Effects of Multifunctional Cross-linkers on Rheology and

Adhesion of Soft Nanostructured Materials

X. Callies^{a,b+*}, C. Véchambre^d, C. Fonteneau^c, F. Herbst^e, J-M. Chenal^d, S. Pensec^c,

L. Chazeau^d, W. H. Binder^e, L. Bouteiller^c, and C. Creton^{a,b*}

^aLaboratoire de Sciences et Ingénierie de la Matière Molle, CNRS, ESPCI Paris, PSL Research University, 10 Rue Vauquelin, 75005 Paris, France

^bLaboratoire Sciences et Ingénierie de la Matière Molle, Université Pierre et Marie Curie, Sorbonne-Universités, 10 rue Vauquelin, France

^cSorbonne Universités, UPMC Univ Paris 06, CNRS, IPCM, Chimie des Polymères, F-75005 Paris, France

^dLaboratoire MATEIS, CNRS, INSA Lyon, 7 avenue Jean Capelle, Villeurbanne, 69100, France

^eChair of Macromolecular Chemistry, Institute of Chemistry, Faculty of Natural Science II (Chemistry, Physics and Mathematics), Martin Luther University Halle-Wittenberg, Halle 06120, Germany

⁺current address: IPREM, Technopôle Helioparc, 2 avenue P. Angot, 64053 Pau Cedex 9, France

xavier.callies@univ-pau.fr, costantino.creton@espci.fr

1. Synthesis

For the synthesis of compounds 2 and 3, the procedure was adapted from previous works¹.

Synthesis of **2**

The diallyl poly(isobutene) **1** Epion (Mn = 9990 g/mol, D = 1.25 from Kaneka) (6.1 g, 0.61 mmol) was dissolved in 80 mL of dry THF. The solution was degassed by argon for 10 min. A 0.5 M 9-borabicyclo[3.3.1]nonane solution in THF (13.86 mL, 6.9 mmol) was added dropwise under argon at room temperature. After 10 h of stirring, the mixture was cooled to 0°C. Methanol (0.39 mL) and 3-chloroperoxybenzoic acid (8.66 g, 35.1 mmol) were added carefully. After one night of stirring, hexane was added to the mixture. The solution was washed twice with an aqueous phase saturated with potassium carbonate and three times with a water/methanol (3/1) mixture. The organic layer was dried with

magnesium sulfate. After filtration, the solution was evaporated. The product was dissolved in hexane, precipitated twice in methanol and dried in vacuo at 60°C. 5.3 g of **2** (yield 86%) was obtained.

¹**H NMR** (200 MHz, CD2Cl₂, δ (ppm)): 0.7-1.8 (m, 1610H,(-Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n-(CH₂)₂-), 3.6 (t, 4H, CH₂-OH), 7.18 (s, 4H, Ph).





Figure S1: ¹H NMR spectrum for compound 1 (top) and 2 (bottom) in CDCl₃.

Synthesis of **3**

Compound **2** (2 g, 0.2 mmol) was dissolved in 20 mL of dry dichloromethane and tetrabromomethane (0.763g, 2.3 mmol) and subsequently triphenylphosphine (0.6 g, 2.3 mmol) was added at 5°C. The mixture was then warmed to room temperature and stirred for one night. The solvent was removed under vacuum, the residue was dissolved in 100 mL of hexane and filtrated. After evaporation of the solvent, the product was purified by SiO₂ column chromatography (hexane 40/ethyl acetate 1), dried under vacuum to obtain 1.52 g of **3** (yield 75%).

¹**H NMR** (200 MHz, CD₂Cl₂, δ (ppm) : 0.7-1.8 (m, 1564H,(-Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n-(CH₂)₂-), 3.4 (t, 4H, CH₂-OH), 7.18 (s, 4H, Ph).



Figure S2: ¹H NMR spectrum for compound 2 (top) and 3 (bottom) in CDCl₃.

Synthesis of 4

Compound **3** (1 g, 0.1 mmol) was dissolved in 10 mL of dry THF. 3.5 mL of dry DMF and then potassium phtalimide (0.65 g, 3.5 mmol) were added to the solution. The mixture was stirred and refluxed for one night under argon. After evaporation of THF, methanol was added to the residue. The precipitate was dissolved in hexane, filtrated and re-precipitated in methanol. The product was dried to obtain **4** (0.75 g, Yield 75%).

¹H NMR (200 MHz, CD₂Cl₂, δ (ppm)): 0.8 - 1.5 (m, 1570H,(-Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n-(CH₂)₂-), 3.7 (t, 4H, CH₂-N), 7.26 (s, 4H, Ph), 7.77 (m, 4H, N-CO-C-CH=CH), 7.9 (m, 4H, N-CO-C-CH=CH)

¹³**C NMR** (75 MHz, CDCl₃, δ (ppm) : 29-38 (Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n), 40.1 (CH₂-N), 50-60 (Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n), 123.6 (=CH), 125.36 (Ph-H), 132.7 (=C-CO), 133.1 (=CH), 146.99 (Ph-C(CH₃)₂), 168.3 (N-(CO)₂).



