Supporting Information

On the nitroxide mediated polymerization of methacrylates derived from bio-sourced terpenes in miniemulsion

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Monomer synthesis

Tetrahydrogeraniol methacrylate (THGMA)

A mixture of tetrahydrogeraniol (28.5 g, 0.18 mol), methacrylic acid (25.81 g, 0.30 mol), 2-Methyltetrahydrofuran (250 mL) and propylphosphonic anhydride (57 g, 0.18 mol) and triethylamine (16 g, 0.164 mol) were mixed in the 500 mL round bottom flask and stirred at room temperature for 24 hours. To this mixture, water was added first and the product was then extracted with diethyl ether. Then, the organic phase was washed several times with brine and deionized water. The organic phase was passed through basic alumina and the volatile solvent was removed by rotary evaporation to yield a transparent viscous liquid (35 g, 85 % yield). The ^{1}H NMR ($CDCl_3$, 400 MHz) of the monomer is shown in Figure 1, 6.12 (a) (m, 1H, $C\boldsymbol{H}_2$=CH-C=O), 5.56 (b) (p, 1H, $C\boldsymbol{H}_2$=C-(CH_3)(C=O), 4.21 (d) (ddt, 2H, O=C-O-$C\boldsymbol{H}_2$), 1.96 (c) (t, 3H, CH_2=C-$C\boldsymbol{H}_3$), 1.73 (k) (ddt, 1H, $(CH_3)_2$-$C\boldsymbol{H}$-CH_2), 1.55 (e) (m, 2H, CH-$C\boldsymbol{H}_2$-CH_2-O), 1.54 (f) (m, 1H, CH_3-$C\boldsymbol{H}$-CH_2), 1.31 (i) (m, 2H,CH_2-$C\boldsymbol{H}_2$-CH_2-CH), 1.18 (h) (m, 2H, $C\boldsymbol{H}_2$-CH_2-CH_2-CH), 1.18 (J) (m, 2H, CH_2-CH_2-$C\boldsymbol{H}_2$-CH), 0.92 (g) (dd, 3H, $C\boldsymbol{H}_3$-CH-CH_2-CH_2), 0.91 (l) (dd, 6H, $(C\boldsymbol{H}_3)_2$-CH-CH_2-CH_2).

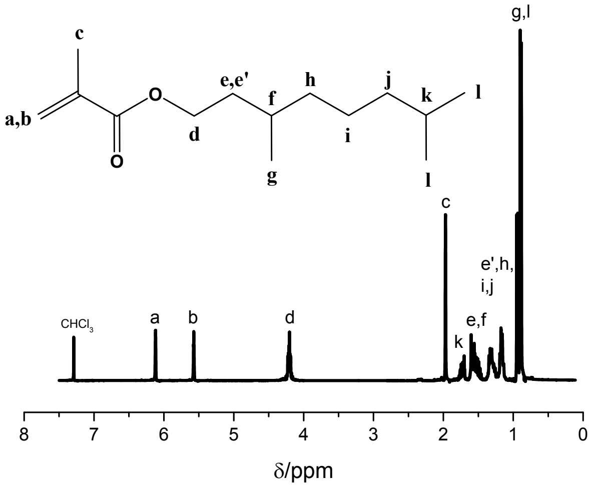

Figure S1. ^{1}H-NMR of THGMA monomer.

Cyclademol methacrylate (CDMMA)

A mixture of cyclademol (28.12 g, 0.18 mol), methacrylic acid (25.81 g, 0.30 mol), 2-Methyltetrahydrofuran (250 mL) and propylphosphonic anhydride (57 g, 0.18 mol) and triethylamine (16 g, 0.164 mol) were mixed in the 500 mL round bottom flask and stirred at room temperature for 24 hours. To this mixture, water was added first and the product was then extracted with diethyl ether. Then, the organic phase was washed several times with brine and deionized water. The organic phase was passed through basic alumina and the volatile solvent was removed by rotary evaporation to yield a transparent viscous liquid (33 g, 82 % yield). The ^{1}H NMR ($CDCl_3$, 400 MHz) of the monomer is shown in Figure 2, 6.1 (a) (s,1H, $O{=}C{-}C(CH_3){=}C\boldsymbol{H}_2$), 5.5 (b) (s,1H, $O{=}C{-}C(CH_3){=}C\boldsymbol{H}_2$), 4.7 (d) (m, 1H, $C\boldsymbol{H}{-}O{-}C{=}O$), 1.95 (c,f) (s, 4H, $C\boldsymbol{H}{-}CH{-}O{-}C{-}C(C\boldsymbol{H}_3)$)), 1.5 (h, k, m) (m, 4H, $C\boldsymbol{H}_2{-}C\boldsymbol{H}_2{-}C\boldsymbol{H}_2{-}CH(C\boldsymbol{H}_2{-}C){-}CH{-}O{-}C{=}O$), 1.2 (e, i) (m, 4H, $C\boldsymbol{H}_2{-}CH_2{-}CH{-}CH(C\boldsymbol{H}_3){-}O{-}C{=}O$), 1.05 (j, g) (m, 2H, $C\boldsymbol{H}_2{-}CH_2{-}C\boldsymbol{H}_2{-}CH{-}CH(CH_3){-}O{-}C{=}O$), 0.95 (l) (s, 1H, $CH(C\boldsymbol{H}_2{-}C){-}CH{-}O{-}C{=}O$), 0.9 (n) (s, 6H, $C(C\boldsymbol{H}_3)_2$).

