Supplementary Information

Synthesis of 2-acetoxy-3-cardanylpropyl methacrylate (ACPM)

To a THF solution (20 mL) of HCPM (2.00 g, 4.50 mmol) and acetyl chloride (0.53 g, 6.75 mmol), triethylamine (0.911 g, 9.00 mmol) was slowly added in an ice bath. The solution mixture was reacted in nitrogen atmosphere for 14 h and the solvent was evaporated. The crude product was dissolved in methylene chloride (MC) and transferred to a separatory funnel. After extraction with 0.5 *N* HCl solution, the MC layer was dried over anhydrous magnesium sulfate and filtered. Crude product was purified by silica gel column chromatography (ethyl acetate : n-hexane = 1 : 6). The yield was 33.8 % (0.74 g).

^{1}H NMR (300 MHz, $CDCl_3$, TMS ref): δ = 0.88 (t, 3 H, $–C\mathit{H}_3$), 1.20–1.40 (m, $CH_3(C\mathit{H}_2)12CH_2$–), 1.59 (m, 2 H, $CH_3(CH_2)_{12}C\mathit{H}_2CH_2$–), 1.94 (s, 3 H, $–OC(O)C(C\mathit{H}_3)=CH_2$), 2.02 (m, $–CH_2CH_2C\mathit{H}_2CH=CHCH_2$–), 2.11 (s, 3 H, $–OC(O)C\mathit{H}_3$), 2.56 (t, 2 H, $–OC_6H_4C\mathit{H}_2$–), 2.77–2.83 (m, $–CH_2CH=CHC\mathit{H}_2CH=CH$–), 4.12-4.53 (m, 5 H, $–OC\mathit{H}_2C\mathit{H}(OAc)C\mathit{H}_2OC(O)$–), 5.32–5.46 (m, $–CH_2C\mathit{H}=C\mathit{H}CH_2$–), 5.60 and 6.12 (s, 2 H, $–OC(O)C(CH_3)=C\mathit{H}_2$), 6.70–6.81 (m, 3 H, aromatic), 7.19 (t, 1 H, aromatic). FT-IR: 3010 cm^{-1} (C-H vibration of the unsaturated hydrocarbon), 1747 cm^{-1} (C=O stretching vibration (acetate), 1724 cm^{-1} (C=O stretching vibration (α,β-unsaturated ester), 1257 cm^{-1} (C(Ar)-O-C asymmetric stretching vibration (m-alkyl phenol)), 1054 cm^{-1} (C(Ar)-O-C symmetric stretching vibration (m-alkyl phenol)), 775 cm^{-1} ($-CH_2-$ rocking vibration), 721 cm^{-1} ($-(CH_2)_n-$, n>3; rocking vibration), 694 cm^{-1} (aromatic out of plane C-H deformation vibration of meta-substituted benzene). Mass *m/z* calculated: $C_{30}H_{46}O_5^+$: 486.33, found 486.

Synthesis of poly(2-acetoxy-3-cardanylpropyl methacrylate) (PACPM)

ACPM (1.10 g, 2.26 mmol), AIBN (5 wt%, 0.055 g), and THF (10 mL) were added to a round-bottomed flask fitted with a condenser. The mixtures were heated with stirring and refluxed in nitrogen atmosphere for 24 h, and then poured into distilled water. The flask was purged with N_2 and sonicated for 10 min to degas the mixture and remove dissolved oxygen. Then, the mixture was heated with stirring and refluxed. After 24 h of polymerization, the solution was exposed to air. The crude product was poured into excess of distilled water/methanol (2/1). The dissolution-precipitation procedure was repeated three times, yielding a yellowish wax (0.67 g). The M_n and PDI of synthesized P-ACPM by GPC (polystyrene standards, THF as an eluent) were 14,000 g mol^{-1} and 2.50, respectively.

