Supporting Information

Paving the way to sustainable waterborne pressure-sensitive adhesives using terpene-based triblock copolymers

Sayrung Noppalit[a,b,c †], Alexandre Simula[a †], Laurent Billon[b,c] and José M. Asua[*a]*

[a] *POLYMAT, University of the Basque Country UPV/EHU, Kimika Aplikatua saila, Kimika Zientzien Fakultatea, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018 Donostia-San Sebastián, Spain*

[b] *Université de Pau et des Pays de l'Adour IPREM-CNRS, UMR 5254, Hélioparc Pau-Pyrénées, 2 avenue Président Angot, 64053 PAU CEDEX 9, France*

[c] *Université de Pau et des Pays de l'Adour, Bio-inspired Materials Group : function, Hélioparc Pau-Pyrénées, 2 avenue Président Angot, 64053 PAU CEDEX 9, France*

† These authors contributed equally to this work.

**Corresponding authors: Prof. Laurent Billon (laurent.billon@univ-pau.fr) and Prof. José M. Asua (jm.asua@ehu.eus)*

The supporting information contains, the characterization of the purity of THGA and CDMA monomers by $_1$H NMR and $_{13}$C NMR. The stability of the dispersion is characterized by scanning every 30 min for 5 hours. The detail of the experimental data is provided to calculate the theoretical molecular weights of homo and block copolymers by RAFT miniemulsion polymerization. The SEC traces evolution, AFM image and rheological analysis of triblock copolymers are the evidence of the good chain extension and the polymer film casted at 23 ºC.

This supporting information contains

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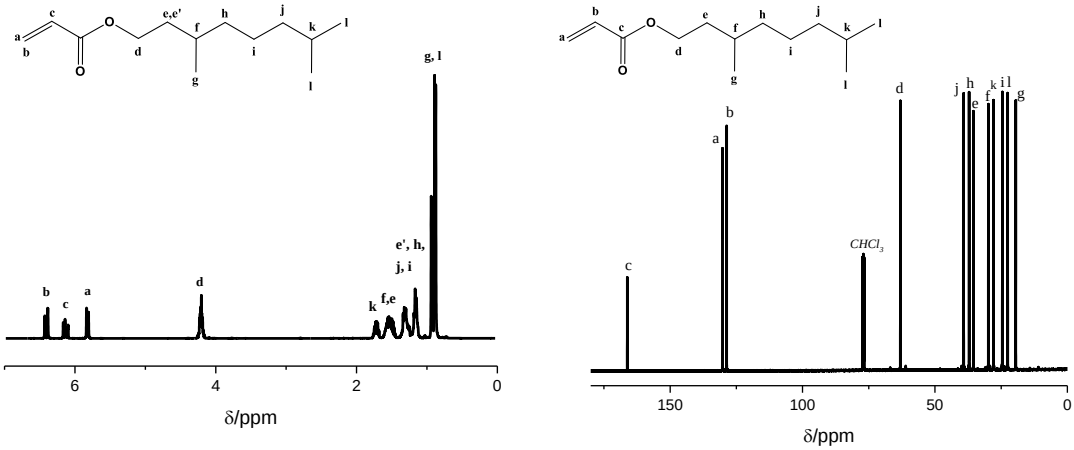

Figure S1. 1H NMR and 13C NMR of tetrahydrogeraniol acrylate (THGA).

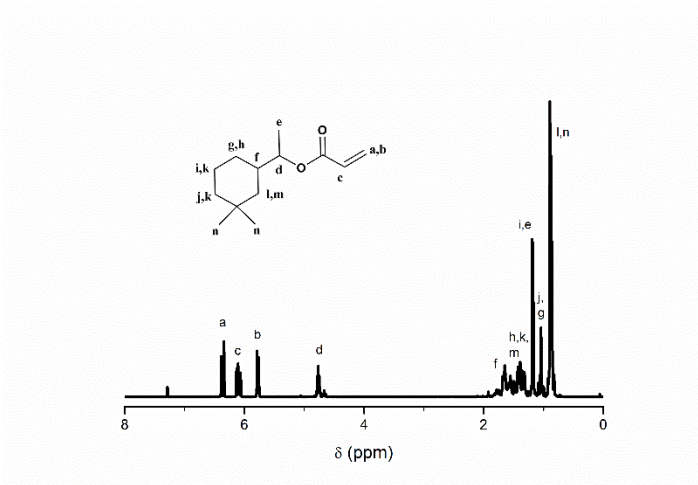

Figure S2. 1H NMR of cyclademol acrylate (CDMA).

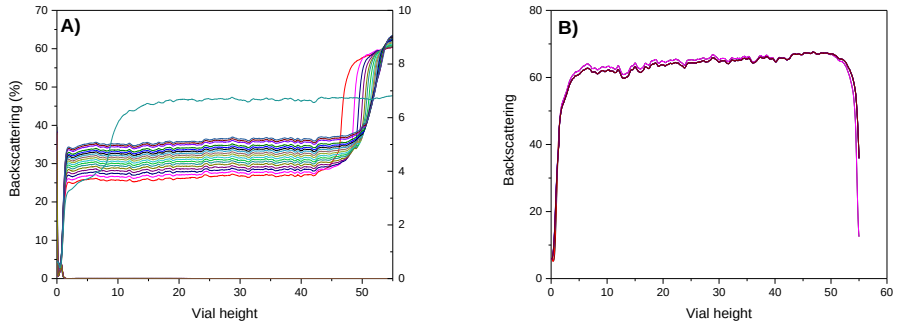

Figure S3. Stability of the THGA dispersion at 60 ˚C. (A) entry 1. (B) entry 2

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Table S1. Preparation of the styrene based soft-hard-soft triblock copolymer by RAFT miniemulsion polymerization.

