermal history within the sample. Samples were then heated to 125°C at a rate of 10 at 10°C/min. The nematic to isotropic transition temperature (T_i) was defined as the minimum value of the endothermic peak. All samples were run in triplicate (n=3) and representative curves can be seen in **Figure S3**. It should be noted that the tan ∂ functions of the samples were much broader compared to traditional elastomeric materials, which typically display a relatively symmetric single peak. Furthermore, both Stage 1 and Stage 2 LCE samples exhibited a distinct dip (i.e. minimum) in the rubbery modulus regime, which was appears to be associated with T_i. This behavior has previously been reported by Warner and Terentjev when testing LCEs under relatively low frequencies.[3] The T_i was difficult to detect using DSC for the Stage 2 samples. A broad and weak transition appears to occur at approximately 70ºC and is best illustrated in Figure S3c.

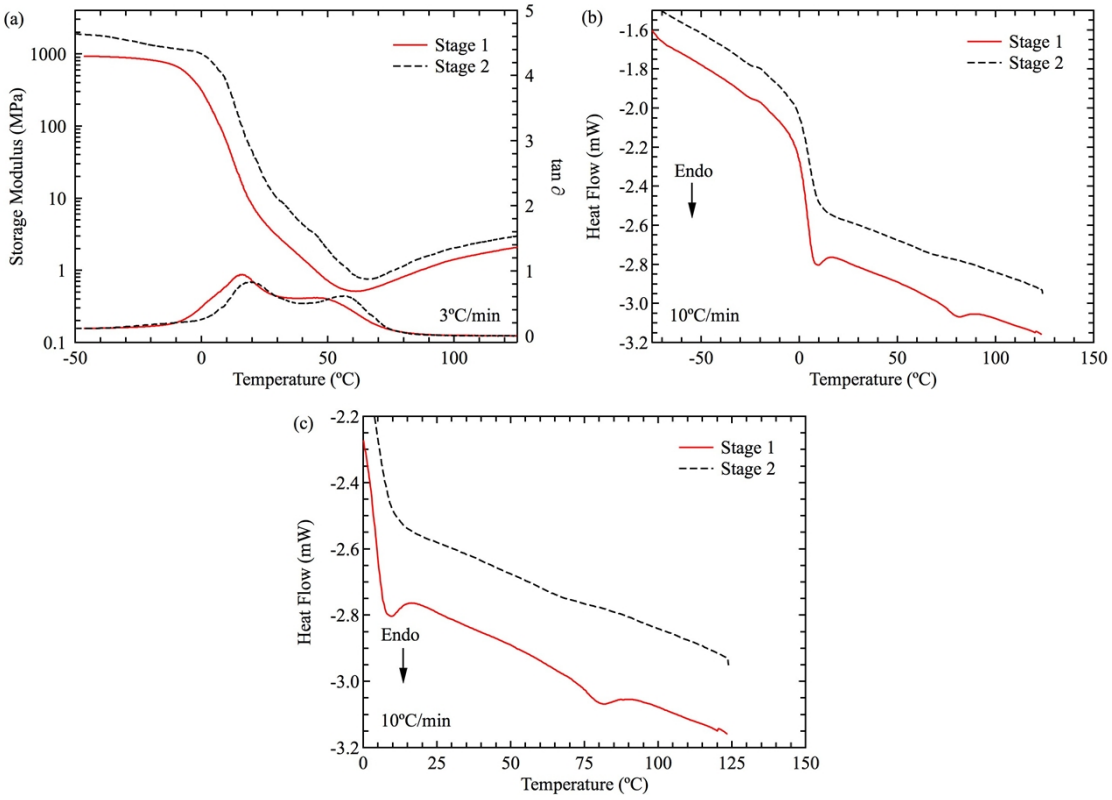

Figure S3: *Polydomain LCE samples are tested after completion of Michael-addition reaction (Stage 1) and photo-polymerization reaction (Stage 2). (a) Storage modulus and tan ∂ are plotted as a function of temperature to characterize glass transition. (b) Heat flow is plotted as a function of temperature to identify isotropic transition. (c) An expanded view of heat flow as a function of temperature for the LCE samples shown in (b).*

Photo-Dynamic Mechanical Analysis

The storage modulus was calculated as a function of UV exposure time using a dynamic mechanical test in a Bose ElectroForce 3200 (Eden Prarie, MN, USA). Samples were cycled at 1 Hz between 0.2 and 3.5% strain. The phase lag (∂) was determined by curve fitting of the sinusoidal waves using Igor Pro (Wavemetrics, Lake Oswego, OR, USA). Storage modulus (E') was calculated as:

$$E' = \frac{\sigma_o}{\varepsilon_o} cos(\partial) \tag{1}$$

where σ_o and ε_o are the maximum stress and strain values during cyclic loading. The storage modulus was calculated from 2 cycles of test data taken every 15 seconds for 10 minutes of UV exposure time. UV light was produced by a 365 nm UV lamp (B100AP, UVP, Upland, CA, USA).