^{1}H NMR (300 MHz, $CDCl_3$, TMS ref): δ = 0.88 (t, 3 H, $–C\mathit{H}_3$), 1.20-1.40 (m, $CH3(C\mathit{H}_2)12CH_2$– and backbone), 1.55 (m, 2 H, $CH_3(CH_2)_{12}C\mathit{H}_2CH_2$–), 2.01 (m, $–CH_2CH_2C\mathit{H}_2CH=CHCH_2$–), 2.11 (s, 3 H, $–OC(O)C\mathit{H}_3$), 2.52 (t, 2 H, $–OC_6H_4C\mathit{H}_2$–), 2.70–2.85 (m, $–CH_2CH=CHC\mathit{H}_2CH=CH$–), 3.90–4.50 (m, 5 H, $–OC\mathit{H}_2C\mathit{H}(OAc)C\mathit{H}_2OC(O)$–), 5.32–5.46 (m, $–CH_2C\mathit{H}=C\mathit{H}CH_2$–), 6.60–6.81 (m, 3 H, aromatic), 7.13 (t, 1 H, aromatic). FT-IR: 3010 cm^{-1} (C-H vibration of the unsaturated hydrocarbon), 1742 cm^{-1} (C=O stretching vibration (saturated aliphatic ester), 1257 cm^{-1} (C(Ar)-O-C asymmetric stretching vibration (m-alkyl phenol)), 1054 cm^{-1} (C(Ar)-O-C symmetric stretching vibration (m-alkyl phenol)), 775 cm^{-1} ($-CH_2-$ rocking vibration), 721 cm^{-1} ($-(CH_2)_n-$, n>3; rocking vibration), 694 cm^{-1} (aromatic out of plane C-H deformation vibration of meta-substituted benzene)

Synthesis of cardanyl acrylate (CA)

Cardanyl acrylate (CA) was synthesized by the procedure reported.[1] Cardanol (30 g, 0.1 mol) and toluene (200 mL) were placed in a three-necked round-bottom flask (500 mL) equipped with a dropping funnel and a Dean-Stark trap. Sodium hydroxide aqueous solution (0.11 mol, 4.4 g, in 5 mL H_2O) was drop-wised to it via the dropping funnel, while the solution was heated with stirring and refluxed. Refluxing was continued until the azeotropic removal of water was complete (4 h). The mixture solution was cooled to 45 ^{o}C and hydroquinone (1 % of the weight of cardanol) was added. Later, acryloyl chloride (0.12 mol, 10.86 g) was slowly drop-wised to mixture solution and reacted overnight at 45 ^{o}C. After the reaction was finished with dropping few drops of a concentrated HCl solution, toluene was evaporated. The crude product was dissolved in methylene chloride (MC) and transferred to a separatory funnel. After extraction with 0.5 *N* HCl solution, the MC layer was dried over anhydrous magnesium sulfate and filtered. The obtained product was purified by silica gel column chromatography (ethyl acetate : *n*-hexane = 1 : 30). The yield was 65 % (25.1 g).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.88 (t, *J* = 6.78 Hz, 3 H, $–CH_3$), 1.20–1.40 (m, $CH_3(CH_2)_{12}CH_2–$), 1.60 (m, 2 H, $CH_3(CH_2)_{12}CH_2CH_2–$), 1.97 (s, 3 H, $–OC(O)C(CH_3)=CH_2$), 2.02 (m, $–CH_2CH_2CH_2CH=CHCH_2–$), 2.57 (t, *J* = 8.04 Hz, 2 H, $–OC_6H_4CH_2–$), 2.75–2.90 (m, $–CH_2CH=CHCH_2CH=CH–$), 3.94–4.40 (m, 5 H, $–OCH_2CH(OH)CH_2OC(O)–$), 5.20–5.50 (m, $–CH_2CH=CHCH_2–$), 5.62 and 6.26 (s, 2 H, $–OC(O)C(CH_3)=CH_2$), 6.67–6.83 (m, 3 H, aromatic), 7.19 (t, *J* = 7.5 Hz, 1 H, aromatic)

Synthesis of poly(cardanyl acrylate) (PCA)

