Supporting Information

Tuning Thermal Properties of Cross-Linked DCPD Polymers by Functionalization, Initiator Type and Curing Methods

No.	Content	Page
1.	General	S-2
2.	Synthesis and characterization of DCPD derivatives	S-3 – S-4
	2.1 Synthesis of endo-DCPD-OH (2)	S-3
	2.2 Synthesis of endo-DCPD-OAc (3)	S-3
	2.3 Synthesis of endo-DCPD-OPr (4)	S-4
3.	General procedure for homo-polymerization of monomers 1-4	S-4
	Table S1. Comparison between T_g values obtained by DMA analysis	
4.	following curing of monomer 2 for 1 and 5 h in the presence of either G-II	S-4
	or Ru-CAAC catalysts.	9.5
5.	Determination of cross-linking density for polymeric films $T_{\rm eff} = S_{\rm eff}^2 - T_{\rm eff} + C_{\rm eff}^2 + C$	5-5
	Table S2. I_g and E values at the rubbery plateau obtained from DMA curves at 10 Hz and calculated cross-linking density values therefrom for	
	selected polymeric films produced from all three catalysts (0.01 and 0.1	S-5
	mol-%) under thermal conditions	
	Table S3. T_{a} and E' values at the rubbery plateau obtained from DMA	
	curves at 10 Hz, and calculated cross-linking density values therefrom, for	
	selected co-polymeric films produced by all three catalysts (0.1 mol-%)	S-6
	under thermal conditions.	
	Figure S1. Comparison between calculated cross-linking values and $T_{\rm g}$	5.6
	values for polymeric films produced in both initiator	5-6
6.	General procedure for co-polymerizations	S-7
	Table S4. T_g values obtained by DMA analysis of polymeric films	S-7
	produced from mixture of DCPD-OH and DCPD-OPr (3:1).	5-7
	Table S5. T_g values obtained by DMA analysis of polymeric films	S-8
	produced from mixture of DCPD-OH and DCPD-OPr (1:1).	5 0
	Table S6. T_g values obtained by DMA analysis of polymeric films	S-8
	produced from mixture of DCPD-OH and DCPD-OPr (1:3).	~ -
7.	References	S-8
8.	Storage modulus (E') and Tan delta (δ) curves of homo-polymeric films	S-9 – S-30
9.	Storage modulus (E') and Tan delta (δ) curves of co-polymeric films	S-31 – S-47
10.	Table S7 . T_g values obtained by DMA and DSC analyses of selected poly-	S-48
11	DCPD samples	G 40 G 70
11.	DSC inermograms of selected poly-DCPD samples	5-49 - 5-38

Table of Content

1. General

Materials.

Solvents, reagents and DCPD monomer are commercially available and used without any further purification unless described otherwise. DMF and dichloromethane were dried by passing through a solvents drying machine.

NMR.

¹H and ¹³C NMR spectra of monomers **2-4** were recorded with either Avance-DPX 400 or DPX 500 Bruker instruments. Analyses were performed in CDCl₃ by using residual solvent signals: CDCl₃: $\delta_{\rm H} = 7.26$ ppm, $\delta_{\rm C} = 77.23$ ppm. Coupling constants (*J*) are reported in Hz. Signal multiplicities use the following abbreviations or combinations thereof: *s*-singlet, *d*-doublet, *t*-triplet, *m*-multiplet and *b*-broad.

DMA.

DMA measurements were performed using Mettler-Toledo Dynamic Mechanical Analyzer (DMA) 1 STAR^e instrument provided with rotatable measuring head. For polymeric films that display higher degree of rigidity, we used the single cantilever bending approach for determining the loss factor tan δ and semi-rigid polymeric films were examined by using the tension mode approach. Runs with frequencies at 1, 5 and 10 Hz were performed at a constant heating rate of 1-3 °C/min over pre-determined temperature range. Perceptibly inelastic polymeric films (length: 10 mm; width: 10 mm; thickness: 1 mm) were run over a temperature range of 30 °C to 150 °C. More elastic texture films (length: 10 mm; width: 5 mm; thickness: 1 mm) were run over a temperature range of -90 °C to 100 °C. Viscoelastic properties of the cured polymeric films were estimated from the changes in the storage modulus (E'), mechanical loss (E'') as well as from the changes of tan δ (tan $\delta = E''/E'$) at constant frequency depending on temperature. The T_g was identified as the maximum of the tan δ and the half of the full-width from the tan δ curve.

