Highly transparent and colorless self-healing polyacrylate coatings based on Diels-Alder chemistry

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Keywords: transparent coatings, self-healing polymers, Diels-Alder, acrylates

Abstract

The efficient integration of reversible polymer networks into acrylate-based polymeric materials is of peculiar interest for the development of coatings who combine high transparency with self-healing ability. In this work, reversible networks are obtained by reacting a series of linear copolymers of furfuryl methacrylate with aliphatic bismaleimides through Diels-Alder (DA) reaction between furan and maleimide moieties. Owing to dynamic crosslinking, the obtained coatings exhibit thermal reversibility, as determined by differential scanning calorimetry and dissolution experiments. Furthermore, upon heating over the retro-DA temperature, an excellent recovery of mechanically-induced surface damages proves successful thermal remendability. Compared to previous reports on DA-based acrylate networks, the presented thermally-responsive coatings exhibit outstanding transparency and absence of colour, as a result of an accurate choice of suitable monomeric precursors. In addition, a pronounced hydrophobic behaviour and excellent adhesive properties make the proposed material particularly suitable for optical applications.

Introduction

Acrylic polymers established themselves in the coating industry due do their low cost, improved properties (e.g., adhesion, filmability, processability) and outstanding durability, particularly in outdoor environments.[1] Moreover, it is easy to tailor their physical properties by judiciously selecting the appropriate monomers for polymer network formation. A further improvement in adhesion and solvent resistance can be achieved by using functional acrylic monomers like hydroxyethyl methacrylate, amenable to postreaction processes such as chemical crosslinking.[2] Unfortunately, these thermosetting acrylic systems generally lack the ability to be repaired after a mechanical damage, as a consequence of their irreversibly crosslinked nature.

In this context, dynamic covalent chemistries have emerged as an efficient tool to embed reversible linkages into acrylate networks, in order to provide healing ability under a suitable external stimulus. While recent efforts have been addressed to the development of approaches based on disulfide bond exchange [3], alkoxyamine dissociation [4], thiol-Michael reaction [5], Alder-Ene addition [6] and bulky urea bonds [7], the most widely reported systems are based on the well-established Diels-Alder (DA) cycloaddition [8-23].

DA is a click-type addition reaction between a dienophile and a diene, typically a maleimide and a furan. The design of a polymer network where crosslinks are constituted by DA adducts would result in the ability to cleave the crosslinks at mild-to-high temperature through a retro Diels-Alder process (r-DA), while enabling their reformation upon cooling through the direct DA reaction. Therefore, the r-DA/DA sequence can be exploited to repair cracks or to remold the crosslinked material.[24] The concept, firstly described in a patent[25] and then in the milestone work of Wudl[26] has been exploited for the dynamic crosslinking of different polymer matrices like epoxies[27, 28], elastomers[29, 30], polyesters[31, 32] and polyketones.[33, 34]

A straightforward strategy to design DA crosslinked acrylates is based on the combination of linear copolymers of furfuryl methacrylates with difunctional maleimide linkers. [8-10, 12, 16, 20] The reported

systems are typically characterized by high healing efficiency. However, they lack of transparency and usually exhibit a yellow-to-orange color, predominantly due to the use of aromatic bismaleimide linkers. This feature factually forbids the utilization of DA-based acrylates for optical applications, where high levels of transmittance in the visible wavelength range are inevitably required.

To bridge this gap, a straightforward strategy to prepare colorless and transparent thermo-responsive acrylates based on the DA chemistry is proposed in this work. Furan functional polyacrylates were synthetized *via* free radical polymerization of furfuryl methacrylate (FMA) with methacrylates bearing different aliphatic groups. Two aliphatic bismaleimides, with different chain length, were synthesized starting from the respective diamines. The obtained linear copolymers containing furan moieties were combined with the bismaleimides in solvent, and colorless, high-transmittance, crosslinked coatings were obtained. The thermal reversibility of the DA-coatings was assessed by means of differential scanning calorimetry (DSC) and solubility experiments. After assessing the self-healing ability of the acrylic-based polymeric materials, the effect of network structure (i.e. type of comonomer, functionality and crosslinker) on thermal properties, wettability and adhesion strength was studied. To the best of our knowledge, this is the first demonstration of transparent, colorless DA-based acrylates for coating applications.