Poly(cardanyl acrylate) (PCA) was synthesized by the procedure reported.[2] CA (1.5 g, 4.21 mmol), AIBN (2 wt %, 0.030 g), and toluene (10 mL) were added to a round-bottomed flask fitted with a condenser. The flask was purged with N_2 and sonicated for 10 min to degas the mixture and remove dissolved oxygen. Then, the mixture was heated with stirring and refluxed. After 24 h of polymerization, the solution was exposed to air. The crude product was poured into excess of methanol. The dissolution-precipitation procedure was repeated three times, yielding a yellowish wax (0.9 g). The M_n and PDI of synthesized PCA by GPC (polystyrene standards, THF as an eluent) were 6,700 g mol^{-1} and 1.40, respectively.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.88 (t, 3 H, –CH3), 1.20-1.40 (m, $CH_3(CH_2)_{12}CH_2–$ and backbone), 1.55 (m, 2 H, $CH_3(CH_2)_{12}CH_2CH_2–$), 2.01 (m, $–CH_2CH_2CH_2CH=CHCH_2–$), 2.11 (s, 3 H, $–OC(O)CH_3$), 2.52 (t, 2 H, $–OC_6H_4CH_2–$), 2.70-2.85 (m, $–CH_2CH=CHCH_2CH=CH–$), 3.90-4.50 (m, 5 H, $–OCH_2CH(OAc)CH_2OC(O)–$), 5.32-5.46 (m, $–CH_2CH=CHCH_2–$), 6.60-6.81 (m, 3 H, aromatic), 7.13 (t, 1 H, aromatic)

Characterization

Wide-angle X-ray scattering was used to analyze the chemical structures of polymer samples. The measurements were carried out using Rigaku Model Smart Lab.

Table S1. Results of gel fraction test of PHMC films.

Sample	$W_1{}^a$ (mg)	$W_2{}^b$ (mg)	Gel fraction (%)
PHM100C	34.8	32.8	94.3
PHM47C	36.0	31.9	88.6
PHM10C	23.3	17.6	75.5

[a] W_1: weight of the dry film before the gel fraction test.

[b] W_2: weight of the dry film after the gel fraction test.

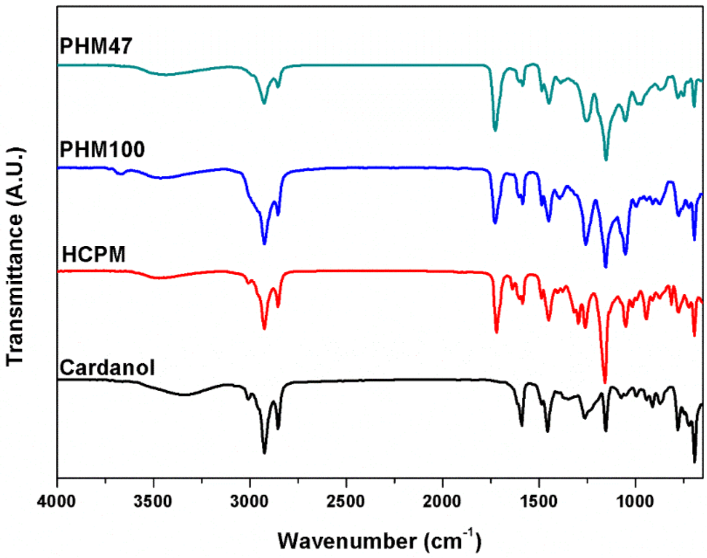

Fig. S1. FT-IR/ATR spectra of cardanol, HCPM, PHM100, and PHM47.

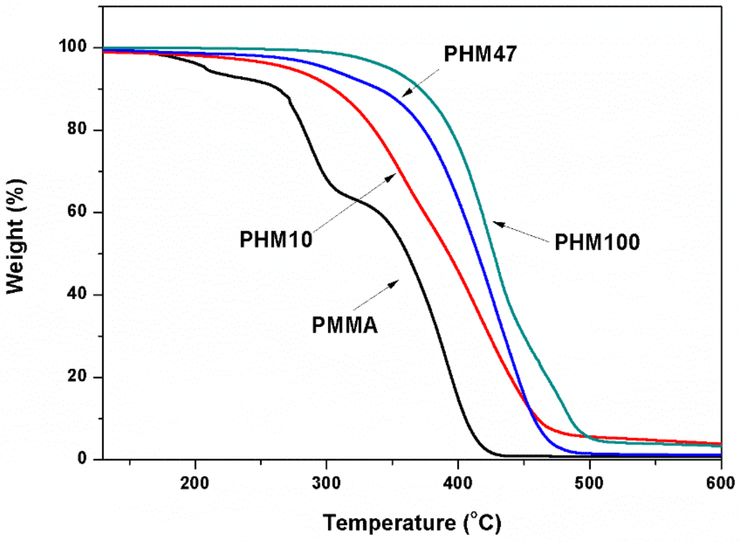

Fig. S2. TGA thermograms of PHMs under N_2 atmosphere.

