Supporting Information for

A Polymer with Mechanochemically Active Hidden Length

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Methods

Quantum-chemical calculations

All calculations were performed with the Gaussian09.E01 software package. The Berny algorithm was used to locate stationary points. Very tight convergence criteria and ultrafine integration grids were used in all optimizations. Thermodynamic corrections to electronic energies of individual conformers were calculated statistically mechanically in the harmonic oscillator/rigid rotor/ideal gas approximations, as 3RT + ZPE + U_vib − TS, where ZPE is the zero-point energy, U_vib is the vibrational component of the internal energy and S is the total entropy. Vibrational frequencies below 500 cm⁻¹ were replaced with 500 cm⁻¹ as previously recommended, to avoid the artifactually large contribution of such low-frequency modes to vibrational entropy. The calculations of analytical frequencies on converged constrained molecules is valid because the molecule plus its infinitely compliant constraining potential is a stationary point. The free energies of ensembles were calculated as $G_{\text{min}} - RT \ln \sum g_i e^{-\Delta G_i / RT}$, where $G_{\text{min}}$ is the free energy of the conformational minimum, $\Delta G_i$ is the excess free energy of conformer $i$ relative to this minimum, and $g_i$ is its degeneracy. The energy barriers separating individual strain-free conformers were <4 kcal/mol, justifying the use of Boltzmann statistics in calculating properties of ground and transition states and energies of activation. Ensemble averaging was done as $\langle \alpha \rangle = \frac{\sum \alpha_i g_i e^{-\Delta G_i / RT}}{\sum g_i e^{-\Delta G_i / RT}}$, where $\alpha$ is the quantity of interest (e.g., end-to-end distance) and the remaining terms are defined above.

The converged wavefunctions were stable as determined by outcome of the testing with the “stable” key word in Gaussian. All converged conformers of the reactant or intermediate states had 0 imaginary frequencies and all converged conformers of the transition states had a single imaginary frequency with the nuclear motion consistent with dissociation/rotation as appropriate. Unconstrained conformational ensembles of the structures in Fig. 2 (main text), including the transition states, were built systematically as previously described. The transition state conformers were first optimized at BLYP/6-31G(d) with constraints of the coordinates that dominate the reactive motion (e.g., scissile bond and bond angles around them, and/or torsions), followed by analytical frequency calculations and optimizations at each functional listed in the main text. Force-dependent properties of individual conformers and the conformational ensembles were calculated following the described procedures.

Intrinsic reaction path calculations were performed on all minimum-energy conformers of the strain-free transition states except one for the conversion of h,Z,Z and s,Z,Z which terminated after <5 steps due to the flat energy surface around the transition state (reactive frequency of >-50 cm⁻¹ at all functionals tested). The final geometries of all IRC calculations optimized to the expected minima. In addition, we calculated IRCs originating from the closed-shell and open-shell transition states leading to Z-2 at ~$f_{cs}^{\text{max}}$ − 0.25 nN and ~$f_{os}^{\text{min}}$ for the closed-shell TS; and at ~$f_{os}^{\text{min}}$+0.1 nN, ~$f_{os}^{\text{min}}$+0.4 nN, ~$f_{os}^{\text{min}}$+1 nN, 3.5 nN and 4.5 nN, for the open-shell TS (see Table 1 in the main text for the values of critical forces for the open- and closed-shell TSs). These calculations confirmed that the closed-shell transition state leads to Z,E diene at any force and the open-shell transition state leads to E,E diene at any force.

General experimental procedures

1,2-diphenylacetylene, benzophenone, acetophenone, 3-(4-hydroxyphenyl)-2-propenoic acid, diethylene glycol,
potassium perchlorate were purchased from Energy. Maleic anhydride, 1,5-pentanedioic acid, 4-dimethylaminepyridine, N,N'-methane-tetraylbis(1-methylethylamine) were obtained from Alladin. THF was dried with Na before use. Dichloromethane and chloroform were distilled over CaH₂ under nitrogen. All other reagents were purchased from Sinopharm and used without further purification.

¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ (δ = 7.26 (¹H) and 77.16 (¹³C)) or DMSO-d₆ (δ = 2.50 (¹H)) and referenced to the residual solvent signals on a 500 MHz Brucker AvanceII spectrometer at 25 °C. All chemical shifts were given in ppm (δ) as singlet(s), doublet (d), triplet (t), quartet (q), multiplet (m), or broad (br).

Gel permeation chromatography (GPC) data were calibrated on two columns in series (7.8 × 300 mm, 2 GMHHRM17932 and 1 GMHHRH17360) with tetrahydrofuran (THF, HPLC grade) as eluent at 40 °C with a LC-20AD pump. The facility was equipped with two detectors (RID-10A refractive index detector; SPD-20A UV detector) and the molecular weight was calibrated against polystyrene standards.

Silicon substrate and silicon nitride AFM tips (Veeco Instruments, now Bruker Nano, Santa Barbara, CA, MLCT) were used in the SMFS experiments. Before modification, the AFM tips and silicon slides were treated with piranha solution (H₂SO₄ (98%)/H₂O₂ (30%) = 7:3 in volume), and thoroughly rinsed with deionized water, followed by drying in an oven at 115 °C for 90 min to remove any remaining water. (Caution: Piranha solution that may result in explosion or skin burns is a very hazardous oxidant. This solution must be handled with extreme care.) The vapor-phase deposition method was used for the silanization of clean AFM tips and silicon slides by placing them in the atmosphere of the 3-amino-propyltrimethoxysilane (APDMMMS) in a dry nitrogen-purged desiccator for 1.5 h at 25 °C. Immediately after being taken out, the silanized tips and silicon slides were rinsed three times with methanol and then placed in a 110 °C oven for 10 min for activation. The silanized substrates and AFM tips were immersed in 1 mL DMF solution of P1 (0.5 umol/mL) and N,N'-dicyclohexylcarbodiimide (DCC) (0.75 umol/mL) and kept for 2.5 h at room temperature. Then the they were rinsed with DMF thoroughly to remove any loosely adsorbed molecules. Both the amino functionalized AFM tips and polymer anchored substrates were newly prepared just before SMFS experiments.

Ultrasound experiments were performed on a Vibra Cell 505 liquid processor with a 12.8 mm (diameter) titanium solid probe (Sonics and Materials). For typical sonication experiment, polymers were dissolved in THF with a concentration of 5 mg/mL in 15 mL of solvent. The solution was then transferred to a 3-necked Suslick cell in an ice bath and sparged with nitrogen for 20 min. A pulse sequence of 1 s on/1 s off was applied to the solution at a power of 8.7 W/cm². The temperature of the system was maintained at 0 - 5 °C. The sonication was carried out under a nitrogen atmosphere. Aliquots (0.5 mL, 4 mg/mL) at given time were removed from the Suslick cell for GPC and UV-Vis test. To monitor the cinnamic moiety, UV absorbance at 280 nm in GPC test was recorded. After sonication, the residual solution was precipitated by methanol and redissolved in CH₂Cl₂ (~ 25 mg/mL) for ¹H NMR measurement.

## Synthesis

### Synthesis of compound 2′

bis(2-(2-hydroxyethoxy)ethyl) (1R,2S)-3,4-diphenylcyclobut-3-ene-1,2-dicarboxylate, 2′:² a solution of 1,2-diphenylacetylene (5.34 g, 30 mmol, 3 equiv.), maleic anhydride (0.98 g, 10 mmol, 1 equiv.), benzophenone (5.5
g, 30 mmol, 3 equiv.) in acetonitrile (200 mL) placed in a cylindrical water-cooled reactor was degassed with a nitrogen stream for 15 min, then sealed. The solution was then irradiated for 24 h with a 400 W medium-pressure mercury lamp fitted with a Pyrex filter. The solution was then evaporated under reduced pressure to get a yellow oil. Then it was diluted with 30 mL dry THF in a 100 mL round bottom flask and added 8 mL diethylene glycol. Concentrated H₂SO₄ (1.5 mL) was carefully added, then the solution was heated at 75 °C overnight. After cooling, the reaction was quenched by pouring into 100 mL sat. NaHCO₃ and extracted with CH₂Cl₂ (100 mL). The organics were washed with 200 mL sat. NaCl and dried over Na₂SO₄, then evaporated under reduced pressure to give a crude product which was purified with column chromatography (ethyl acetate) to give compound 2' (1.5 g) as a yellow oil in 30% yield.