Figure S3: ¹H NMR spectrum for compound 3 (top) and 4 (bottom)) in CDCl₃.

Synthesis of 5

The procedure was adapted from the study of Ummadisetty et al². Compound **4** (0.75 g, 0.075 mmol) was dissolved in 30 mL of an ethanol /hexane (50/50) mixture. The solution was heated to reflux, then hydrazine (2.25 mL, 43 mmol) was added and stirred for 5 hours. 40 mL of hexane was added to the mixture. The solution was washed three times with water. The organic layer was dried over MgSO₄, filtrated and the solvent was evaporated. The compound **5** (0.6 g, yield 85%) was obtained.

¹**H NMR** (200 MHz, CD_2Cl_2 , δ (ppm) : 0.8-1.5 (m, 1621H, Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n), 2.7 (t, 4H, CH₂-NH₂), 7.26 (s, 4H, **Ph**).

¹³**C NMR** (75 MHz, $CDCl_3$, δ (ppm) : 29-38 (Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n), 43.2 (CH₂-NH₂), 50-60 (Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n), 125.36 (Ph-H), 146.99 (Ph-C(CH₃)₂).



Figure S4: ¹H NMR spectrum for compound 4 (top) and 5 (bottom)) in CDCl₃.

Synthesis of M-PIBUT

Compound **5** (0.55 g, 0.057 mmol) was dissolved in 5 mL of dry THF in an oven-dried flask. 2,4-toluenediisocyanate (TDI 98% from Aldrich) (18 μ L, 0.125 mmol) was added via a syringe under argon. After 24h of stirring at room temperature, the mixture was transferred with a degassed syringe into a second flask charged with the amino-functionalized poly(isobutene) (0.35g, Kerocom PIBA, 60% in hydrocarbon, from BASF) dissolved in 5 mL of dry THF. The reaction was followed by FT-IR until the disappearance of isocyanate band (2270 cm⁻¹). Then the solution was concentrated and **M-PIBUT** (0.6g, yield 67%) was recovered by precipitation in ethyl acetate and drying under vacuum at 60°C.

SEC: Decomposition of the chromatogram (figure 2) was performed with 3 exponential-Gaussian hybrid peaks, with 10 adjustable parameters (peak height, retention volume and dispersity for each peak and a common time constant of the exponentials) (see reference³).

¹H NMR (200 MHz, CDCl₃/d6-DMSO, δ (ppm) : 0.8 - 1.5 (m, Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n-CH₂-CH₂ and CH₂-CH(CH₃)-CH₂-(C(CH₃)₂-CH₂)_n-C(CH₃)₃), 1.7 (CH₂-C(CH₃)₂-Ph), 1.99 (s, Ph-CH₃), 3.2 (m, CH₂-NH), 5.3-5.6 (m, CO-NH-CH₂), 6.7 (s, Ph-NH-CO), 6.9 (d, Ph-H), 7.18 (s, Ph-H), 7.2 (d, Ph-H), 7.4 (s, Ph-H), 7.6 (s, Ph-NH-CO).

¹³**C NMR** (75 MHz, CDCl₃, δ (ppm) : 16.6 (Ph-CH₃), 22.0 (CH₂-CH(CH₃)-CH₂), 25.7 (CH₂-**C**H(CH₃)-CH₂), 29-38 (Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n + C(CH₃)₃), 34.8 (N-CH₂-CH₂), 50-60 (Ph-C(CH₃)₂-(CH₂-C(CH₃)₂)_n-CH₂), 110.7 (Ph-H), 112.1 (Ph-H), 119.5 (Ph-CH₃), 125.36 (Ph-H), 129.5 (Ph-H), 137 (Ph-NH), 137.7 ((Ph-NH), 146.99 (Ph-C-(CH₃)₂), 155.2 (**C**=O).



Figure S5: ¹H NMR spectrum for compound M-PIBUT in CDCl₃/d6-DMSO

Rheology



Figure S6: Frequency dependence of the complex viscosity $\eta^*(Pa.s)$ at 80°C in the linear regime at small deformation for PIBUT (red markers), Blend_1 (green) and Blend_10 (black).



Figure S7: Frequency dependency of the elastic modulus G' and the damping factor $\tan \delta$ at 25°C after different time intervals following the temperature ramp.

Adhesion





Figure S8: Pictures of cavitation process during probe-tack tests at 100μ m/s for Blend_0.1 (A), Blend_1 (C) and Blend_5 (E). Photos of the steel probe after the adhesion test for Blend_0.1 (B), Blend_1 (D) and Blend_5 (F).



Figure S9: Pictures of the steel probe after the adhesion test at 1μ m/s for Blend_0.1 (A), Blend_1 (B) and Blend_5 (C).

References

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