A major advantage to the two-stage TAMAP approach is that the photo-crosslinking reaction (Stage 2) offers spatio-temporal control to tailor and program LCE networks. The crosslinking density, and subsequently modulus, of the initial polydomain network are increased as a function of UV irradiation time (**Figure S4**), as the excess acrylate groups will react together and establish new crosslinks. For this system, the results show that the photo-crosslinking reaction results in an increase in modulus by approximately one order of magnitude and is completed within 10 minutes. An investigation into the dynamic loading response is shown in **Figure S4b**. Though a hysteresis loop is still present in the networks, the damping function (tan ∂) decreases from 0.62 to 0.25 over the course of the photo-crosslinking reaction. Previous results by Nair *et al.* showed that the increase of modulus in amorphous SMP networks could be increased by up to three orders of magnitude by using a 2:1 ratio of acrylate to thiol functional groups in the initial mixture.[4] This approach can be made compatible with any thermal or UV initiator; however, in this study we chose HHMP for its long-term stability at elevated temperatures above T_i and in the presence of visible light (**Figure S1b**).

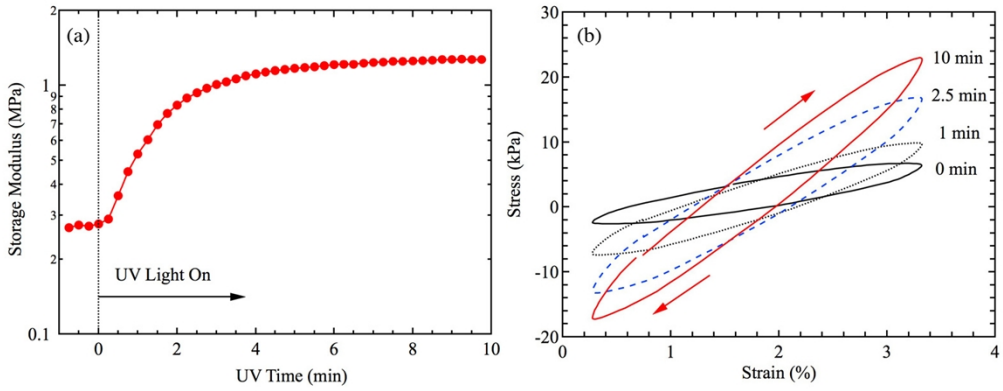

***Figure* S4:** *Mechanical properties of polydomain LCEs evolving during the second reaction. (a) Storage modulus increases as a function of the UV exposure time. (b) Cyclic stress vs. strain shows increased mechanical response as UV time increased. Both plots are a result of increased photo-crosslinks being established due to the conversion of unreacted acrylate groups.*

Spatial Control of Second-Stage Reaction

The second-stage photo-crosslinking reaction could be combined with traditional photo-masking techniques to provide spatial control over tailoring the properties of the LCE materials. To demonstrate this effect, LCE samples were sandwiched between two glass slides with a photo-mask placed on top of the glass. A UV lamp was placed approximately 50 cm from the sample for 10 minutes. For the rectangular sample shown in **Figure 3a**, the photo-mask consisted of alternating stripes and the reaction was carried out at room temperature. For the circular film sample shown in **Figure 3b**, a photo-mask of a laboratory logo was placed on the sample and can be seen in **Figure S5**. In this instance, photo-crosslinking was performed above T_i at 90˚C.

Figure S5: *Image of an LCE sample being covered with a photo-mask and exposed to UV light to spatially control the second-stage photo-crosslinking reaction.*

Polarized Optical Microscopy

Polarized optical microscopy (POM) was taken of three networks to demonstrate the change in birefringence of the LCEs (**Figure S6**) using a BX-51 microscope and cross polarizers (Olympus, Center Valley, PA, USA). Polydomain samples were made with 13, 50, and 100 mol% PETMP and an excess of 15 mol% acrylate functional groups in each sample. Samples with the lowest amount of crosslinking exhibited clear patterns of birefringence, which decreased with increasing crosslinking density.

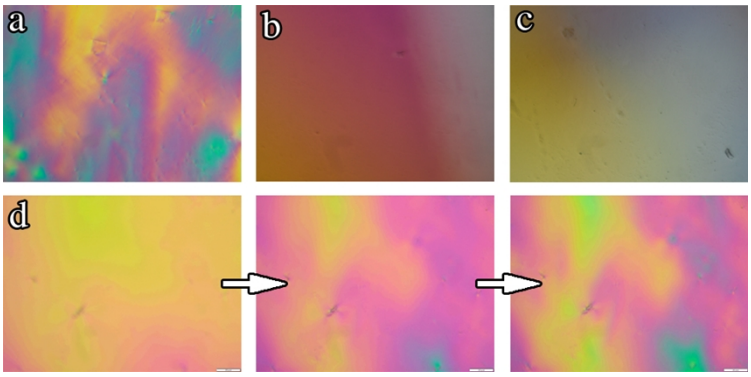

Figure S6*: POM at 20x magnification is performed using cross polarizers at room temperature for a). 13 mol%, b). 50 mol%, and 100 mol% PETMP samples with 15 mol% excess acrylate functional groups. d). The sample from (a) is cooled from the isotropic*

state to room temperature over the course of three images.