Results and discussion

Copolymers of FMA and one comonomer among n-butyl methacrylate (BMA), 2-ethylhexyl methacrylate (EHMA) and lauryl methacrylate (LMA) were prepared by free radical polymerization in the presence of azobisisobutyronitrile (AIBN) as an initiator (experimental procedure reported in Supporting Information). The composition of copolymers was calculated from ^{1}H-NMR spectra in terms of molar content of furfuryl units, according to the equation:

$$FMA\ (mol\%) = \frac{A_{Fu}}{A_{Fu}+A_C} \cdot 100 \quad (1)$$

where A_{Fu} and A_C are the integrated areas of the signals at 4.9 ppm (-OCH_2 protons of FMA) and 4.0 ppm (-OCH_2 protons of the aliphatic methacrylate comomoner) respectively. For all the copolymers, FMA content was close to the feed composition (see Table S1 in Supporting Information), owing to the similar reactivity of methacrylate precursors [35]. By comparing copolymers with the same furan content, the glass transition temperature (T_g) strongly decreased by increasing the length of the pendant alkyl chain of the methacrylate comonomer, as expected. As shown in Table S1 (Supporting Information), the lowest and highest T_g values were observed in LMA (-49 °C) and BMA (36 °C), respectively. Aliphatic bismaleimides (1,6-bismaleimido hexane (C6) and 1,12-bismaleimido dodecane (C12)) were repeatedly recrystallized from acetone in order to achieve a thorough removal of colored byproducts. Indeed, dissolution in THF and subsequent addition of furan-functionalized co-polyacrylates resulted in transparent and colorless solutions. Equimolar ratio between maleimide and pending furan groups was employed for all coating formulations in order to target full crosslinking through DA cycloaddition, as schematically depicted in **Figure 1**A. Solid coatings were obtained after deposition on glass substrates and suitable thermal treatment (150 °C, 20 min).

Investigation of the thermal properties of the obtained coatings through differential scanning calorimetry (DSC) measurements provided insights into the dynamically crosslinked polymer networks. First, all samples exhibited a single glass transition and a broad endothermic transition between 120 °C and 170 °C (Figure 1B). T_g values of the DA-based acrylate coatings (**Table 1**) were systematically higher than their parent copolymers, owing to the physical constraint exerted by DA crosslinks to chain mobility. In this context, the free volume (*viz.*, T_g) of the parent copolymer played a key role: more rigid networks were obtained from poly(BMA-*co*-FMA) copolymers, compared to the others with same furan content. Furthermore, crosslinked EHMA20 samples exhibited the highest T_g, due to their higher furan/maleimide functionality. Lastly, molecular length of maleimide linkers had a significant influence on the network mobility: samples crosslinked with C6 (more rigid) systematically showed higher T_g (+ 6-7 °C) than their counterparts crosslinked with C12. [36]. In all

coating formulations, the broad endotherm starting at 120 °C and peaking at 150 – 160 °C indicated the occurrence of the r-DA reaction [37], *i.e.* the cleavage of the furan/maleimide adducts, and proved the reversibility of the formed crosslinks. The observed temperature ranges for the r-DA process in the different coating samples were not affected by the network rigidity, being this a peculiar feature of the furan/maleimide couple.[38] Direct evidence of crosslinking was gained from gel content experiments (Figure 1C). Coating deposited on glass substrates underwent swelling when immersed in THF. Recovered solids, after filtration and evaporation were > 99% of the original sample, given their insolubility at rt due to covalent crosslinking. Conversely, when crosslinked samples were firstly swelled at rt in dichlorobenzene (good, high boiling solvent for both furan-containing polyacrylates and aliphatic bismaleimides) and then heated at 150 °C (r-DA range), complete dissolution was achieved (Figure 1D), further proving the thermal reversibility of the polymer networks.

In order to assess the thermally induced self-healing of the dynamically crosslinked polyacrylates, coatings were manually damaged on the surface with a scalpel, producing cuts with up to 30-40 μm average width and 1-2 μm thickness. After a thermal treatment at 150 °C (90 min) followed by slow cooling to rt, scratches were found to heal (**Figure 2**). The best results in terms of visual repair were obtained in the case of softer polymer networks (EHMA- and LMA-based), likely due to better macromolecular flow at higher temperatures compared with BMA-based systems. Temperature for thermal treatment was chosen in accordance with the peak of r-DA endotherm, while avoiding thermal degradation of the material (*i.e.*, the maximum temperature for the healing cycle was maintained ≈ 50 °C lower than the onset of thermal degradation as assessed by TGA in air, see Figure S1 Supporting Information). Notably, the time required for the healing treatment in this work was slightly shorter (90 min) compared to the majority of furan polyacrylates/maleimide networks previously reported in the literature (typically, > 2h).[8, 12, 16, 17]

