Thermo-Resettable Cross-Linked Polymers for Reusable / Removable Adhesives

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Experimental Section:

Materials and Purification:

The monomer *n*-hexyl methacrylate (HMA), and 2-hydroxyethyl methacrylate (HEMA) were bought from Wako chemicals and Tokyo Chemical Industry Co. Ltd. (TCI), respectively and was purified by passing through alumina column in order to remove inhibitors. The cross-linker 1,1'-(Methylenedi-4,1phenylene)bismaleimide (BMI) was purchased from Wako Pure Chemical Industries Ltd. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Furfuryl isocyanate was purchased from Sigma-Aldrich, USA and used as received. The catalyst dibutyltin diacetate (DBTDA) was bought from TCI used without any purification. and was Super dehydrated dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from Wako Pure Chemical Industries Ltd. The NMR solvent N, Ndimethylformamide (DMF- d_7) and tetrahydrofuran- d_8 (THF- d_8) were bought from Sigma-Aldrich and TCI, respectively. Other chemicals and solvents were purchased from commercial sources and were used without further purification. All substrates were purchased from commercial sources.

Instrumentation:

¹H-NMR & Fourier Transform Infrared Spectra (FT-IR):

The ¹H-NMR spectra of the random copolymers (P1-P5) and furyl-modified copolymers (FMP1-FMP5) were recorded in DMF-d₇ at 25 °C on JEOL ECS-400 spectrometer (for P6 and FMP6, THF-d₈ was used as a solvent). To investigate the progress of DA reaction time dependent ¹H-NMR was made. For that purpose, the reaction was performed under preheated oven and the spectra were recorded at room temperature (immediately).

The actual compositions of the two monomers within copolymers were calculated from their respective ¹H-NMR spectra using following relation.

Mol (%) of HEMA = $100 / [1 + \{ \text{area of } (c+c') - \text{area of } (d) \} / \text{area of } (d)]$ (as number of c and d proton is same).

 $Mol (\%) of HMA = \{100 - Mol (\%) of HEMA\}$

The fourier transform infrared (FT-IR) spectra of the samples were performed in a JASCO (FT-IR 6100) instrument from KBr pellets. The heat induced crosslinking/decrosslinking reaction between FMP4 and BMI was also monitored by FT-IR spectroscopy. In a typical experiment, the mixture of FMP4 and BMI $(I_{mal/fur} = 1)$ in chloroform was drop casted on a KBr pellet and then another KBr pellet was placed on it. Finally, the spectra were collected under several conditions (before curing, after curing and after heat treatment).

Gel permeation chromatography (GPC):

The molar mass of all the random copolymers (P1-P6) and FMPs were calculated using GPC. The GPC experiments were performed using Viscotek TDA302 (Triple Detector Array) equipped with a two-column system (TOSOH, TSKgel GMH_{HR}-M) at 30 $^{\circ}$ C and flow rate 1 mL min⁻¹. The instruments were calibrated by polystyrene standards (1.01 kDa to 706 kDa) and tetrahydrofuran (THF) was used as eluent.

Differential scanning calorimetry (DSC):

A SHIMADZU DSC-60 plus instrument (serial no-C309454) was used to monitor the thermal property and glass transition temperature (T_g) of all FMPs under nitrogen atmosphere. Temperature range was from -80 to 120 °C with heating and cooling rate 10 °C min⁻¹ (Cycle 1: heat up to 100 from 25 °C and cool to -80 °C, Cycle 2: heat up to 120 °C from -80 °C and cool to -80 °C from 120 °C and cycle 3: heat up to 120 °C from -80 °C and cool to 25 °C from 120 °C. Aluminum pan was used as a sample holder and α -alumina (Al₂O₃) was used in these studies as a reference. The T_g values were determined from the second heating cycle. The progress of the rDA reaction also monitored by DSC study. For that purpose cross-linked network of FMP4 (xIFMP4¹) is prepared by simple mixing of FMP4 with BMI ($I_{mal/fur} = 1$) in chloroform, followed by 2 h heating at 80 °C in air. DSC of xIFMP4¹ was performed and the reported plots and values were estimated from the first and second heating cycle. Temperature range was from -80 to 170 °C with heating and cooling rate 10 °C min⁻¹. The T_g values of all adhesives (xIFMP1¹-xIFMP6¹) were determined from the first heating cycle.

Lap-shear test:

The lap-shear bonding property of all FMPs was measured by Shimadzu autograph AG-X plus instrument with a 10000 N load cell. The crosshead speed was 2 mm \min^{-1} for all cases. The reported values are the average of four measurements with standard error for each study. The lap shear strength was determined using following equation.