Copolymer	M_n macro-RAFT th [a] (g.mol-1)	M_n macro-RAFT exp [b] (g.mol-1)	Conv. (%)	M_n triblock th [a] (g.mol-1)	M_n triblock exp [b] (g.mol-1)	Đ	dp (nm)	Coagulation (*wt.*%)
PTHGA-*b*-PS-*b*-PTHGA	52300	50000	96	98400	120,000	2.64	310	n/a

[a] The theoretical molar masses were calculated as $M_n^{Th} = M_{CTA} + \frac{[M]_0 \times p \times M_M}{[CTA]_0 + 2 \times f \times [I]_0 \times (1 - e^{-k_D t}) \times (1 - \frac{f_C}{2})}$.[b] Extracted from SEC-MALS analysis using the measured *dn/dc* values for poly(THGA) (*dn/dc* = 0.0678 mL.g-1) and poly(S) (*dn/dc* = 0.19 mL.g-1). The *dn/dc* of the tri block copolymers were determined using eq (1)

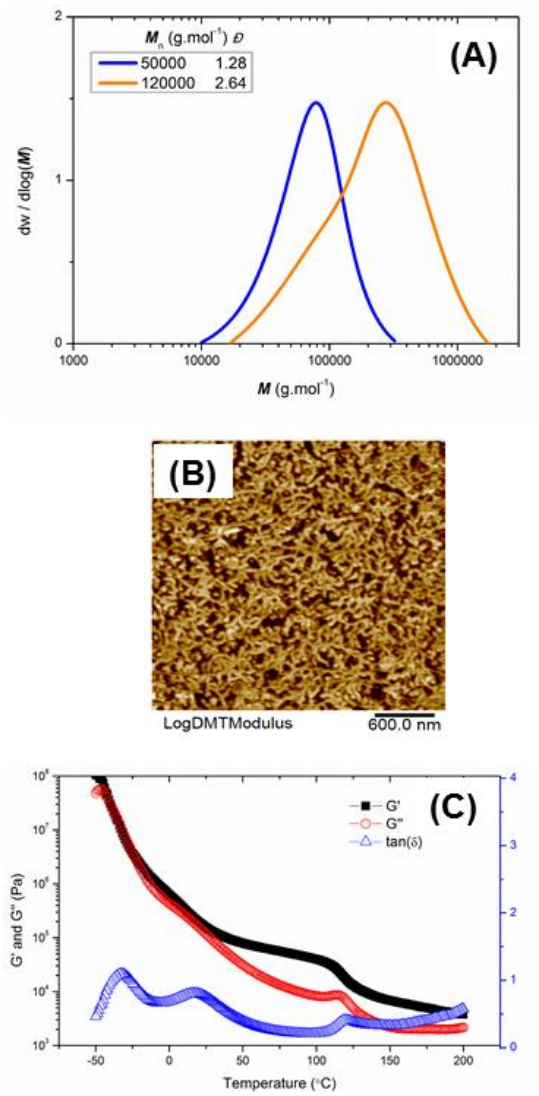

Figure S4. (A) SEC traces evolution; **(B)** AFM image (PeakForce QNM mode) and **(C)** Rheological behavior of PTHGA-*b*-PS-*b*-PTHGA.

Table S2. Rheological properties of the triblock copolymers.

Triblock copolymer	Soft phase (*wt.*%)*a*	Hard phase (*wt.*%)*a*	T_gs (ºC)*b*	G' / G'' cross over (ºC)
PTHGA-*b*-PS-*b*-PTHGA	43	57	-32; 19; 120	-37
PTHGA-*b*-PCDMA-*b*-PTHGA	46	54	-42; 91	n/a
PCDMA-*b*-PTHGA-*b*-PCDMA	66	34	-33; 6; 93	62

a- extracted from ^{1}H NMR. *b*- extracted from the local maxima of tan(δ).

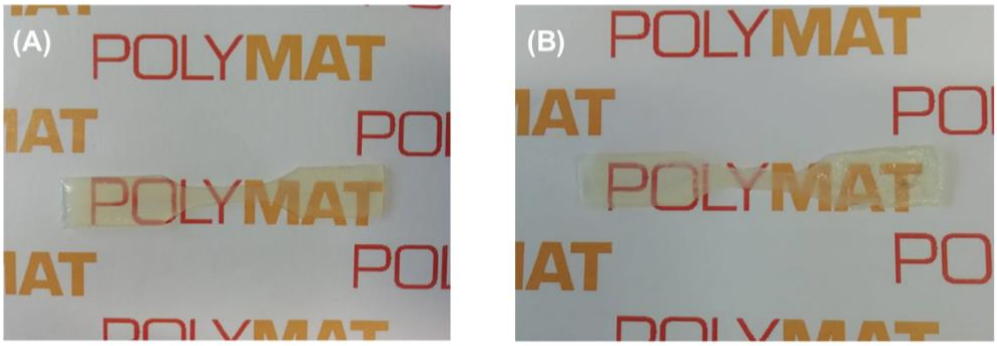

Figure S5. Films casted at 23 ºC and 55 % humidity. (A) PTHGA-*b*-PCDMA-*b*-PTHGA. (B) PCDMA-*b*-PTHGA-*b*-PCDMA.