The suitability of the presented systems as transparent thermally healable coatings for optical applications was studied through the evaluation of some selected, relevant technological properties,

namely optical transparency, wettability and adhesion. As of transparency, the latter considered one of the primary targets of the present study, all DA-coatings exhibited a transmittance > 90% throughout the visible (400 – 700 nm) range, independently of the co-monomer, the crosslinker and the content of furan/maleimide functionality (**Figure 3**A and 3B). This key property of optically clear polymers is intrinsically related to their molecular structure, their chain conformation and the presence of impurities in the formulation. In the presented systems, besides the judicious choice of precursors bearing no chromophore species capable of absorbing light in the visible range (namely, the functional polyacrylates and the aliphatic bismaleimides) [39], transparency can be attributed to the completely amorphous nature of the developed DA-based polymeric networks. Moreover, differently from other dynamic covalent networks recently reported, [40, 41] systems based on the DA chemistry do not require catalysts, which could cause unwanted coloring of the resulting solid material. [42]

Wettability was studied in terms of static optical contact angle (OCA) measurements. All DA-based crosslinked coatings displayed high values of water contact angles ϑ_{H2O}, ranging from 97 ° to about 120 ° (Figure 3C), directly indicating their moderate to pronounced hydrophobic character. Surface properties were clearly affected by the structure of the parent copolymers. First, by comparing samples with the same FMA content (BM10, EHMA10, LMA10), ϑ_{H2O} was found to increase to about 120° as the alkyl chain of the comonomer increased its length from butyl to lauryl groups.[43, 44] Furthermore, considering samples with same comonomer (EHMA), coatings with a higher furfuryl content (20 mol.%) exhibited lower ϑ_{H2O} values, as a result of the higher polarity of the system imparted by the more abundant furan pendant groups. Conversely, the maleimide linker did not influence significantly the wettability of the coatings. Comparatively, calculated values of surface energy γ followed a reverse trend and they were largely determined by the dispersive component γ_d (Table 1), likely due to the prevalence of the non-polar pendant groups over the polar ones in the copolymer structure. Finally, the adhesion strength of all DA-coatings was evaluated through pull-

off tests after deposition on glass substrates. For all the tested samples, the failure mode was completely cohesive, either within the coating layer or in the glass substrate, indicating excellent coating-substrate adhesion (see Figure S2 Supporting Information). In particular, adhesive strength values >16 MPa, >7 MPa and >4 MPa were recorded for BMA10_C6, EHMA10_C6, and LMA10_C6 respectively (Table 1), in accordance with the trends observed for the surface tension values.

