Rapid Synthesis of Elastomers and Thermosets with Tunable Thermomechanical Properties

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ABSTRACT: Rapid, solvent-free synthesis of poly(1,4-butadiene) in ambient conditions is demonstrated by frontal ring-opening metathesis polymerization (FROMP) of 1,5-cyclooctadiene (COD). Furthermore, cross-linked copolymers with a wide range of tunable properties are readily prepared by FROMP of mixtures of COD and dicyclopentadiene (DCPD). Specifically, glass transition temperature and tensile modulus are varied from −90 to 114 °C and 3.1 MPa to 1.9 GPa, respectively, by controlling the comonomer ratio. Copolymers with subambient glass transition temperature exhibit robust elastomeric behavior, with the ability to repeatedly recover from large elastic deformations. As a demonstration of the capability of this manufacturing strategy, gradient materials are fabricated in less than a minute with spatially controlled properties for multistage shape memory actuation. This simple yet powerful manufacturing strategy enables rapid synthesis of copolymers ranging from elastomers to thermosets with precise control over thermomechanical properties.

The conventional manufacturing of synthetic rubbers is a multistep, energy-intensive process. For example, polybutadiene rubbers are typically prepared by solution-based polymerization of butadiene, followed by solvent removal (e.g., stripping with steam), dewatering, and oven drying.‡ The subsequent processing steps (compounding, shaping, and vulcanization) require large mechanical forces and/or high temperature.‡ An alternative synthetic route toward polybutadiene is the polymerization of 1,5-cyclooctadiene (COD) into poly(1,4-butadiene) in the presence of an olefin metathesis catalyst.‡ This method offers several advantages including easy handling of COD monomer as a high boiling point liquid, improved control of polymer microstructure (exclusively 1,4-structure with controllable cis/trans configuration), and capability for side-chain and/or chain-end functionalization.§ However, the synthesis of poly(1,4-butadiene) from COD typically is performed in solution and has been limited to the laboratory scale.

Frontal polymerization (FP) has emerged as a promising technique for rapid, energy-efficient preparation of bulk polymeric materials in ambient conditions without solvents. In FP, the monomer is converted to a polymer within a localized reaction zone that propagates spatially as a consequence of heat transfer from the exothermic polymerization to unreacted monomer. FP requires a minimal amount of energy to initiate the process, after which the polymerization front continues to propagate without further energy input. The applications of FP include micropatterning,¹⁰ and free-form 3D printing,¹⁰ as well as the fabrication of cure-on-demand adhesives,¹¹ gradient materials,¹² hydrogels,¹³ and nanocomposites.¹⁴ FP has been demonstrated for a wide variety of monomers including acrylates,¹²,¹⁵−¹⁷ epoxies,¹⁸,¹⁹ and cyclic olefins such as dicyclopentadiene (DCPD).¹⁰−²⁵

Recently, structural thermoset polymers and composites were produced by frontal ring-opening metathesis polymerization (FROMP) of DCPD with properties comparable to conventionally manufactured materials but with energy savings of up to 10 orders of magnitude.¹⁰ However, the rapid manufacturing of robust elastomers with mechanical properties comparable to commercial rubbers using FP has not yet been achieved.

Herein, we report the rapid, solvent-free synthesis of poly(1,4-butadiene) by FROMP of neat COD. Moreover, we find that FROMP of comonomer mixtures of COD and DCPD produces mechanically robust cross-linked polymeric materials having a wide range of properties, from soft elastomers to rigid thermosets, which can be tuned simply by varying the comonomer ratio. We use the ability to spatially control copolymer composition, and henceforth properties, to rapidly fabricate materials with spatially varying properties capable of multistage shape memory actuation.