Differential Scanning Calorimetry (DSC) measurements.

All measurements were carried out with Thermal Analysis DSC instrument (METTLER TOLEDO) under a flow of nitrogen (80 mL/min). The samples was placed in a standard sealed aluminum pan of the type: DSC821e (40 μ L). The following temperature program was used in two cycles: equilibrate at 30 °C (10 min), ramp up to 150 °C at a heating rate of 5 °C /min., equilibrate at 150 °C (5 min) and then ramp down to 30 °C at a cooling rate of 10 °C /min. The data were recorded and analyzed on a TA program.

Cross-linking density calculations.

Cross-linking density of polymeric film, V_e was calculated by applying the equation derived from the theory of rubber elasticity: $E' = 3 \times V_e RT$, where E' (Mpa×9.8692 converts to atm unit) is the storage modulus in the rubbery plateau, R (82.057 cm³×atm×mol⁻¹×K⁻¹) is the gas constant and T (K) is the absolute temperature (T>> T_g).

2. Synthesis and characterization of the monomers:

2.1 *endo*-DCPD-OH (2):

The synthesis of endo-DCPD-OH was carried out as described previously.¹ endodicyclopentadiene (1) (0.303 mol) was dissolved in 120 ml of dioxane/H₂O (9:1, v/v) solution. Selenium dioxide (0.361 mol) was added in one portion; the solution was refluxed for 3 hours and cooled to room temperature. The solvent was removed under reduced pressure and the viscous brown oil was dissolved in 200 ml of diethyl ether, dried on magnesium sulfate, filtered and the solvent again evaporated. The crude brown oil was distilled at 1.5 mbar, the fraction at 74-76°C was collected to afford a pale yellow oil which crystallized at 4°C to a pale yellow solid, m.p. 30-35°C (isolated yield 67%).

Boiling point: 216 -217°C; ¹H NMR (400 MHz, CDCl₃, δ ppm): 5.91 (dd, J = 5.7, 3.0 Hz, 1H), 5.82 (dd, J = 5.7, 3.0 Hz, 1H), 5.78 – 5.71 (m, 1H), 5.61 – 5.55 (m, 1H), 4.04 (m, 1H), 3.35 (m, 1H), 3.03 (m, 1H), 2.77 (m, 1H), 2.51 (m, 1H), 1.95 (s, 1H), 1.54 (m, 1H), 1.37 (m, 1H); ¹³C NMR (100 MHz, CDCl3, δ ppm): 137.76, 135.41, 134.63, 132.38, 78.92, 54.64, 53.37, 51.23, 44.77 and 44.62.

2.2 *endo*-DCPD-OAc (3):

The synthesis of endo-DCPD-OAc (**3**) was carried out as described previously.¹ A three necked round bottom flask was charged with endo-DCPD-OH (**2**) (5 gm, 33.7 mmol) and was subjected to vacuum and then nitrogen consecutively three times. Then, dry DCM (250 ml) and Et₃N (8 ml) were added to it and the solution was stirred at 0°C for 10 min. Subsequently, the acetyl chloride (40.5 mmol) was added through syringe in dropwise fashion. It was then kept for 12 h stirring at room temperature. After that, it was washed with water. The organic layer was separated and dried over MgSO₄. It was finally concentrated and subjected to flash column chromatography for purification. The expected product *endo*-DCPD-OAc (**3**) was eluted with ethyl acetate/petroleum ether (1:19) on neutral alumina stationary phase. Colorless liquid (isolated yield: 85%).

Boiling point: 224-226°C; ¹H NMR (500 MHz, CDCl₃, δ ppm): 6.03 (dd, J = 5.5, 3.0 Hz, 1H), 5.88 (bd, J = 5.5 Hz, 1H), 5.86 (dd, J = 5.5, 3.0 Hz, 1H), 5.57 (bd, J = 5.5 Hz, 1H), 4.96 (bs, 1H), 3.38- 3.37 (m, 1H), 3.10 (bs, 1H), 2.82 (bs, 1H), 2.61 – 2.59 (m, 1H), 2.02 (s, 3H), 1.58 (bd, J = 8.2 Hz, 1H), 1.40 (bd, J = 8.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl3, δ ppm): 171.22, 140.15, 135.48, 132.68, 130.86, 82.23, 54.67, 51.47, 50.37, 44.94, 44.84 and 21.51.