Conclusion

In conclusion, the development, characterization and functional testing of novel thermo-responsive polymer networks for transparent and colorless coatings is presented in this work. A series of dynamic covalent networks based on the DA chemistry was prepared by reacting linear copolymers of furfuryl methacrylate and aliphatic methacrylates with aliphatic bismaleimides. The thermal reversibility of the crosslinked polymeric structure, assessed by solubility tests and DSC, allowed excellent aesthetic recovery of the surface smoothness after the coatings were manually scratched. The type of comonomer, the length of the maleimide crosslinker and the degree of furan functionality in the copolymer significantly influenced the thermal properties of the resulting DA-coatings, so that their T_g could be tuned over a wide range from 7 °C to 63 °C. Owing to the careful choice of appropriate synthetic precursors, the obtained self-healing polyacrylate coatings were completely colorless and exhibited excellent transparency in the visible range. Combined with a marked hydrophobicity and exceptional adhesive strength, the presented coatings can be considered a promising platform for the development of advanced stimuli-responsive systems for optical applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Authors thank Gigliola Clerici for her kind support with the thermal analysis.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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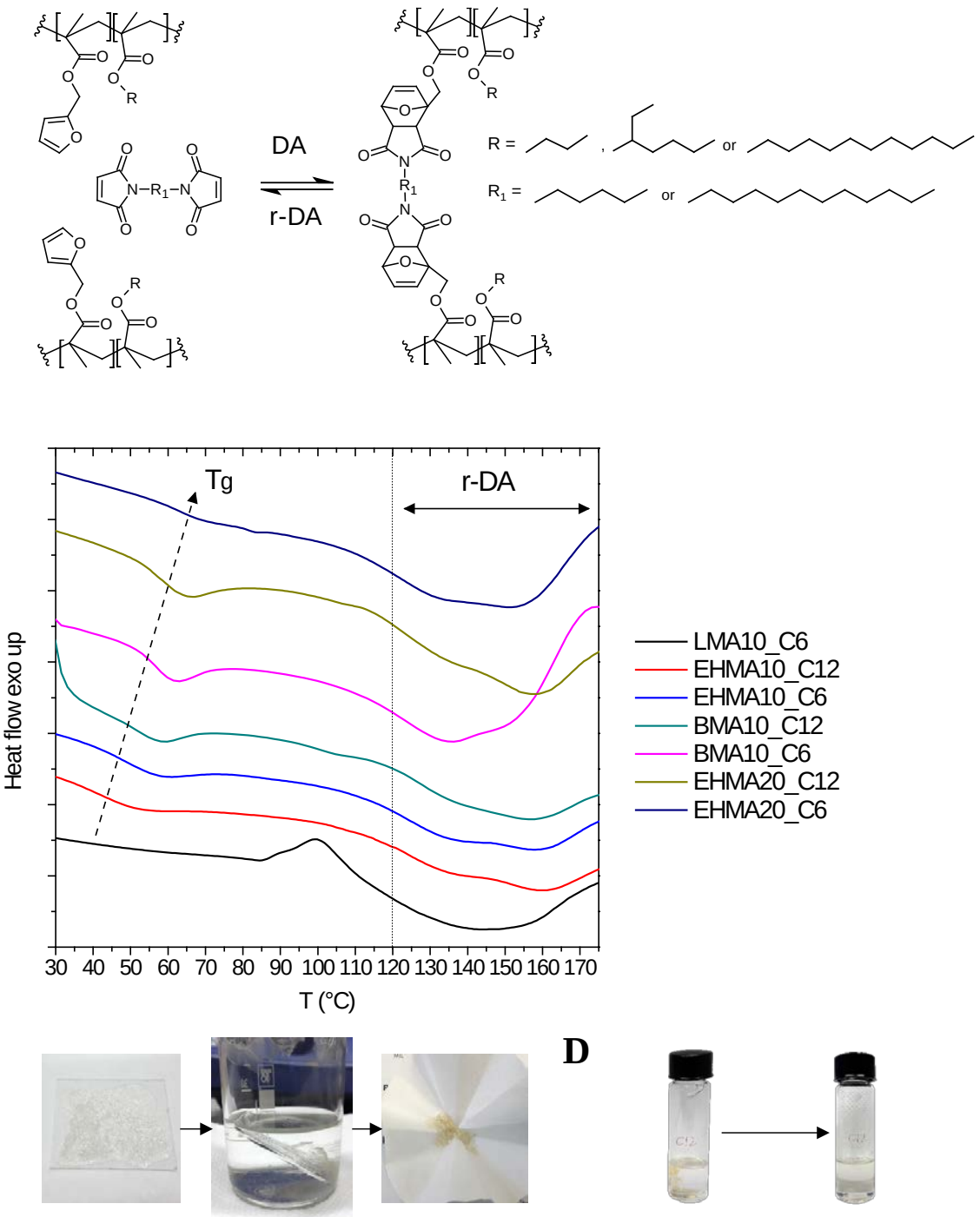

Figure 1. (A) Reaction scheme of reversible crosslinking of furan functionalized polymethacrylates with aliphatic bismaleimides through DA. (B) DSC traces (heating scan) of crosslinked coatings. (C) Determination of insoluble fraction after crosslinking. (D) Solubilization through r-DA.