Lap shear strength (MPa) = Load (N)/Area (mm^2) [Used area=250 mm^2]. Substrate cleaning for lap-shear test: Metal substrates were prepared as per ASTM D2651 standard protocol and was used immediately for attachment.¹ The dimensions of aluminum (Al) and copper (Cu) substrates are same (10 cm x 2.5 cm x 0.1 cm). Glass substrate with dimensions of 7.5 cm \times 2.5 cm \times 0.2 cm and polypropylene (PP) with dimensions of 10 cm \times 2.5 cm \times 0.3 cm, were also purchased from commercial sources. The dimensions of wood (WD) substrate is 10 cm x 2.5 cm x 0.3 cm. Glass and polymer substrates were cleaned by soapy water followed by sonication in ethanol, *n*-hexane, and acetone for two to three minutes each. Substrates were dried in room temperature and used immediately.

Single-lap bonding method:

The adhesive property of all FMPs was monitored by most common lap-shear test and all primary adhesion tests were carried out on Al substrate. First of all, FMPs were dissolved in CHCl₃ (40 wt% solution) and then 60 μ L solution was spread over both substrates by using a syringe. The solvent was removed by heating at 80 °C for 30 min. The substrates were joined and again cured at 80 °C for 30 min and the test was performed after 24 hours. The overlapped area was fixed (250 mm²) for all cases. Adhesives were prepared by simple mixing of FMPs with BMI in CHCl₃ (40 wt% solution). The adhesive solution (60 μ L) was spread onto the both substrates were overlapped in a single lap-shear configuration and the overlapped area of the specimen was fixed by a pair of metal clamp. Finally, the attached specimens were cured at 80 °C for specified time (2 h). After curing, samples were allowed to cool down at room temperature and lap-shear test was performed after several hours.

Stress relaxation:

Stress relaxation experiments of xlFMP4¹ ($I_{mal/fur} = 1$) were conducted with an Anton Paar (MCR 302) rheometer using a 8 mm parallel-plate geometry at different temperatures (80, 100 and 140 °C). For the stress-relaxation experiments a constant shear strain of 0.5% was applied.

Synthesis of random copolymers poly(2-hydroxyethyl methacrylate-*co*-hexyl methacrylate) (P1-P6):

AIBN (2 mol%) was taken in a 100 ml two-necked round bottom flask, purged with argon and equipped with a water condenser. The flask was backfilled with argon two times and dehydrated DMF (1.5 ml/mmol) was injected into the flask and stirred for 15 min. The monomers HEMA (m mmol) and HMA (n mmol) (**Table S1**) were next

added into the reaction mixture by using a syringe and the reaction mixture was degassed by argon bubbling for 1 h. The reaction was carried out under argon atmosphere at 75 °C for 8 h. After the desired time period the reaction mixture was cooled and the solvent DMF was removed under reduced pressure. The solid (sticky) residue was dissolved in small amount THF and then precipitated in excess water. The solid polymer was isolated, re-dissolved in THF, and re-precipitated into excess water to remove trace amount of monomer (if any) entrapped with in the polymer. The solid product was then dried under vacuum at 60 °C for overnight and finally a color less solid/sticky residue was obtained as a final product (**Scheme 1A**).

Synthesis of furyl-modified copolymers (FMP1-FMP6):

In 100 ml, argon purged, round bottom two-neck flask equipped with water condenser 1 g random copolymers (P1-P6) was taken and the flask was backfilled with argon two times. 10 ml super dehydrated DMF was injected into the flask and stirred for 30 min and argon purging was continued (for P5 and P6, THF was used as a solvent instead of DMF). A small amount DBTDA was then added into the reaction mixture. Furfuryl isocyanate (slight excess) was added slowly into the reaction mixture and stirred at room temperature for 15 min. Finally, the reaction was carried out at 55 °C for 2 h with continuous stirring. After the desired time period the reaction mixture was allowed to cool at room temperature. The solvent (DMF) was removed under reduced pressure. The brown color sticky material was dissolved in small amount of THF and was precipitated in excess water. The solid product was separated and again dissolved in THF followed by precipitated in excess water to remove the trace amount of unreacted furfuryl isocyanate (if any). The solid/sticky product was then dried under vacuum at 60 °C (6 h) and then overnight at room temperature. Finally a light brown color solid (sticky) was obtained as a final product (**Scheme 1A**).²

Delever	Feed (mol%) ^c		Observed (mol%) ^d		ме	PDI
Polymer	HEMA	HMA	HEMA	HMA	l vi n°	(M_w/M_n)
P1 ^a	50	50	48	52	10300	2.1
P2 ^a	33	66	30	70	11600	2.9
P3 ^a	25	75	20	80	12500	2.6
P4 ^a	20	80	18	82	15400	2.2
P5 ^a	9	91	9	91	13200	2.5
P6 ^a	5	95	4	96	15000	2.2
FMP1 ^b	_		-		12100	2.9
FMP2 ^b	_		-		12300	3.4
FMP3 ^b	-		-		13400	2.4
FMP4 ^b	-		-		15100	2.5
FMP5 ^b	-		-		13600	2.5
FMP6 ^b	-		-		14700	2.3

^aCopolymer = poly(HEMA-*co*-HMA)

^bFuryl modified poly(HEMA-*co*-HMA)

^cFeeding ratio of HEMA and HMA(Taken)

^dMolar ratios of HEMA and HMA in copolymers determined from ¹H-NMR ^eNumber average molecular weight (GPC)

Table S1: Copolymerization of HEMA/HMA and properties of the random

copolymers (P1-P6) and furyl-modified copolymers (FMP1-FMP6).