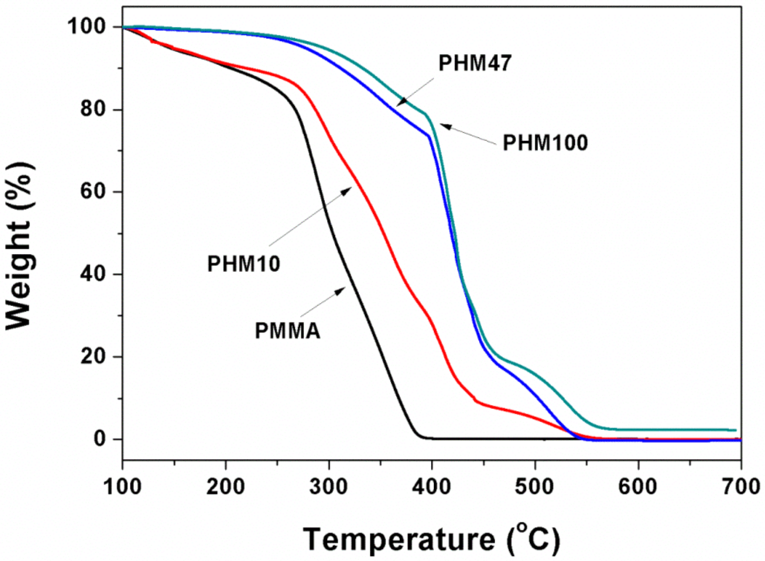

Fig. S3. TGA thermograms of PHMs under air atmosphere.

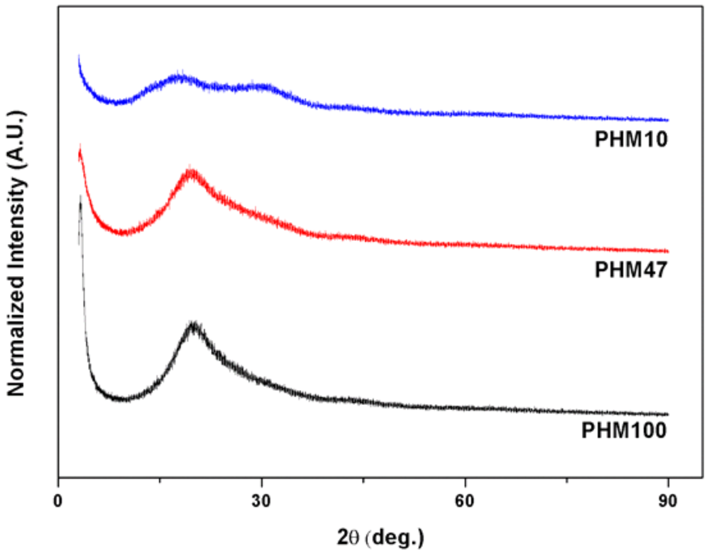

Fig. S4. Line profiles of WAXS diffractograms of PHM100, PHM47, and PHM10.

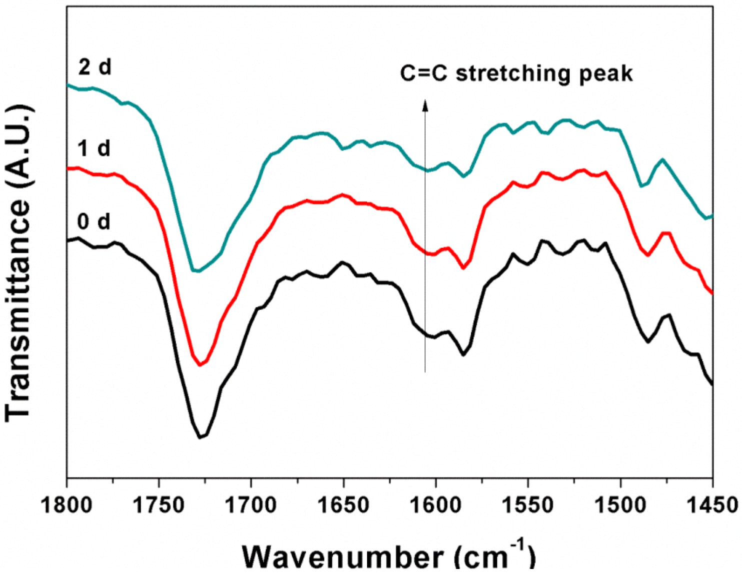

Fig. S5. FT-IR/ATR spectra of PHM100 film in the low frequency region after UV irradiation for 1 and 2 days.