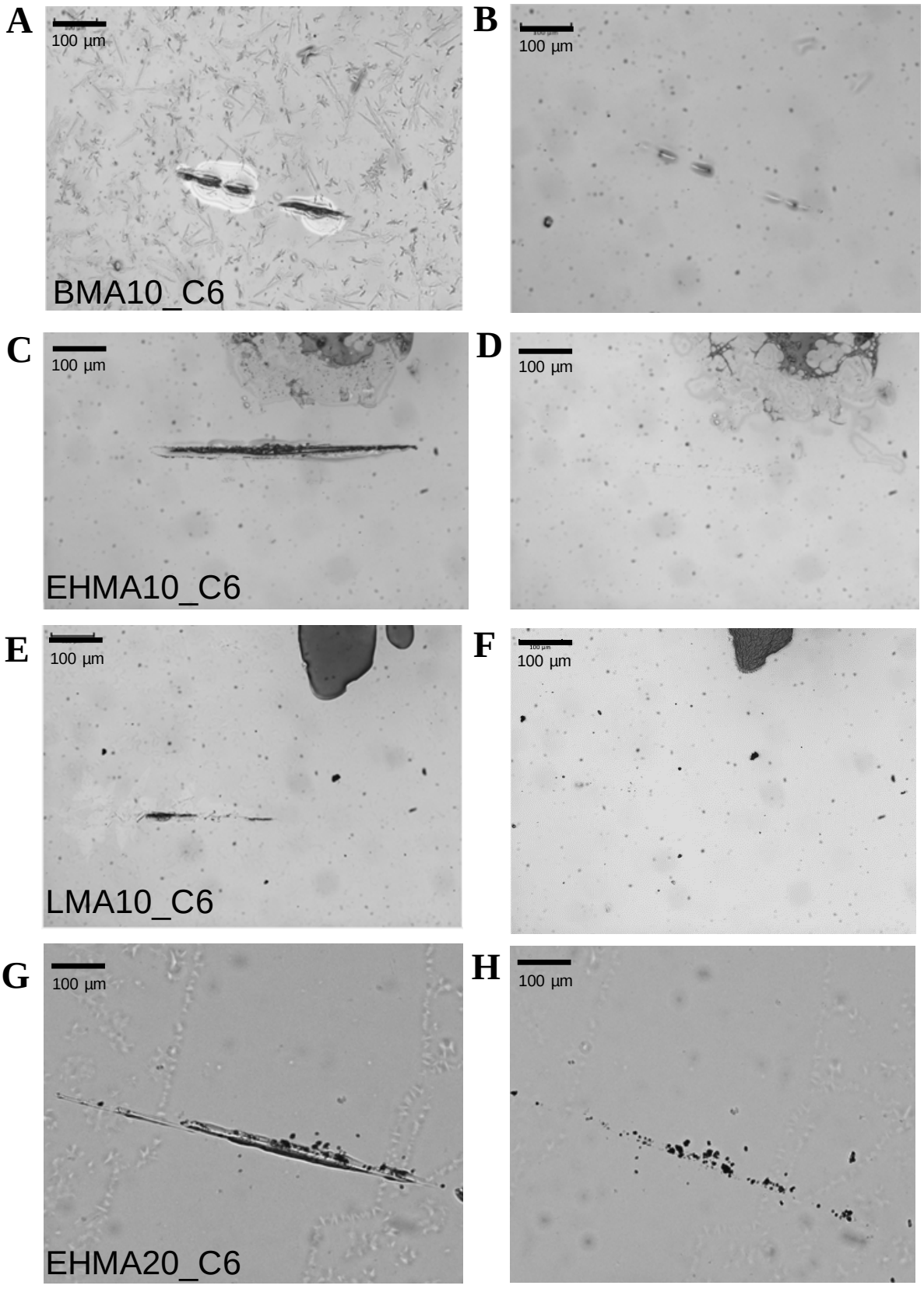

Figure 2. Optical microscope images of coating obtained from copolymers of FMA (10 mol% or 20 mol%) crosslinked with C6 bismaleimide: (A, C, E, G) damaged by scratching with a scalpel and (B, D; F, H) after thermal treatment at 150 °C and slow cooling to rt.