Entry	Furyl-modified copolymer (FMP)	Furan:Maleimide unit (mol/mol)	Lap shear strength (MPa)
xlFMP1 ¹	FMP1	1:1	6.5 ± 0.7
xlFMP2 ¹	FMP2	1:1	7.5 ± 0.7
xlFMP3 ¹	FMP3	1:1	7.2 ± 0.7
xlFMP4 ¹	FMP4	1:1	6.5 ± 0.8
xlFMP5 ¹	FMP5	1:1	0.5 ± 0.2
xlFMP6 ¹	FMP6	1:1	0.2 ± 0.04
xlFMP4 ^{0.2}	FMP4	1:0.2	1.3 ± 0.4
xlFMP4 ^{0.5}	FMP4	1:0.5	3.6 ± 0.9
xlFMP4 ¹	FMP4	1:1	6.5 ± 0.8
xlFMP4 ^{1.1}	FMP4	1:1.1	7.9 ± 1.1
xlFMP4 ^{1.4}	FMP4	1:1.4	7.5 ± 1.1
xlFMP4 ^{2.8}	FMP4	1:2.8	6.6 ± 1.1
xlFMP4 ^{5.6}	FMP4	1:5.6	2.5 ± 0.9

Table S2: Formulation of different adhesives by the heat induced DA reaction

 between FMP and BMI.



Figure S1: ¹H-NMR spectra of P1, P2, P3 and P4 (*=Solvent DMF-d₇; x=water) [Molar ratios of HEMA and HMA in different copolymers (P1-P4) determined from ¹H-NMR].



Figure S2: ¹H-NMR spectra of FMP1, FMP2 and FMP3 (*=Solvent DMF-d₇; x=water).



Figure S3: ¹H-NMR spectra of P5 and FMP5 (*=Solvent DMF-d₇; x=water). [Molar ratios of HEMA and HMA in P5 determined from ¹H-NMR].



Figure S4: ¹H-NMR spectra of P6 and FMP6 (*=Solvent THF-d₈; x=water).



Figure S5: FT-IR spectra of P4 and FMP4.



Figure S6: Gel permeation chromatography (GPC) traces of all copolymers (P1-P6) and furyl modified copolymers (FMP1-FMP6).



Figure S7: DSC thermograms of furyl-modified copolymers (FMP1-FMP6).



Figure S8: ¹H-NMR spectra of the mixture of FMP4 and BMI in solvent DMF-d₇ (maleimide unit /furan unit ratio, $I_{mal/fur} = 1$).



Figure S9: DSC thermograms of xIFMP4¹ exhibiting two endothermic peaks for exo and endo adduct rDA reactions.



Figure S10: Raw profiles (load versus extension plot) of lap-shear tests for different FMPs.



Figure S11: The effect of curing temperature and time on lap-shear strength of $xIFMP4^{1.1}$ ($I_{mal/fur}=1.1$). **A**) Curing temperature was maintained 80 °C for all cases; **B**) Curing time was maintained 2 h for all cases; (aluminum substrates were used for all experiment).

For further study we have selected 2 h as curing time and 80 °C as curing temperature.



SI Figure 12: Plot of composition ratio (HMA/HEMA) vs. ratio of lap-shear strength (after cross-linking/before cross-linking) for different FMPs.

xlFMP1¹



Figure S13: Failure pattern for different adhesive materials after lap shear test (substrate-aluminum).



Figure S14: FTIR spectra of different cross-linked FMP4 (xlFMP4^{0.2}-xlFMP4^{5.6}) after 2 h curing at 80 °C.



Figure S15: Lap-shear strength of various substrates under (A) similar and (B) dissimilar attachments (C) images of substrate failure [Adhesive: xlFMP4^{1.1}, curing time 2 h, temperature 80 °C].



'c': Lap-shear test

Scheme S1: Lap-shear strength of xIFMP4^{1.1} initially, after first and second reattachment.

Reference:

1. American society for testing and materials (ASTM) Standard D2651, Preparation

of metal surfaces for adhesive bonding, ASTM International, West Conshohocken,

PA 2008.

2. P. Berto, A. Pointet, C. L. Coz, S. Grelier and F. Peruch, *Macromolecules*, 2018, **51**, 651-659.