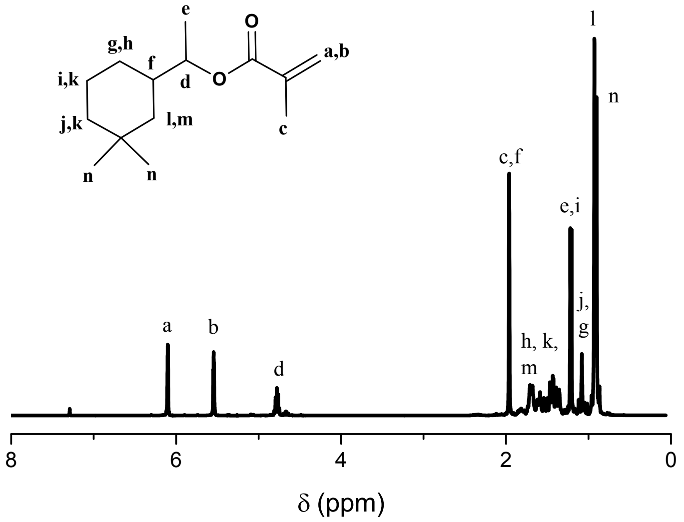

Figure S2. ^{1}H-NMR of CDMMA monomer.

Poly(THGMA)-*b*-poly(S) diblock copolymer in miniemulsion

The formulations utilized for the synthesis of all diblock copolymers are summarized in Table S1. A poly(THGMA) seed latex 10 wt% solids ($[M]_0/[\text{Dispolreg 007}]_0 = 225$, $M_{n,th} = 50\,400$ g.mol^{-1}) was first prepared via NMP in miniemulsion as described above. The reaction was stopped at 98 % monomer conversion, yielding a polymer with $M_n = 50\,000$ g.mol^{-1} and $Đ = 1.13$. The poly(THGA) seed latex (25 g) was charged to the reactor equipped with rubber seals and magnetic stirring. Subsequently, the mixture of styrene monomer (3.5 g, $[M]_0/[\text{macro initiator agent}]_0 = 672$) and acetone (10 *wt.*% b-o-m) was added to the reactor and stirred for 30 min before deoxygenation with purging nitrogen gas for an additional 30 min. The reactor was then placed into an oil bath at 97°C and left to polymerize for 8 hours. After polymerization, the reaction was cooled to room temperature.

Table S1. Recipes for synthesis the soft/hard diblock copolymer.

Entry	macro-initiator seed latex (g)	Monomer	Monomer (g)	Acetone (10 *wt.*% b-o-m)
14	25	Styrene	3.5	0.35
15	25	Styrene	1.5	0.15