Figure 1a shows the reaction scheme for FROMP of neat COD to produce poly(1,4-butadiene) in the presence of second-generation Grubbs catalyst (GC2). Mixtures of COD
with 90 ppm of GC2 and 90 ppm of tributyl phosphite (TBP)
inhibitor were stable at room temperature. FROMP was
initiated with a small amount of heat to trigger the activation of
inhibited GC2, and the heat released due to polymerization of
COD ($H_r = 204 \pm 5 \text{ J g}^{-1}$, see Figure S1) was sufficient to
activate GC2 ahead of the polymerization front, thereby
sustaining stable propagation of the reaction front without
further energy input (Figure 1b and Video S1). The
temperature of the front was 140 °C, and the front velocity
was ca. 0.6 mm s$^{-1}$ (see Figure S2), which is suitable for a
time-efficient bulk manufacturing process. For example, at this
speed of front propagation, a 12 in. rubber shoe sole could be
manufactured in less than 9 min.

Poly(1,4-butadiene) prepared by FROMP of COD (FPCOD) had a degree of cure ($\alpha$) of 95.6 ± 0.2% (see Figure S3) with no postcuring needed. The number-average molecular weight of FPCOD was ca. 220 kg mol$^{-1}$, which is comparable to commercial high molecular weight polybutadiene (100–300 kg mol$^{-1}$), with dispersity of ca. 2.0 (by gel permeation chromatography, GPC, vs polystyrene standards, see Figure S4). Tensile testing of freshly prepared FPCOD samples revealed strain-hardening behavior and very large elongation before failure (ca. 1280%) (see Figure 1c and Figure S5). The deformation was not recoverable due to macroscopic flow of polymer chains and strain-induced crystallization (see Figure S6).

In the absence of applied load, FPCOD samples also slowly crystallized at room temperature into an opaque rigid polymer with a melting point of ca. 40 °C (see Figures S7–S9). The crystallization behavior is due to the strictly linear constitution and predominant trans conformation (ca. 88% by $^1$H NMR, Figure S10), due to secondary metathesis reactions promoted by high temperature during FROMP that convert alkenes in the polymer backbone from cis to trans.$^{26}$ The $T_g$ of FPCOD was ca. −90 °C (see Table S1 and Figure S3), which is slightly higher than the literature value (ca. −100 °C) for most commercial poly(1,4-butadiene)s, possibly due to microstructure differences or the formation of microcrystalline regions.$^{27}$ The $T_g$ of FPCOD is sufficiently low to provide good elastomeric properties as long as crystallization is prevented.

To suppress crystallization and access polymers with a wider range of thermomechanical properties, one strategy is copolymerization of COD with a norbornene derivative.$^{28,29}$ Herein, we investigated the FROMP of comonomer mixtures of COD and DCPD (Figure 2a). Due to the higher ring strain of DCPD (90 kJ mol$^{-1}$)$^{30}$ compared to COD (56 kJ mol$^{-1}$),$^5$ these comonomer mixtures have increased reactivity, and

Figure 1. Poly(1,4-butadiene) prepared by FROMP of neat COD (FPCOD). (a) Scheme of polymerization reaction. (b) Images with time stamps showing the propagation of a polymerization front through a reaction vessel (see Video S1). (c) Representative tensile test data for freshly prepared FPCOD. True stress vs stretch is plotted for the same data in Figure S5. From five independent tests, the measured tensile modulus and tensile strength were 3.1 ± 0.8 MPa and 1.5 ± 0.4 MPa, respectively (see Table S1).

Figure 2. Copolymers prepared by FROMP of COD−DCPD comonomer mixtures. (a) Scheme of copolymerization reaction. (b) Front velocity and maximum front temperature (six independent tests for front velocity, three independent tests for front temperature, and error bars represent standard deviation). (c) $T_g$ of copolymers with varying COD volume fraction (three independent tests and error bars represent standard deviation). Numerical values and corresponding mole fractions are given in Table S1. The literature value for the $T_g$ of amorphous poly(1,4-butadiene) (−100 °C) is used in the Fox equation since all copolymers are amorphous, and the $T_g$ of FPCOD (−90 °C) is slightly increased due to crystallization.
FROMP copolymerization showed higher front velocity (ca. 0.6–1.2 mm s\(^{-1}\) with 1 equiv of TBP to GC2) and maximum front temperature (ca. 140–210 °C), both of which increased monotonically with DCPD fraction (Figure 2b and Video S2). Furthermore, the DCPD monomer has two reactive sites for metathesis, enabling the formation of chemical cross-links. We observed that the degree of cross-linking in copolymers prepared by FROMP increased with DCPD fraction, based on swelling tests (Figure S11) and dynamic mechanical analysis (DMA) (Figure S12). The presence of a second monomer and cross-linking sites successfully prevents the polymer chains from organizing into crystalline domains when the DCPD fraction exceeds 15 vol %.