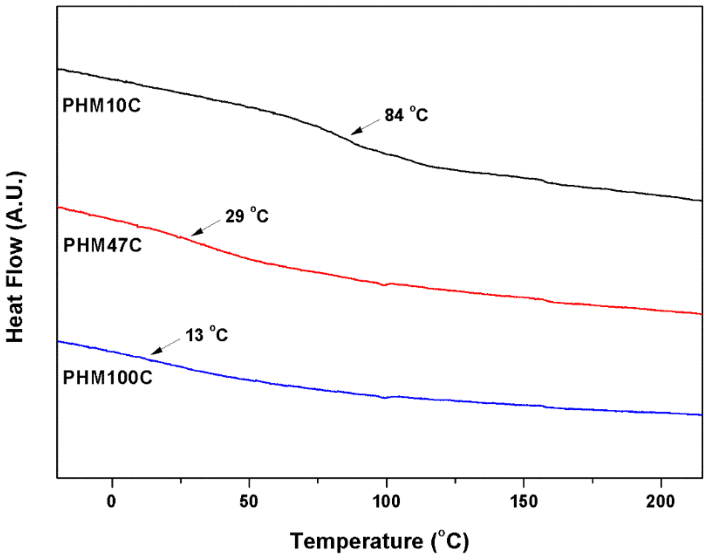

Fig. S6. DSC traces of the cross-linked PHMs (PHMCs) coatings.

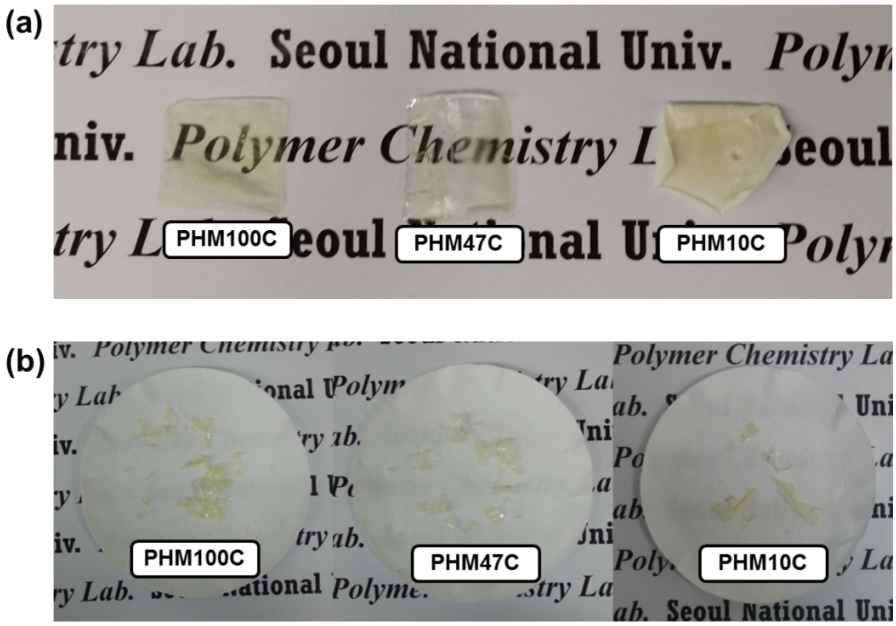

Fig. S7. Photographic results of gel fraction test of PHMC films (a) before and (b) after.