2.3 *endo*-DCPD-OPr (4):

The synthesis of endo-DCPD-OPr (4) was carried out as described previously.¹ A three necked round bottom flask was charged with endo-DCPD-OH (2) (5 gm, 33.7 mmol) and NaH (1.75 gm, 43.9 mmol, 60%) and it was subjected to vacuum and then nitrogen consecutively three times. Then, dry DMF (100 ml) was added to it and was stirred at 0°C for 10 min, a purple colored solution was observed. Subsequently, 1-bromopropane (40.5 mmol) was added through syringe in dropwise fashion, the purple color disappeared and a pale white solution was observed. It was then kept for 12 h stirring at room temperature. After that, it was diluted with ethyl acetate (100 ml) and washed with saturated aq. NH₄Cl solution. The organic layer was then separated and dried over MgSO₄. It was finally concentrated and subjected to flash column chromatography for purification. The expected product endo-DCPD-OPr (4) was eluted with ethyl acetate/ petroleum ether (1: 19) on silica gel stationary phase. Colorless liquid (isolated yield: 91%).

Boiling point: 216-218°C; ¹H NMR (400 MHz, CDCl₃, δ ppm): 5.96 (bdd, J = 5.8 Hz, 3 Hz, 1H), 5.86 (bdd, J = 5.8, 3.0 Hz, 1H), 5.80 (bd, J = 5.6 Hz, 1H), 5.65 – 5.63 (m, 1H), 3.78-3.76 (m, 1H), 3.47- 3.31 (m, 3H), 2.99 (bs, 1H), 2.79 (bs, 1H), 2.63-2.59 (m, 1H), 1.63 – 1.56 (m, 3H), 1.42 (d, J = 8 Hz, 1H), 0.92 (t, 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl3, δ ppm) (4b): 138.24, 135.58, 132.54, 132.50, 86.61, 70.33, 54.85, 51.47, 50.18, 45.37, 44.67, 23.44 and 10.84.

3. General procedure for homo-polymerizations:

Monomer (0.5 g) was introduced to a 4 mL glass vial and then solution of Ru-catalyst (0.10, 0.05, or 0.01 mol %) dissolved in dry CH_2Cl_2 (~50 µl) was added. After mixing the solution very quickly, the solvent was removed by gentle blowing of argon and the remaining mixture was transferred into a rectangular shaped aluminum mold (50x10x1 mm³) and placed in a preset oven at temperature of 90 °C for 1 or 5h depending on used catalyst (see Tables 1-4 and text in MS). Homo-polymerization induced by light were performed in a Luzchem photo reactor (LZC-ORG model) equipped with ten lamp tubes (350 nm).

4. Comparison between T_g values obtained by DMA analysis following curing of monomer 2 for 1 and 5 h in the presence of either G-II or Ru-CAAC catalysts.

Initiator	Curing	Polymer	7	$\mathcal{F}_{g}(\mathbf{K})$ ons	et	$T_g(\mathbf{K}) \tan \delta$			
(mol %)	duration (h)	films	1 Hz	5 Hz	10 Hz	1 Hz	5 Hz	10 Hz	
		·	G-II at	90 °C					
0.10	1	2c	380.7	382.3	383.0	405.4	411.1	417.3	
5	5	2c	377.1	378.0	379.4	401.3	409.3	410.0	
		Н	G-CAA	C at 90 °C	, ,				
0.10	1	2f	358.4	359.1	359.4	383.4	395.8	400.3	
0.10	5	2c	353.2	356.1	356.1	386.7	398.5	404.1	

Table S1.

5. Determination of cross-linking density for polymeric films.

Table S2. T_g and E' values at the rubbery plateau obtained from DMA curves at 10 Hz, and calculated cross-linking density values therefrom, for selected polymeric films produced from all three catalysts (0.01 and 0.1 mol-%) under thermal conditions.