**1H NMR (500 MHz, CDCl₃) δ (ppm):**
- 7.52 (d, J = 6.98 Hz, 4H)
- 7.32 (m, 6H)
- 4.25 (m, 6H)
- 3.64 (m, 8H)
- 3.50 (m, 4H)
- 2.97 (br, 2H)

**13C NMR (500 MHz, CDCl₃) δ (ppm):**
- 170.75
- 138.39
- 133.53
- 128.56
- 128.39
- 126.78
- 72.52
- 68.67
- 64.35
- 61.62
- 46.55

**ESquire 3000 Plus Suplementary (m/z):**
- Calculated for C₂₆H₃₀O₈ [MNa⁺] 493.18; found 492.90.

**Synthesis of (E)-4-acetoxy-cinnamic acid chloride 3**

**((E)-3-(4-acetoxyphenyl)acrylic acid 3a**: (E)-3-(4-hydroxyphenyl)acrylic acid (5 g, 30.4 mmol, 1 equiv.) was slowly (in 10 min) added to a cold solution of dimethylaminopyridine (DMAP) (0.09 g, 0.78 mmol, 0.025 equiv.) and acetic anhydride (4.28 mL, 45.6 mmol, 1.52 equiv.) in pyridine (10 mL). The mixture was stirred at room temperature for 1 h and then poured over crushed ice. A white solid formed when the solution was acidified (pH = 2). The white solid was collected via vacuum filtration to provide compound 3a (6.7 g, 27.3 mmol) in 91% yield.

**1H NMR (DMSO-d₆, 500 MHz):**
- δ (ppm) = 7.74-7.72 (d, J = 8.5 Hz, 2H)
- 7.60-7.57 (d, J = 16.1 Hz, 1H)
- 7.18-7.16 (d, J = 8.6 Hz, 2H)
- 6.52-6.48 (d, J = 16.1 Hz, 1H)
- 2.27 (s, 3H)

**((E)-4-(3-chloro-3-oxoprop-1-en-1-yl)phenyl acetate, 3b**: thionyl chloride (SOCl₂) (1.35 ml, 38 mmol, 2.6 equiv.) and two drops of dimethylformamide (DMF) were added to a stirred solution of compound 3a (3 g, 14.55 mmol, 1 equiv.) in dry chloroform (CHCl₃) (20 mL). The mixture was refluxed for 6 h and allowed to cool to room temperature. The solvent and the unreacted SOCl₂ were removed under vacuum. The acid chloride derivative 3b was directly used in the next step. **1H NMR (CDCl₃, 500 MHz):**
- δ (ppm) = 7.83-7.80 (d, J = 15.5 Hz, 1H)
- 7.61-7.59 (d, J = 8.50 Hz, 2H)
- 7.20-7.18 (d, J = 8.6 Hz, 2H)
- 6.22-6.99 (d, J = 15.6 Hz, 1H)
- 2.33 (s, 3H)

**Synthesis of compound 3**

bis(2-(2-(((E)-3-(4-acetoxyphenyl)acryloyloxy)ethoxy)ethyl) (1R,2S)-3,4-diphenylcyclobut-3-ene-1,2-dicarboxylate, 3c: a solution of compound 3b (1.6 g, 7 mmol, 2.5 equiv.) in dry CH₂Cl₂ (50 mL) was added dropwise to a stirred solution of 2' (1.5 g, 3.2 mmol, 1 equiv.) and triethylamine (TEA) (0.9 mL, 6.5 mmol, 2.1 equiv.) in dry dichloromethane (CH₂Cl₂) (30 mL). The reaction mixture was stirred at room temperature
overnight. The organic layer was then washed sequentially with 1 M chlorhydric acid (HCl) (50 mL), 10% sodium hydrogenocarbonate (NaHCO₃) (50 mL) and saturated brine (50 mL), and dried over Na₂SO₄. The solvent was further evaporated under vacuum to give a crude product which was purified with column chromatography (hexane/ethyl acetate = 2:1) to give compound 3c (2.4 g, yield 77%) as a yellow oil. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.67 (d, J = 16.13 Hz, 2H), 7.52 (m, 8H), 7.31 (m, 6H), 7.10 (d, J = 8.63 Hz, 4H), 6.41 (d, J = 15.82 Hz, 2H), 4.29 (m, 8H), 4.24 (s, 2H), 3.61 - 3.69 (m, 8H), 2.3 (s, 6H).