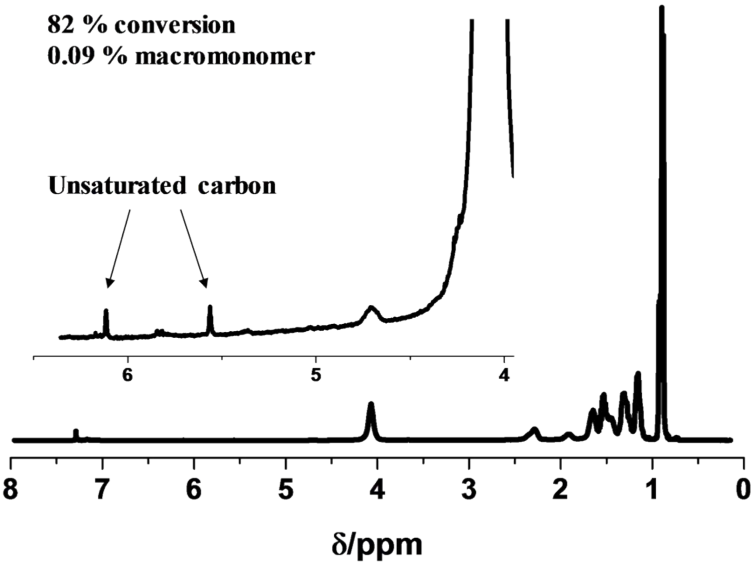

Figure S3. ^{1}H NMR ($CDCl_3$, 400 MHz) of PTHGMA ($[M]_0/[\text{Dispolreg 007}]_0 = 400$, $M_n = 70\,000$ g.mol^{-1}, $Đ = 1.50$ at 82 % conversion) prepared by NMP in toluene at 97 ºC.

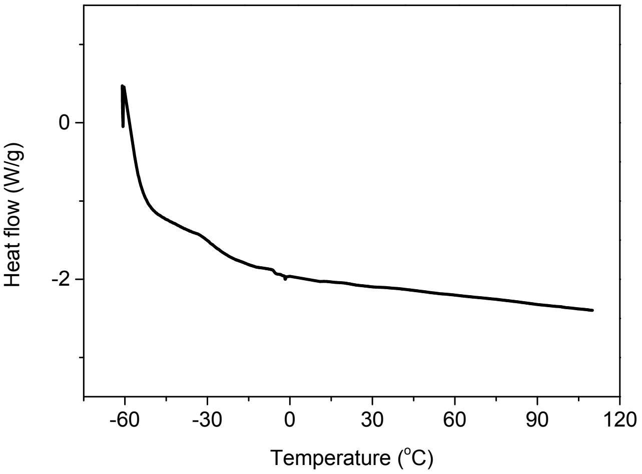

Figure S4. DSC thermogram of PTHGMA, ($[M]_0/[\text{Dispolreg 007}]_0 = 400$, $M_n = 70\ 000$ g.mol^{-1}, $Đ = 1.50$ at 82 % conversion) prepared by NMP in toluene at 97 ºC

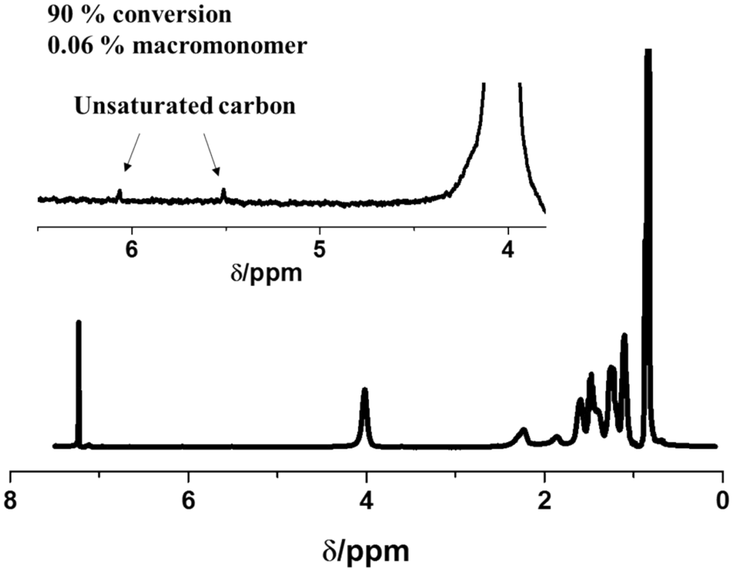

Figure S5. ^{1}H NMR ($CDCl_3$, 400 MHz) of poly(THGMA) ($[M]_0/[\text{Dispolreg 007}]_0 = 400$, M_n = 81700 g.mol^{-1}, at 90 % conversion) prepared by NMP in miniemulsion at 97 ºC.