Catalyst type	Monomer	<i>T</i> g (K)	T (K) at rubbery plateau	′ E' (Mpa at 10 Hz)	E' (atm)	<i>V</i> e (mol cm⁻³)10⁻³
	1a	369.2	409.4	11.43	112.81	1.12
G-II	2a	353.3	390.7	32.81	323.85	3.37
(0.01 mol-%)	3a	369.8	393.85	15.71	155.05	1.60
	4a	341.8	355.35	2.72	26.85	0.31
	1d	366.8	393.8	63.46	626.29	6.46
HG-CAAC	2d	250	279.4	21.88	215.90	3.14
(0.01 mol-%)	3d	330.9	399.1	16.67	164.48	1.67
	4d	342.3	359.2	4.03	39.78	0.45
	1g	366.8	385.8	15.06	148.67	1.57
<i>cis-</i> Ru-SPh	2g	337.4	372.4	7.39	72.95	0.80
(0.01 mol-%)	3g	ND				
	4g	342.3	376.7	10.3402	102.0495018	1.10
Catalyst type	Monomer	<i>T</i> g (K)	T (K) at rubbery plateau	/ E' (Mpa at 10 Hz)	E' (atm)	V _e (mol´cm ⁻³)10 ⁻³
Catalyst type	Monomer 1c	7g (K) 378.9	T (K) at rubbery plateau 417.1	/ E' (Mpa at 10 Hz) 14.09	E' (atm) 139.10	V _e (mol´cm ⁻³)10 ⁻³ 1.35
Catalyst type G-ll	Monomer 1c 2c	Tg (K) 378.9 383	T (K) at rubbery plateau 417.1 419	(Mpa at 10 Hz) 14.09 20.76	E' (atm) 139.10 204.88	V _e (mol´cm ⁻³)10 ⁻³ 1.35 1.99
G-II (0.1 mol-%)	Monomer 1c 2c 3c	7g (K) 378.9 383 376.5	T (K) at rubbery plateau 417.1 419 413.7	E' (Mpa at 10 Hz) 14.09 20.76 24.62	E' (atm) 139.10 204.88 242.96	V _e (mol´cm ⁻³)10 ⁻³ 1.35 1.99 2.39
Catalyst type G-II (0.1 mol-%)	Monomer 1c 2c 3c 4c	7g (K) 378.9 383 376.5 359.2	T (K) at rubbery plateau 417.1 419 413.7 376.4	E' (Mpa at 10 Hz) 14.09 20.76 24.62 10.83	E' (atm) 139.10 204.88 242.96 106.91	V _e (mol´cm ⁻³)10 ⁻³ 1.35 1.99 2.39 1.15
Catalyst type G-II (0.1 mol-%)	Monomer 1c 2c 3c 4c 1f	7g (K) 378.9 383 376.5 359.2 ND	T (K) at rubbery plateau 417.1 419 413.7 376.4	E' (Mpa at 10 Hz) 14.09 20.76 24.62 10.83	E' (atm) 139.10 204.88 242.96 106.91	Ve (mol´cm³)10 ⁻³ 1.35 1.99 2.39 1.15
Catalyst type G-II (0.1 mol-%) HG-CAAC	Monomer 1c 2c 3c 4c 1f 2f	7g (K) 378.9 383 376.5 359.2 ND 359.4	T (K) at rubbery plateau 417.1 419 413.7 376.4 399.3	<pre>c E' (Mpa at 10 Hz) 14.09 20.76 24.62 10.83 49.81</pre>	E' (atm) 139.10 204.88 242.96 106.91 491.62	Ve (mol´cm ⁻³)10 ⁻³ 1.35 1.99 2.39 1.15 5.00
Catalyst type G-II (0.1 mol-%) HG-CAAC (0.1 mol-%)	Monomer 1c 2c 3c 4c 1f 2f 3f	7g (K) 378.9 383 376.5 359.2 ND 359.4 372.5	T (K) at rubbery plateau 417.1 419 413.7 376.4 399.3 386.7	<pre></pre>	E' (atm) 139.10 204.88 242.96 106.91 491.62 164.05	Ve (mol´cm ⁻³)10 ⁻³ 1.35 1.99 2.39 1.15 5.00 1.72
Catalyst type G-II (0.1 mol-%) HG-CAAC (0.1 mol-%)	Monomer 1c 2c 3c 4c 1f 2f 3f 4f	7g (K) 378.9 383 376.5 359.2 ND 359.4 372.5 342.6	T (K) at rubbery plateau 417.1 419 413.7 376.4 399.3 386.7 351.8	E' (Mpa at 10 Hz) 14.09 20.76 24.62 10.83 49.81 16.62 0.27	E' (atm) 139.10 204.88 242.96 106.91 491.62 164.05 2.62	Ve (mol´cm ⁻³)10 ⁻³ 1.35 1.99 2.39 1.15 5.00 1.72 0.03
Catalyst type G-II (0.1 mol-%) HG-CAAC (0.1 mol-%)	Monomer 1c 2c 3c 4c 1f 2f 3f 4f 1i	7g (K) 378.9 383 376.5 359.2 ND 359.4 372.5 342.6 374.4	T (K) at rubbery plateau 417.1 419 413.7 376.4 399.3 386.7 351.8 388.8	<pre>c E' (Mpa at 10 Hz) 14.09 20.76 24.62 10.83 49.81 16.62 0.27 34.17</pre>	E' (atm) 139.10 204.88 242.96 106.91 491.62 164.05 2.62 337.21	Ve (mol´cm ⁻³)10 ⁻³ 1.35 1.99 2.39 1.15 5.00 1.72 0.03 3.52
Catalyst type G-II (0.1 mol-%) HG-CAAC (0.1 mol-%) <i>cis</i> -Ru-SPh	Monomer 1c 2c 3c 4c 1f 2f 3f 4f 1i 2i	7g (K) 378.9 383 376.5 359.2 ND 359.4 372.5 342.6 374.4 362.7	T (K) at rubbery plateau 417.1 419 413.7 376.4 399.3 386.7 351.8 388.8 388.8 388.7	<pre></pre>	E' (atm) 139.10 204.88 242.96 106.91 491.62 164.05 2.62 337.21 1040.17	Ve (mol´cm ⁻³)10 ⁻³ 1.35 1.99 2.39 1.15 5.00 1.72 0.03 3.52 10.87
Catalyst type G-II (0.1 mol-%) HG-CAAC (0.1 mol-%) cis-Ru-SPh (0.1 mol-%)	Monomer 1c 2c 3c 4c 1f 2f 3f 4f 1i 2i 3i	7g (K) 378.9 383 376.5 359.2 ND 359.4 372.5 342.6 374.4 362.7 354.3	T (K) at rubbery plateau 417.1 419 413.7 376.4 399.3 386.7 351.8 388.8 388.7 373.8	<pre>c E' (Mpa at 10 Hz) 14.09 20.76 24.62 10.83 49.81 16.62 0.27 34.17 105.40 2.56</pre>	E' (atm) 139.10 204.88 242.96 106.91 491.62 164.05 2.62 337.21 1040.17 25.26	Ve (mol´cm ⁻³)10 ⁻³ 1.35 1.99 2.39 1.15 5.00 1.72 0.03 3.52 10.87 0.27