Cytotoxicity Testing

Cytotoxicity tests were performed by an independent laboratory, WuXi AppTec (St. Paul, MN, USA). Elution tests (Test #140320) were run on polymer samples after both the first and second stage reactions. Test articles measuring 32 cm^2 in area were extracted in Eagle's minimum essential medium (E-MEM) plus 5% fetal bovine serum. Samples were extracted for 24 hours at 37°C, after which the extract was inoculated onto the L-929 mouse fibroblasts at 37°C. Cells were monitored at 24, 48, and 72 hours. For both samples and at each time point, the response was rated the highest score of compatibility, defined as "discrete intracytoplasmic granules, no cell lysis, and no reduction of cell growth." Direct contact tests (Test #140250) were also run on samples after each reaction. Rectangular test specimens measuring approximately 1 x 1 x 0.1 cm^3 were gently placed on a monolayer of cells and incubated for 24 hours at 37°C. After incubation, the cultures were flooded with neutral red stain for 1 hour. Test articles were examined macroscopically and microscopically and scored relative to the amount of cell lysis displaced by a negative control. Each sample scored the highest grade of compatibility with no reactivity defined by "no detectable zone around or under specimen."

Swelling and Gel Fraction

Swelling and gel fraction experiments were performed to determine the swelling ratio, gel fraction and sol fraction of LCE samples after each stage of the TAMAP reaction. Two batches of the LCE formulation were made into 11 rectangular samples (approximately 22 x 10 x 1 mm^3). Samples were randomly divided and 5 samples underwent the second-stage photo-polymerization reaction in a 365 nm UV crosslinker box for 15 minutes (UVP, CL-1000). All samples were dried in a high vacuum before the initial weight (W_i) was recorded and then placed in individual vials filled with 10 mL of toluene. After 72 hours of soaking, samples were removed from the vials, dabbed dry with a paper towel, and quickly weighed to determine the swollen weight (W_s). Samples were then dried at 100ºC and high vacuum for 24 hours before measuring the final weight (W_f). The following equations were used to determine swelling ratio (q), gel fraction, and sol fraction:

$$q = \frac{W_s}{W_i} \cdot 100 \quad (1) \qquad Gel\ Fraction = \frac{W_f}{W_i} \cdot 100 \quad (2) \qquad Sol\ Fraction = \frac{W_i - W_f}{W_i} \cdot 100 \quad (3).$$

The results of the swelling and gel fraction tests can be seen in **Figure S7**. There was a slight decrease in swelling ratio in samples that experienced both stages of the reaction (149.6 vs. 145.8%), which is to be expected due to the slight increase in crosslinking density. There was no notable difference in gel fraction between the two sets of samples (95.4 vs. 95.1%). These values are notable considering the purity of starting materials ranged between 95 and 97%. The low sol content (< 5%) helps validate the results of the

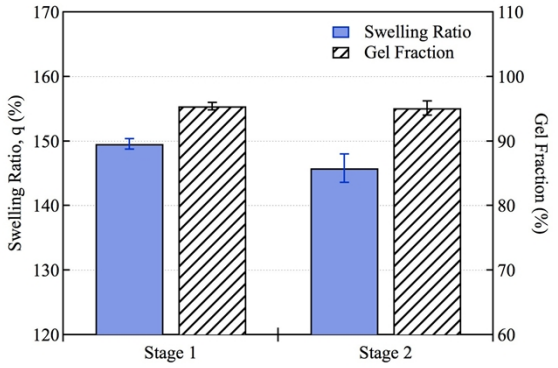

***Figure S7**: Swelling ratio and gel fraction for LCE samples that underwent either the first (Stage 1) or both (Stage 2) stages of the reaction.*

cytotoxicity elution test, in which the extraction did not show a cytotoxic response.

Supplemental References

1. K. M. Lee, T. J. Bunning and T. J. White, *Advanced Materials*, 2012, **24**, 2839-2843.
2. J. W. Chan, C. E. Hoyle, A. B. Lowe and M. Bowman, *Macromolecules*, 2010, **43**, 6381-6388.
3. M. Warner and E. M. Terentjev, *Liquid Crystal Elastomers: Revised Edition*, Oxford University Press, 2007.
4. D. R. Nair, N. B. Cramer, M. K. McBride, J. C. Gaipa, R. Shandas and C. N. Bowman, *Polymer*, 2012, **53**, 2429-2434.