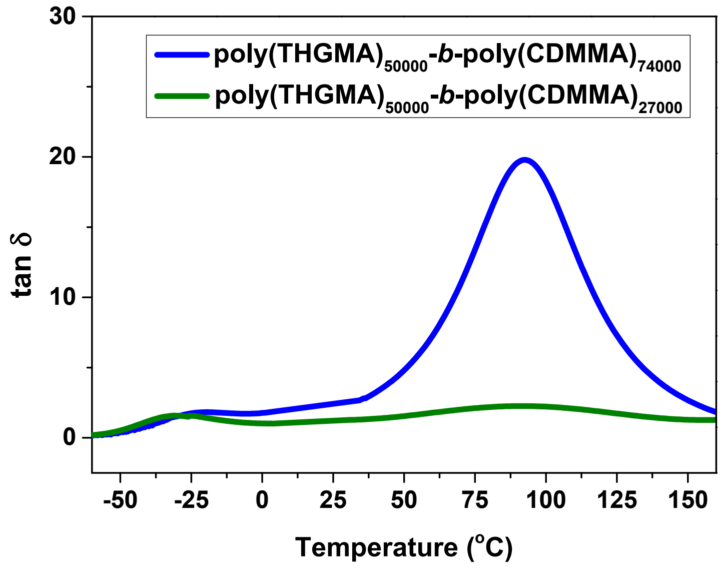

Figure S6. Evolution of tan δ as a function of increasing temperature of the PTHGMA-*b*-PCDMMA "soft"/"hard" diblock copolymers obtained from DMTA with temperature ranging from -60 to 160°C.

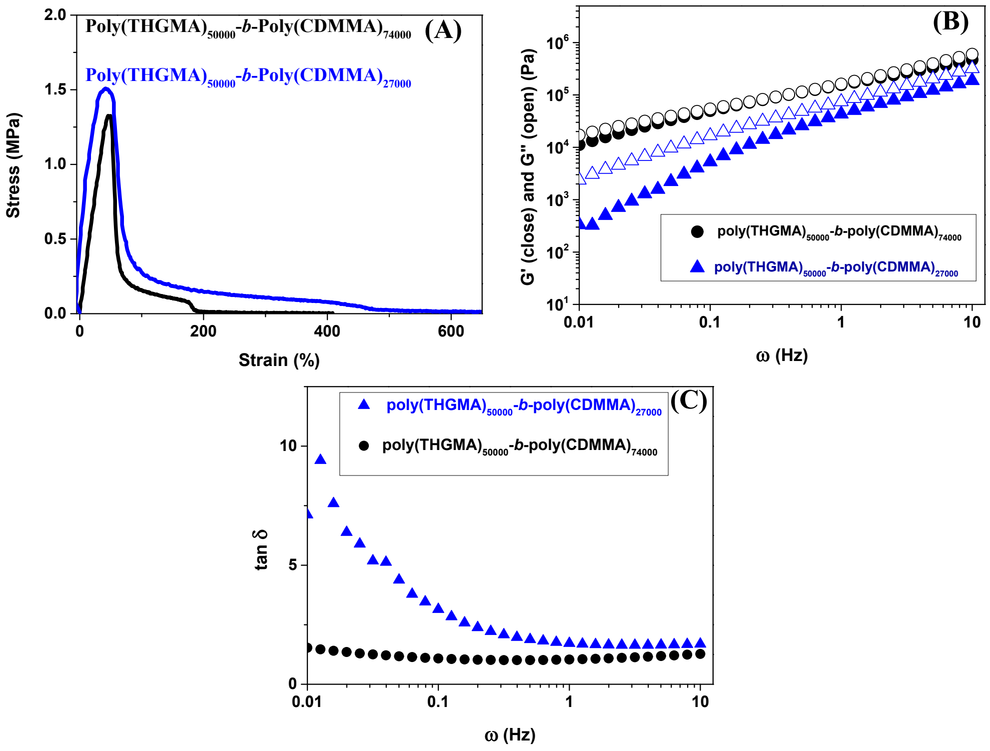

Figure S7. Evolution of adhesive properties for PTHGMA-*b*-PCDMMA diblock copolymer. (A) Stress-strain curve of the probe-tack test. (B) G′ and G′′ as a function of frequency at room temperature. (C) tan δ as a function of frequency at 25 ℃.