Table S3. T_g and E' values at the rubbery plateau obtained from DMA curves at 10 Hz, and calculated cross-linking density values therefrom, for selected co-polymeric films produced by all three catalysts (0.1 mol-%) under thermal conditions.

Catalyst type	Monomer	<i>T</i> g (K)	T (K) at rubbery plateau	E' (Mpa at 10 Hz)	E' (atm)	<i>V</i> ℯ (mol cm⁻³)10⁻³
	2c	383	419	20.76	204.88	1.99
	5c	387.6	420.7	3.70	36.49	0.35
G-II	6c	395.3	416.9	6.88	67.86	0.66
	7c	380	405.4	0.74	7.31	0.07
	4c	359.2	376.4	10.83	106.91	1.15
	2f	359.4	399.3	49.81	491.62	5.00
	5f	363.2	400.9	4.37	43.16	0.44
HG-CAAC	6f	367.3	414.3	2.76	27.25	0.27
	7f	370.6	403.9	1.30	12.88	0.13
	4f	342.6	351.8	0.27	2.62	0.03
	2i	362.7	388.7	105.40	1040.17	10.87
	5i	369.5	409.3	3.12	30.78	0.31
cis-Ru-SPh	6i	364.7	410.8	2.76	27.22	0.27
	7i	364.3	395.9	1.83	18.05	0.19
	4i	351.1	377.7	9.34	92.18	0.99



Figure S1. Glass-transition temperatures *vs.* calculated cross-linking density values of reperesenatative polymeric films produced from monomers **1-4** (see also Tabe S2).