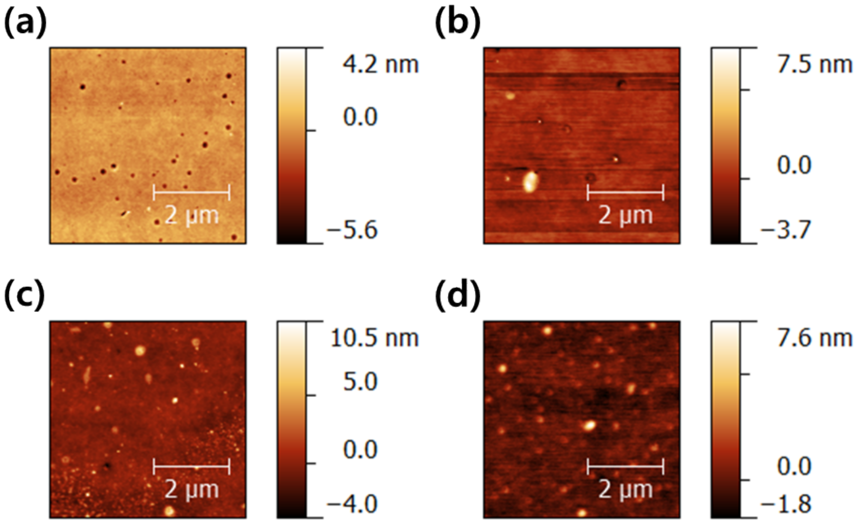

Fig. S8. Surface morphologies of the (a) PMMA, (b) PHM10C, (c) PHM47C, and (d) PHM100C coatings.