13C NMR (500 MHz, CDCl₃) δ (ppm) 170.37, 168.84, 166.50, 151.96, 143.76, 138.28, 133.40, 131.85, 129.07, 128.41, 128.23, 126.66, 121.95, 117.81, 68.91, 68.71, 64.02, 63.46, 46.23. Esquire 3000 Plus-Supplementary (m/z): calculated for C₄₈H₄₆O₁₄ [MNa⁺] 869.28; found 869.30.

bis(2-(((E)-3-(4-hydroxyphenyl)acryloyloxy)ethoxy)ethyl) (1R,2S)-3,4-diphenylcyclobut-3-ene-1,2-dicarboxylate, 3: to a solution of compound 3c (0.5 g, 0.6 mmol, 1 equiv.) in 20 mL CH₃OH/CH₂Cl₂ (1:1) mixture, K₂CO₃ (0.163 g, 1.2 mmol, 2 equiv.) was added, and the resulting solution was stirred for 90 min. Saturated NaCl (aqueous) was added into the mixture. The product was then extracted with CH₂Cl₂ and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the crude product was purified with column chromatography (dichloromethane/acetone = 8:1) to give a compound 3 (0.27 g) as a white solid in 60% yield. ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.58 (d, J = 15.93 Hz, 2H), 7.50 (dd, J = 6.62, 4H), 7.31 (m, 10H), 6.79 (d, J = 8.59 Hz, 4H), 6.42 (br, 2H), 6.21 (d, J = 16.05 Hz, 2H), 4.28 (t, J = 4.6 Hz, 8H), 4.22 (s, 2H), 3.67 (m, 8H).

13C NMR (500 MHz, CDCl₃) δ (ppm) 172.93, 172.82, 170.77, 155.19, 138.40, 133.50, 132.50, 128.67, 128.49, 128.06, 126.81, 115.56, 68.95, 68.89, 68.82, 68.65, 64.35, 64.27, 64.25, 64.11, 46.57, 46.43, 46.40, 46.37, 45.36. Esquire 3000 Plus-Supplementary (m/z): calculated for C₄₄H₄₂O₁₂ [MNa⁺] 785.26; found 785.40.

Polymer synthesis

P1: compound 1 (0.546 g, 0.72 mmol, 1 equiv.), glutaric acid (95 mg, 0.72 mmol, 1 equiv.), and
dimethylaminopyridinium toluenesulfonate (84 mg, 0.28 mmol, 0.4 equiv.) were added to a 25 mL flask. Dry CH$_2$Cl$_2$ (5 mL) was added by syringe, and the solution was heated to 37 °C while stirring until solution became homogenous. After cooling to room temperature, N,N-diisopropylcarbodiimide (0.33 mL, 2.1 mmol, 3 equiv.) was added dropwise by syringe. The mixture was stirred for 96 h. The mixture was precipitated twice from CH$_2$Cl$_2$ into MeOH to afford a yellow solid P1 (0.542 g, 85% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm) 7.52 (d, $J = 6.72$ Hz, 4H), 7.30 (m, 10H), 7.04 (m, 4H), 4.34-4.46 (m, 2H), 4.23-4.31 (m, 2H), 4.10-4.23 (m, 6H), 3.75-3.85 (m, 2H), 3.55-3.71 (m, 8H), 3.33-3.44 (m, 2H), 2.61-2.74 (m, 4H), 2.14 (m, 2H).