6. General procedure for co-polymerizations:

To a mixture of monomers **2** and **4** in ratio of 3:1, 1:1 or 1:3 in a 4 mL glass vial was added solution of Ru-catalyst (0.10, 0.05, or 0.01 mol %) in dry CH_2Cl_2 (~50 µl). After mixing the solution very quickly, the solvent was removed by gentle blowing of argon and the remaining mixture was transferred into a rectangular shaped aluminum mold (50x10x1 mm³) and placed in a preset oven at temperature of 90 °C for 1 or 5h depending on used catalyst (see Tables 5 and S1-S3). Co-polymerization induced by light were performed in a Luzchem photo reactor (LZC-ORG model) equipped with ten lamp tubes (350 nm).

Initiator	Dolumorio filmo	Т	' _g (°K) ons	et	T_{s}	_g (°K) tan	δ
(mol-%)	Foryment mins	1 Hz	5 Hz	10 Hz	1 Hz	5 Hz	10 Hz
		G-II at	90 °C for	[.] 1 h.			
0.01	5a	349.5	350.5	352.8	372.2	377.9	380.8
0.05	5b	370.5	372.3	373.6	390.9	398.5	402.4
0.10	5c	384.4	386.29	387.6	405.0	407.5	412.9
	Η	G-CAA	C at 90 °C	for 1 h.			
0.01	5d	NA	NA	NA	NA	NA	NA
0.05	5e	347.1	348.1	349.3	352.9	359.6	362.5
0.10	5f	358.9	361.7	363.2	385.3	389.9	398.2
	ci	s-Ru-SP	h at 90 °C	C for 5h.			
0.01	5g	322.1	322.1	322.1	347.6	353.7	358.4
0.05	5h	333.8	334.1	334.2	377.8	384.2	388.3
0.10	5 i	365.5	367.8	369.5	398.3	402.5	407.4
	<i>cis</i> -Ru-SPl	h, irradia	tion at λ =	= 350 nm :	for 24h.		
0.01	<u>5</u> g'	205.9	206.3	207.4	259.1	264.9	268.2
0.05	5h'	310.2	312.4	313.6	339.7	343.0	343.6
0.10	5i'	319.6	320.3	321.6	342.0	343.2	348.6

Table-S4. T_g values obtained by DMA analysis of polymeric films produced from mixture of DCPD-OH and DCPD-OPr (3:1).

Initiator	Polymer	Т	' _g (°K) ons	et	Τ	' _g (°K) tan	δ			
(mol-%)	films	1 Hz	5 Hz	10 Hz	1 Hz	5 Hz	10 Hz			
		G-II	at 90 °C f	for 1 h.						
0.01	6a	361.2	362.6	363.0	386.3	394.6	400.3			
0.05	6b	383.0	384.5	385.9	402.0	409.4	411.7			
0.10	6c	392.1	393.9	395.3	410.8	418.1	420.0			
	HG-CAAC at 90 °C for 1 h.									
0.01	6d	355.6	356.3	357.6	380.3	387.2	390.0			
0.05	6e	361.9	363.1	363.5	387.8	397.2	402.1			
0.10	6f	366.4	367.1	367.3	399.2	410.2	414.8			
		cis-Ru-S	SPh at 90	°C for 5h.						
0.01	6g	210.3	212.1	214.5	268.3	274.1	277.0			
0.05	6 h	333.8	333.8	333.9	364.6	371.7	374.8			
0.10	6i	363.3	364.4	364.7	390.1	397.9	402.4			
	<i>cis</i> -Ru-	-SPh, irrac	liation at 7	n = 350 nm	n for 24h.					
0.01	6 g '	NA	NA	NA	NA	NA	NA			
0.05	6h'	320.7	321.1	321.3	334.1	338.7	342.6			
0.10	6i'	325.1	325.1	325.1	325.0	333.1	336.3			

Table-S5. T_g values obtained by DMA analysis of polymeric films produced from mixture of DCPD-OH and DCPD-OPr (1:1).

Table-S6. T_g values obtained by DMA analysis of polymeric films produced from mixture of DCPD-OH and DCPD-OPr (1:3).