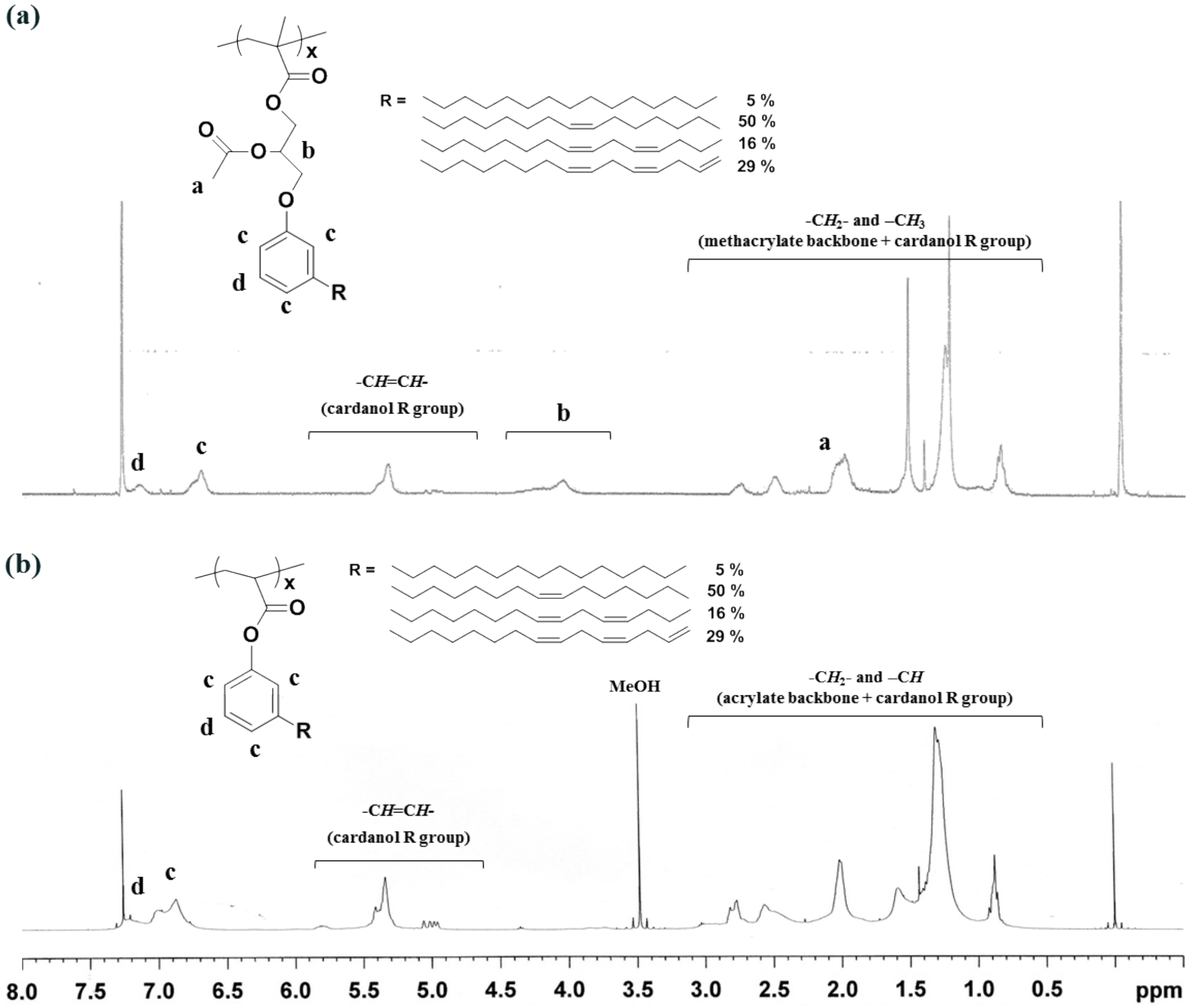

Fig. S9. ^{1}H NMR spectra of (a) PACPM and (b) PCA

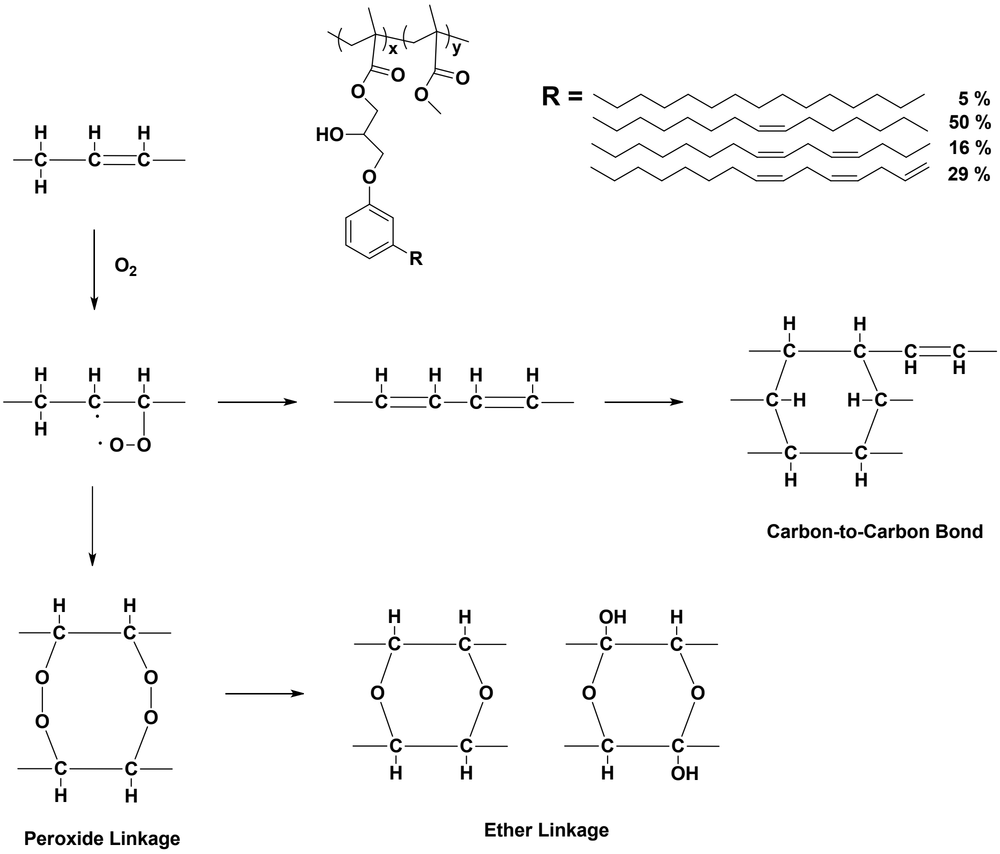

Fig S10. Suggested mechanism for photo-cross-linking of cardanol moieties by oxidation under UV irradiation.

References

[1] John G, Pillai CKS. Die Makromolekulare Chemie, Rapid Communications 1992;13:255.
[2] John G, Pillai C. Journal of Polymer Science Part A: Polymer Chemistry 1993;31:1069.