**P4**: compound 2' (1.412 g, 3 mmol, 1 equiv.), glutaric acid (0.397 g, 3 mmol, 1 equiv.), and dimethylaminopyridinium toluenesulfonate (DPTS) (0.354 g, 1.2 mmol, 0.4 equiv.) were added to a 25 mL flask. Dry CH$_2$Cl$_2$ (10 mL) was added by syringe, and the solution was heated to 37 °C while stirring until solution became homogenous. After cooling to room temperature, N,N-diisopropylcarbodiimide (DIC) (1.4 mL, 9 mmol, 3 equiv.) was added dropwise by syringe. The mixture was stirred for 96 h. The mixture was precipitated twice from CH$_2$Cl$_2$ into MeOH to afford a yellow solid P4 (1.3 g, 71% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm) 7.46 (m, 4H), 7.35 (m, 6H), 4.34 (m, 2H), 4.06 (m, 8H), 3.53 (m, 8H), 2.31 (m, 4H), 1.73 (m, 2H).

**P4 control**: compound 2' (0.353 g, 0.75 mmol, 1 equiv.), glutaric acid (99 mg, 0.75 mmol, 1 equiv.), and dimethylaminopyridinium toluenesulfonate (DPTS) (89 mg, 0.3 mmol, 0.4 equiv.) were added to a 25 mL flask. Dry CH$_2$Cl$_2$ (5 mL) was added by syringe, and the solution was heated to 37 °C while stirring until solution became homogenous. After cooling to room temperature, N,N-diisopropylcarbodiimide (DIC) (0.35 mL, 2.25 mmol, 3 equiv.) was added dropwise by syringe. The mixture was stirred for 24 h. The mixture was precipitated twice from CH$_2$Cl$_2$ into MeOH to afford a yellow solid short P4 control (0.3 g, 66% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm) 7.46 (m, 4H), 7.35 (m, 6H), 4.34 (m, 2H), 4.06 (m, 8H), 3.53 (m, 8H), 2.31 (m, 4H), 1.73 (m, 2H).
# Quantum Chemical Calculation

**Table S1.** Experimental and calculated standard free energies of activation, $\Delta G^{\ddag o}$, and standard reaction free energies of isomerization, $\Delta G^o$ (kcal/mol) of 2 and its diene analogs at different model chemistries; unless noted otherwise, the numbers are for the gas phase. Calculations of direct E,Z isomerization of the dienes were with spin-unrestricted formalism.

| Reaction | Exp. | APFD 6-31+G(d) | BMK 6-311+G(d) | CAM-B3LYP 6-311+G(d) | MPW1K 6-31+G(d) | M06-2X 6-311+G(d) | wB97x-D 6-31+G(d) |
|----------|------|----------------|----------------|----------------------|-----------------|-------------------|-------------------|
| Z-2      |      |                |                |                      |                 |                   |                   |
| MeO₂C[1]CO₂Me $\rightarrow$ MeO₂C[1]CO₂Me | $\Delta G^{\ddag o}$ | 30.6±1.3 $^\ddag$ | 31.1 | 33.8 | 34.6 | 31.2 | 31.6 | 31.8 | 33.5 | 34.0 | 33.9 | 31.3 | 31.4 | 32.9 |
|          | $\Delta G^o$ | -1.7±0.8 $^\ddag$ | 2.2 | 1.9 | 3.0 | -2.9 | -3.0 | -1.7 | 1.7 | 2.2 | 3.4 | -1.1 | -0.9 | 1.0 |
| E-2      |      |                |                |                      |                 |                   |                   |
| MeO₂C[1]CO₂Me $\rightarrow$ MeO₂C[1]CO₂Me | $\Delta G^{\ddag o}$ | 31.8±1.1 $^\ddag$, 32.2 $^\ddag$ | 32.7 | 34.7 | 36.4 | 32.7 | 32.3 | 34.4 | 35.7 | 37.5 | 36.7 | 35.1 | 34.7 | 36.2 |
|          | $\Delta G^o$ | -0.7±0.5 $^\ddag$ | 5.3 | 5.4 | 7.9 | -0.1 | -0.3 | 2.9 | 4.7 | 1.7 | 7.5 | 2.5 | 2.4 | 4.8 |
| E-2      |      |                |                |                      |                 |                   |                   |
| MeO₂C[1]CO₂Me $\rightarrow$ MeO₂C[1]CO₂Me | $\Delta G^{\ddag o}$ | 32.7±0.9 $^\ddag$ | 33.0 | 35.6 | 37.4 | 34.3 | 33.9 | 34.7 | 35.3 | 38.0 | 36.2 | 34.5 | 34.4 | 36.5 |
|          | $\Delta G^o$ | -2.8±0.7 $^\ddag$ | 1.3 | 3.1 | 4.7 | -2.3 | -3.1 | -1.0 | 3.5 | 4.5 | 3.6 | -0.4 | -0.6 | 1.5 |
| E-2      |      |                |                |                      |                 |                   |                   |
| MeO₂C[1]CO₂Me $\rightarrow$ MeO₂C[1]CO₂Me | $\Delta G^{\ddag o}$ | 33.4±1.2 $^\ddag$, 33.9 $^\ddag$ | 26.1 | 34.6 (45.8) | 30.1 | 32.8 | 30.4 | 37.5 | (35.4) | 28.7 | 29.6 (44.8) | 29.1 | (42.8) | 30.4 |
|          | $\Delta G^o$ | -2.0±1.0 $^\ddag$ | -2.9 | -3.0 | -2.8 | -1.7 | -2.4 | -2.6 | -0.94 | -2.9 | -2.8 | -2.3 | -2.4 | 1.5 |