Initiator	Polymer	Т	g (°K) ons	et	T	g (°K) tan	δ		
(mol-%)	films	1 Hz	5 Hz	10 Hz	1 Hz	5 Hz	10 Hz		
		G-II	at 90 °C f	for 1 h.					
0.01	7a	370.1	372.7	373.7	387.7	391.8	394.3		
0.05	7b	376.6	377.5	378.6	393.3	397.3	400.0		
0.10	7c	377.4	378.4	380.0	393.0	398.3	400.9		
	HG-CAAC at 90 °C for 1 h.								
0.01	7d	355.4	356.8	357.2	369.9	373.8	378.9		
0.05	7e	367.1	368.1	369.1	385.6	389.0	391.7		
0.10	7f	367.9	368.7	370.6	387.9	394.5	399.2		
		<i>cis</i> -Ru-S	SPh at 90	°C for 5h.					
0.01	7g	241.9	244.5	246.8	281.3	248.4	287.5		
0.05	7h	351.9	352.2	353.4	365.7	371.3	374.1		
0.10	7i	361.7	363.0	364.3	382.5	389.2	393.0		
	<i>cis</i> -Ru-	SPh, irrad	liation at λ	L = 350 nm	n for 24h.				
0.01	7g'	292.4	294.9	295.6	302.5	308.2	308.9		
0.05	7 h '	329.0	329.0	329.1	345.6	349.6	352.4		
0.10	7i'	332.7	333.8	334.6	381.6	389.0	392.8		

7. References:

 Saha, S.; Ginzburg, Y.; Rozenberg, I.; Iliashevsky, O.; Ben-Asuly, A.; Lemcoff, N. G., Cross-linked ROMP polymers based on odourless dicyclopentadiene derivatives. *Polym. Chem.* 2016, 7, 3071-3075.



8. Storage modulus (E') and Tan delta (δ) curves of homo-polymeric films

Figure S2. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **1a**.



Figure S3. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **1b**.



Figure S4. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of 1c.



Figure S5. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of 1d.



Figure S6. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **1g**.



Figure S7. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **1h**.



Figure S8. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **1i**.



Figure S9. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **1g'**.



Figure S10. Storage modulus (*E*') curves (top) and Tan delta (δ) curves (down) of



Figure S11. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **1i'**.



Figure S12. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **2a**.



Figure S13. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **2b**.



Figure S14. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 2c (1h).



Figure S15. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 2c (5h).



Figure S16. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **2d**.



Figure S17. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 2e.



Figure S18. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 2f (1h).



Figure S19. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 2f (5h).



Figure S20. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **2g**.



Figure S21. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 2h.



Figure S22. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 2i.



Figure S23. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **2g'**.



Figure S24. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **2h'**.



Figure S25. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **2i'**.



Figure S26. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of **3a**.



Figure S27. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **3b**.



Figure S28. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **3c**.



Figure S29. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 3d.



Figure S30. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **3e**.



Figure S31. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 3f.



Figure S32. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **3i**.



Figure S33. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 3i'.



Figure S34. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 4a.



Figure S35. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **4b**.



Figure S36. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **4c**.



Figure S37. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of 4d.



Figure S38. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **4e**.



Figure S39. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 4f.



Figure S40. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **4g**.



Figure S41. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 4h.



Figure S42. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **4i**.



Figure S43. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 4h'.



Figure S44. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **4i'**.



9. Storage modulus (E') and Tan delta (δ) curves for copolymers

Figure S45. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5a**.



Figure S46. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5b**.



Figure S47. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5c**.



Figure S48. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5e**.



Figure S49. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5f**.



Figure S50. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5g**.



Figure S51. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5h**.



Figure S52. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5**i.



Figure S53. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5g'**.



Figure S54. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5h'**.



Figure S55. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **5i'**.



Figure S56. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6a**.



Figure S57. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6b**.



Figure S58. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6c**.



Figure S59. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6d**.



Figure S60. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6e**.



Figure S61. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6f**.



Figure S62. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6g**.



Figure S63. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6h**.



Figure S64. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6**i.



Figure S65. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6h'**.



Figure S66. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **6i'**.



Figure S67. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7a**.



Figure S68. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7b**.



Figure S69. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7c**.



Figure S70. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7d**.



Figure S71. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7e**.



Figure S72. Storage modulus (E') curves (top) and Tan delta (δ) curves (down) of 7f.



Figure S73. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7g**.



Figure S74. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7h**.



Figure S75. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7i**.



Figure S76. Storage modulus (*E*') curves (top) and Tan delta (δ) curves (down) of **7g**'.



Figure S77. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of m **7h'**.



Figure S78. Storage modulus (*E'*) curves (top) and Tan delta (δ) curves (down) of **7i'**.