The \(T_g\) values of the copolymers prepared by FROMP varied monotonically with the comonomer ratio over a wide range between −90 and 114 °C, as measured by differential scanning calorimetry (DSC) (Figure 2c and Table S1, with raw data in Figure S13) and confirmed by DMA (Figure 2c and Table S1, with raw data in Figure S12). The variation of \(T_g\) with comonomer composition closely follows the Fox equation for random copolymers (Equation S1), indicating that the two comonomers are statistically incorporated into the copolymer during FROMP without phase separation.

Control of the \(T_g\) and cross-linking density enabled the tuning of mechanical properties of the copolymers prepared by FROMP. At room temperature, the tensile modulus varied by 3 orders of magnitude, from 3.1 MPa to 1.9 GPa, and the tensile strength varied 40-fold, from 1.3 to 52 MPa (see Figure 3a and Table S1). In contrast to FPCOD samples, copolymers with 33 vol % COD or greater (\(T_g < \text{room temperature}\)) exhibited elastomeric behavior, with recoverable elastic deformation until failure and no observed yielding (Figure 3b and Figure S14). Minimal hysteresis was observed when elastomeric copolymers were unloaded prior to failure and reloaded (Figure S15). Qualitatively, these elastomers exhibited robust behavior, with immediate recovery through multiple cycles of deformation (Video S3). To our best knowledge, these results represent the first demonstration of robust elastomers prepared by frontal polymerization. Among the elastomeric copolymers, the copolymer with 33 vol % COD maximized elongation to failure at 450 ± 70% and tensile strength at 13 ± 3 MPa. Further increasing the DCPD fraction led to dramatically different mechanical behavior for copolymers with 25 vol % COD or less (\(T_g > \text{room temperature}\)). These copolymers were yielded at small strains (ca. 5%) followed by irrecoverable plastic deformation until failure (Figure 3c and Figure S16). This cold drawing behavior is similar to that previously observed for DCPD-based thermosets prepared by FROMP, which have excellent mechanical properties including stiffness and toughness.\(^{10}\)

The facile tuning of \(T_g\) and mechanical properties simply by changing the COD–DCPD comonomer ratio greatly broadens the potential applications of FROMP-prepared materials. As an example, we utilized the ability to control \(T_g\) to enable the fabrication of one-way shape memory polymers with tunable actuation temperature. Shape memory polymers have attracted
attention for sensing, actuation, and biomedical applications because of their low cost, low density, and ability to undergo large deformations compared to metallic shape memory alloys.\(^{31}\) The permanent shape of COD–DCPD copolymers is remembered through chemical cross-links fixed at the time of FROMP. Various temporary shapes are easily set by deforming the sample above \(T_g\) and holding the deformation while cooling to room temperature. The permanent shape is restored upon heating above \(T_g\).

DiOrio et al. previously described a shape memory polymer with a spatial \(T_g\) gradient exhibiting precise shape evolution in response to environmental heating.\(^{32}\) The \(T_g\) gradient was created by application of a temperature gradient during UV postcuring. Here, we introduce a new fabrication method for polymers with discrete spatial variation of \(T_g\) via FROMP of layered comonomer mixtures. Figure 4a illustrates the fabrication process using three layers with COD fractions of 25, 15, and 10 vol %, respectively. Gravity-induced mixing between the layers was prevented by accounting for the density differences between COD (0.88 g mL\(^{-1}\)) and DCPD (0.98 g mL\(^{-1}\)), and diffusion-induced mixing was limited by the rapid FROMP process which converted the liquid mixture into a solid polymer with predetermined compositional gradients in about 1 min (see Video S4). The gradient material part was then cut into a desired shape, such as a hand facsimile, with three different \(T_g\) values of 40, 74, and 94 °C (estimated by the Fox equation).