* the numbers in parentheses are for direct isomerization

$^\ddag$ this work

& from refs. 9
Table S2. Strain-free ensemble-average $\text{MeO-C-} \text{C}_{\text{OMe}}$ distances in cyclobutenes 2 and its diene analogs at CAM-B3LYP/6-311+G(d)/CPCM=DMSO.

| Minimum | Å | Transition state of reaction: | Å |
|---------|---|------------------------------|---|
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( Z-2 \) | 5.490 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( Z-2 \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( Z-2 \) & 5.013 |
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( E-2 \) | 8.000 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( E-2 \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( E-2 \) & 7.115 |
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( h,E,Z \) | 6.682 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( h,E,Z \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( h,E,Z \) & 7.512 |
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,Z,Z \) | 9.056 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,Z,Z \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,Z,Z \) & 7.769 |
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( h,E,E \) | 7.618 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( h,E,E \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( h,E,E \) & 6.836 |
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( eq-Pyran \) | 5.378 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( eq-Pyran \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( eq-Pyran \) & 6.520 |
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( ax-Pyran \) | 6.835 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( ax-Pyran \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( ax-Pyran \) & 5.378 |
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,E,E \) | 10.815 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,E,E \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,E,E \) & 10.318 |
| [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,E,Z \) | 10.307 | [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,E,Z \) & [\( \text{Ph-} \text{Ph} \text{MeO}_2\text{C-CO}_2\text{Me} \)] \( s,E,Z \) & 10.307 |
| Minimum | Å | Transition state of reaction: | Å |
|---------|---|------------------------------|---|
| ![Structure](image1.png) | 9.044 | ![Structure](image2.png) | 7.841 |
| ![Structure](image3.png) | 8.167 | ![Structure](image4.png) | 8.841 |
Spectroscopy and chromatography

Figure S1. (A) $^1$H NMR (500 M) spectrum of compound 2’ (CDCl$_3$, 7.26 ppm) and (B) $^{13}$C NMR (500 M) spectrum of compound 2’ (CDCl$_3$, 77 ppm).
Figure S2. $^1$H NMR (500 M) spectrum of compound 3a (DMSO-d$_6$, 2.50 ppm).

Figure S3. $^1$H NMR (500 M) spectrum of compound 3b (CDCl$_3$, 7.26 ppm).
Figure S4. (A) $^1$H NMR (500 M) spectrum of compound $3c$ (CDCl$_3$, 7.26 ppm) and (B) $^{13}$C NMR (500 M) spectrum of compound $3c$ (CDCl$_3$, 77 ppm).
Figure S5. (A) $^1$H NMR (500 M) spectrum of compound 3 (CDCl$_3$, 7.26 ppm) and (B) $^{13}$C NMR (500 M) spectrum of compound 3 (CDCl$_3$, 77 ppm).
Figure S6. (A) $^1$H NMR (500 M) spectrum of compound 1 (CDCl$_3$, 7.26 ppm) and (B) $^{13}$C NMR (500 M) spectrum of compound 1 (CDCl$_3$, 77 ppm).
Figure S7. $^1$H NMR (500 M) spectrum of polyester P1 (CDCl$_3$, 7.26 ppm).