Polymeric films	T_g (K) onset (DMA)			7	T_g (K) tan δ (DMA)	T_g (K) Onset (DSC)	
	1 Hz	5 Hz	10 Hz	1 Hz	5 Hz	10 Hz	(_ ~ -)
1a	365.4	368.5	369.2	380.7	387.0	390.3	367.9
1c	376.7	377.2	378.9	405.7	408.7	409.9	352.5
1d	366.0	366.4	366.8	380.5	383.0	384.0	362.9
1g	366.0	366.4	366.8	380.5	383.0	384.0	351.4
1i	373.2	373.3	374.4	402.2	413.6	418.4	396.6
2a	351.2	351.9	353.3	360.0	373.4	375.8	380.8
2c	380.7	382.3	383.0	405.4	411.1	417.3	397.7
2 f	358.4	359.1	359.4	383.4	395.8	400.3	377.7
2g	334.7	336.4	337.4	353.8	358.3	361.6	367.0
2i	361.6	362.2	362.7	380.1	386.1	392.8	387.8
3 a	369.4	369.6	369.8	373.6	374.8	376.5	371.8
3c	373.8	375.5	376.5	389.8	392.7	395.1	364.2
3d	330.8	330.8	330.9	359.4	363.6	367.1	378.1
3f	368.3	367.0	372.5	385.0	386.3	391.1	362.1
<u>3i</u>	352.0	353.0	354.3	374.7	378.3	381.2	407.2
4a	340.5	341.5	341.8	344.9	349.5	351.8	339.0
4c	354.1	357.2	359.2	362.3	367.5	371.3	332.3
4f	341.7	342.2	342.6	354.8	359.6	362.9	332.1
4g	340.0	341.6	342.3	359.3	362.8	365.5	333.6
4 i	350.0	350.6	351.1	365.4	370.4	372.8	348.1

10. Table S7. $T_{\rm g}$ values obtained by DMA and DSC analyses of selected poly-DCPD samples

11. DSC thermograms of selected poly-DCPD samples



Figure S79. DSC analysis graph of 1a



Figure S80. DSC analysis graph of 1c



Figure S81. DSC analysis graph of 1d



Figure S82. DSC analysis graph of 1g



Figure S83. DSC analysis graph of 1i



Figure S84. DSC analysis graph of 2a



Figure S85. DSC analysis graph of 2c



Figure S86. DSC analysis graph of 2f



Figure S87. DSC analysis graph of 2g



Figure S88. DSC analysis graph of 2i



Figure S89. DSC analysis graph of 3a



Figure S90. DSC analysis graph of 3c



Figure S91. DSC analysis graph of 3d



Figure S92. DSC analysis graph of 3f



Figure S93. DSC analysis graph of 3i



Figure S94. DSC analysis graph of 4a



Figure S95. DSC analysis graph of 4c

`exo			RSP-4F-DSC	≻Tg		31.12	.2019 (09:33:0
Sample: RSP-4F, 22.2200 mg Experiment: RSP-4F, 31.12.20	19 07:13:31	Module:	DSC823e/700/484 Air, 18.04.	2007 11:15:04		Methu dt 1.0 30.0 150. 30.0 30.0 Synch	ad: DSC-30-150 0 s ⊢150.0°C 5.00° 0°C 5.0 min 0°C 5.0 min 0°C 10.0 min ⊢150.0°C 5.00° ronization enab	-30-5-Air=0 C/min 0°C/min C/min led
Ng^1 15[8:IRSP-4F RSP-4F, 22.2200 mg	Glass Transition Onset Midpoint Deta Cp Midpoint ASTM,IEC Midpoint ASTM,IEC Deta cp ASTM,IEC Deta cp Richardson	58.94 ℃ 64.63 ℃ 0.160 Jg^1K^1 63.64 ℃ 63.85 ℃ 0.164 Jg^1K^1 0.120 Jg^1K^1 0.120 Jg^1K^1						Heating
]1[&IRSP-4F RSP-4F, 22:2200 mg	Integral -28 normalized -1.1. Onset 34. Peak Height 15. Peak 40. Extrapol. Peak 40. Endset 45. Peak Width 6.7	27 mJ 27 Jg^-1 28 °C 63e-03 Wg^-1 49 °C 44 °C 47 °C 9 °C						Heating
<u>30 40</u> ah: Δna	50 60	70	80 90	100	110	120 1	30 STARe	140 SVV/Q(

Figure S96. DSC analysis graph of 4f



Figure S97. DSC analysis graph of 4g



Figure S98. DSC analysis graph of 4i