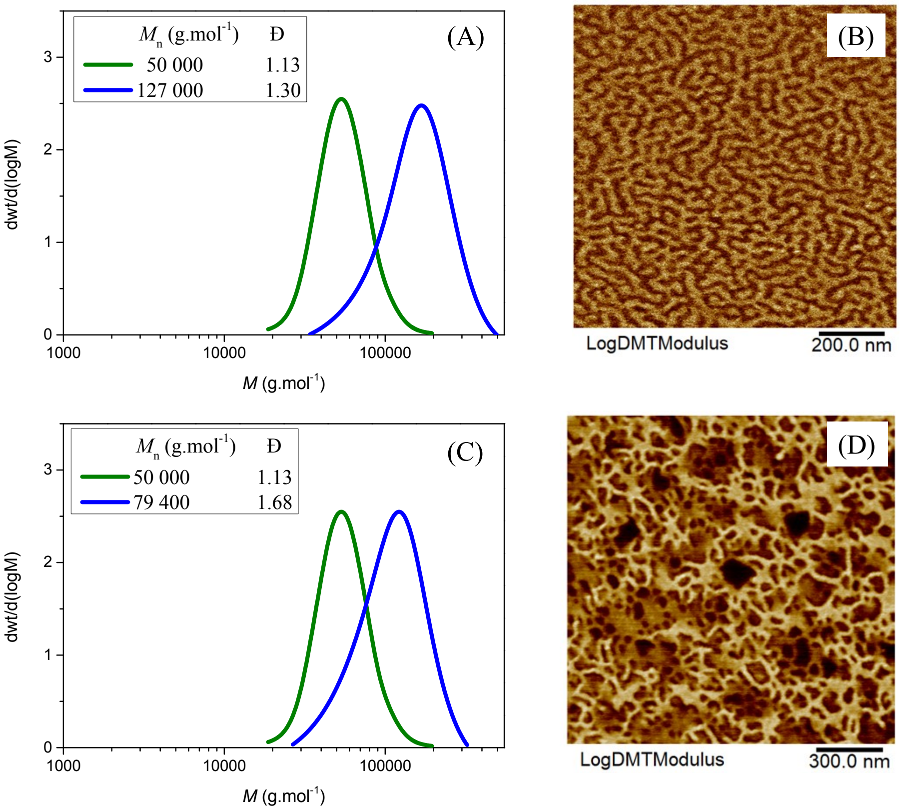

Figure S8. (A) SEC traces and (B) AFM picture of a poly(THGMA)$_{50000}$-b-poly(styrene)$_{77000}$ diblock copolymer via chain extension of poly(THGMA) macro-initiator agent with styrene. (C) (A) SEC traces and (D) AFM picture of a poly(THGMA)$_{50000}$-b-poly(styrene)$_{25000}$ AB diblock copolymer via chain extension of poly(THGMA) macro-initiator agent with styrene.

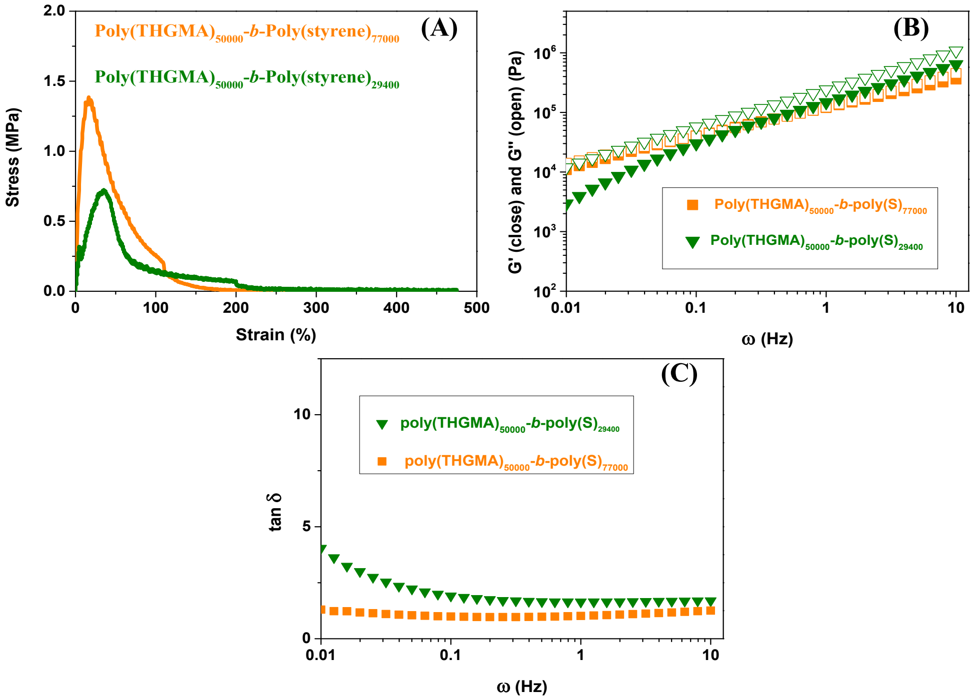

Figure S9. Evolution of adhesive properties for poly(THGMA)-b-poly(S) soft/hard diblock copolymer. (A) Stress-strain curve of the probe-tack test. (B) G´ and G´´ as a function of frequency at room temperature. (C) tan δ as a function of frequency at room temperature.