Figure S8. GPC traces of polyester P1 (RI signal).
Figure S9. $^1$H NMR (500 M) spectrum of polyester P4 (DMSO-$d_6$, 2.50 ppm).
Figure S10. GPC traces of polyesters. (A) P4 and (B) P4S (RI signal).

Table S3. Molecular parameters of P1, P4 and P4S. $X_n$ is number -average degree of polymerization.

| Entry      | $M_n$ (g/mol)* | $M_w$ (g/mol)* | $D_M$ | $X_n$ |
|------------|----------------|----------------|-------|-------|
| P1         | 48,000         | 84,000         | 1.7   | 54    |
| P4         | 33,000         | 52,000         | 1.6   | 55    |
| P4 control | 6,800          | 9,600          | 1.4   | 10    |

* nominal mass in polystyrene mass equivalents.
Figure S11. Representative force-extension curves for P1 and P4 from SMFS experiments.
Figure S12. The distribution of (A) the dissociation force and (B) the peak-to-peak separations of the saw-tooth pattern of the plateau in the force-extension curves of P1 from SMFS experiments. The x axis is the upper limit of each bin, i.e., the bar centered at 1.8 nN (A) gives the fraction of observed dimer dissociations that occurred between 1.751 and 1.8 nN and the bar between 2.6 and 2.8 nm (B) contains the fraction of transitions with elongations of 2.61 to 2.8 nm. The solid line in (A) is the expected distribution based on the calculated mechanochemical kinetics and the lengths of the stretched chain segments studies experimentally, calculated according to the described procedure. The solid line in (B) is a Gaussian fit of the experimental distribution with $\mu = 2.93$ nm and $\sigma = 0.34$ nm.
Calculations of the fractions of conversion

The fraction of dissociated cinnamate dimers was calculated by the ratio of the integrals of peaks $h'$ and $h''$ at various times (see Figure 4A-B) to half that of peak $l$ (the proton of methylene group, $\delta=2.70$ ppm, see Figure S7). The fraction of isomerized cyclobutene was calculated by the ratio of the integrals of peaks $(d'+d''+d^*)$ at various times (see Figure 4A,C) to half that of peak $l$ (the proton of methylene group, $\delta=2.70$ ppm, see Figure S7).

The ratios of the two products of cyclobutene isomerization were calculated by the ratios of peak $d^*$ of the $E,E$-diene to the sum of peaks $d'$ and $d''$ of the $E,Z$-diene, Fig. S13.

![Graph](image_url)

Figure S13. The ratio of the fractions of dissociated cinnamate dimer to isomerized cyclobutene moieties at various sonication times.
Molecular weight dependence

Figure S14. Molecular weight dependence of sonication. The $^1$H NMR spectra of short P4 control with 3 h ultrasonication (red) and without ultrasonication (black).

To exclude the thermal effect during ultrasonication, we sonicated a shorter counterpart P4, which should experience much less stretching force but the same thermal effect. No change of $^1$H NMR was seen therefore the two dienes solely come from the mechanochemical ring-opening of Z-2.
Figure S15. Evolution of GPC traces of P1 as a function of sonication. (A) Refractive index traces, (B) UV traces.
The various sonication times are indicated in the legend. The concentration of P1 is 5 mg/mL in THF.

Table S4. Change of nominal molecular weight and dispersity of P1 during sonication.

| Sonication time (h) | $M_n$ (kDa) | $\bar{D}_M$ |
|---------------------|-------------|-------------|
| 0                   | 48          | 1.70        |
| 1                   | 38          | 1.43        |
| 2                   | 34          | 1.29        |
| 3                   | 30          | 1.28        |
| 4                   | 29          | 1.28        |
| 5                   | 28          | 1.27        |
| 6                   | 25          | 1.26        |
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