Sequential shape memory actuation of the FROMP-prepared gradient hand structure is demonstrated in Figure 4b. At 120 °C (above the highest \(T_g\)), the hand was deformed into a fist, followed by rapid cooling to 20 °C (below the lowest \(T_g\)) to fix the temporary shape. Then, the digits of the fist opened in a predetermined order in response to uniform environmental heating from 20 to 120 °C, restoring the original shape of the hand (Video S5). Additional shape memory cycles were carried out with the same sample programmed into different temporary shapes (Figure S17 and Videos S6 and S7).

To further investigate the shape memory recovery process, the transition behavior was studied by monitoring the unfolding of a three-layer gradient strip with the same spatial variation in \(T_g\). As shown in Figure 4c (also see Video S8), the end-to-end length of the strip rapidly increased in the temperature ranges corresponding to \(T \approx T_g + 10 \, ^\circ\text{C}\) for each of the three layers, demonstrating that shape memory actuation of the FROMP-prepared gradient material encompasses three distinct and sequential processes, rather than a continuous process. The wide temperature range between actuation events allows selected actuation of specific regions, enabling the fabrication of materials for complicated, multi-stage shape-memory tasks via a facile manufacturing toolbox.

In conclusion, we have demonstrated the rapid preparation of poly(1,4-butadiene) by FROMP of COD. This method has the potential to drastically reduce the time and energy input for the manufacturing of bulk poly(1,4-butadiene), which is widely used in the automotive and sporting goods industries. Without postprocessing, FPCOD samples exhibited a \(T_g\) of \(-90 \, ^\circ\text{C}\) and very high elongation at failure (ca. 1280%). Due to the linear constitution and predominance of translational C=C bonds in the backbone, the polymer tended to partially crystallize at room temperature. Further investigations of kinetics and the extent of crystallization may provide even greater control over the properties of poly(1,4-butadiene) prepared by FROMP. We have also demonstrated the rapid preparation of amorphous cross-linked copolymers with tunable thermomechanical properties by FROMP of COD–DCPD mixtures. The ratio of the two comonomers governs FROMP parameters such as front velocity and the maximum front temperature, as well as copolymer properties including \(T_g\) (from \(-90\) to 114 °C) and mechanical behavior. Copolymers of different compositions exhibited mechanical behavior ranging from elastomeric to cold drawing at room temperature, with tensile modulus varying almost 3 orders of magnitude (3.1 MPa to 1.9 GPa).

Figure 4. Sequential one-way shape memory actuation of a gradient material. (a) Rapid fabrication of a three-layer gradient material with temporally tuned \(T_g\) via FROMP in about 1 min. (b) Snapshots of sequential one-way shape memory actuation of the gradient material structure (see Video S5). Additional shape memory cycles are performed after resetting the structure into a different temporary shape (see Videos S6 and S7). (c) End-to-end length measurements of a gradient strip during uniform environmental heating. Scale bars = 10 mm (see Video S8).
Importantly, elastomeric compositions exhibited recoverable elastic deformation until failure, which occurred as high as 450% elongation for 33 vol % COD samples. Precise spatial control of the \( T_g \) enabled the sequential one-way shape memory actuation of gradient material structures with three distinct transition temperatures. We envision that the ability to tune \( T_g \) and mechanical properties of FROMP-prepared copolymers will enable further advances in the rapid, energy-efficient manufacturing of functional elastomers, gradient materials, and composites, as well as the 3D printing of multifunctional objects.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00233.

Video S1: FROMP of COD (MP4)
Video S2: FROMP of COD–DCPD mixture (MP4)
Video S3: Robust elastomeric behavior (MP4)
Video S4: FROMP of layered COD–DCPD mixture (MP4)
Video S5: Sequential shape memory actuation: first cycle (MP4)
Video S6: Sequential shape memory actuation: second cycle (MP4)
Video S7: Sequential shape memory actuation: third cycle (MP4)
Video S8: Sequential shape memory actuation of strip (MP4)

Materials and experimental methods and additional tables and figures (PDF)

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**Notes**

The authors declare no competing financial interest.

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