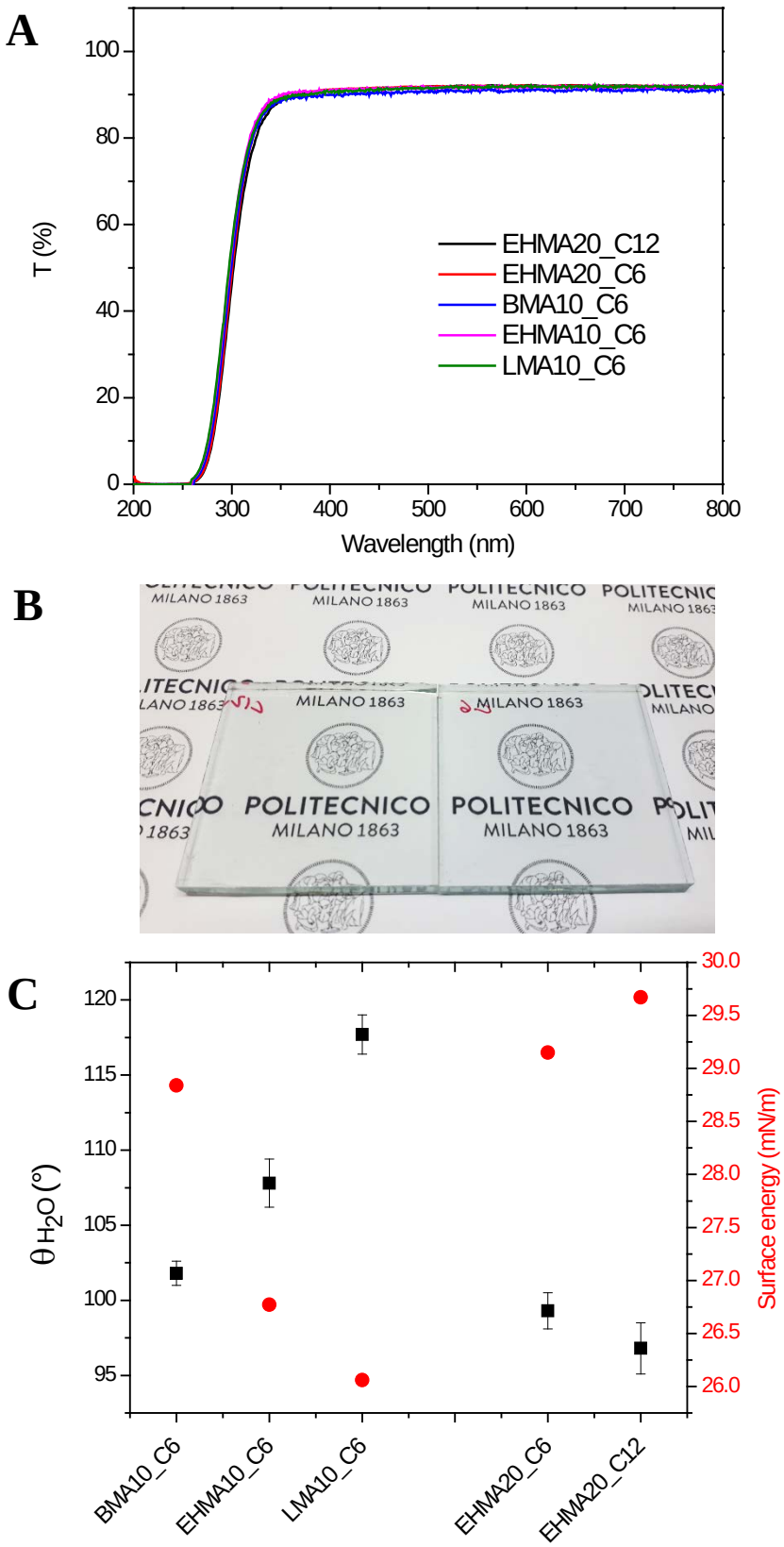

Figure 3. (A) UV-Vis transmittance spectra of different coating formulations. (B) picture of copolymer EHM20 crosslinked with C6 and C12, coated on glass slabs (C) Static contact angle in water and calculated surface energy.

Table 1. Thermal properties of copolymers after crosslinking with C6 or C12 aliphatic bismaleimides, determined from DSC; static contact angle measurements in water (ϑ_{H2O}), diodomethane (ϑ_{DIM}), calculated dispersive (γ_d) and polar (γ_p) component of surface energy and pull-off adhesion strength for selected coatings;

Polymer	linker	T_g [°C]	$T_{r\text{-}DA}$ [°C]	ϑ_{H2O} [°]	ϑ_{DIM} [°]	γ_d [mN/m]	γ_p [mN/m]	Adhesion [MPa]
LMA10	C6	7	120-160	117.7±1.3	68.3±3.6	25.84	0.22	>4
LMA10	C12	nd	120-160					
EHMA10	C6	48	120-170	107.8±1.6	63.9±1.8	26.69	0.08	>7
EHMA10	C12	42	120-170					
BMA10	C6	57	120-160	101.8±0.8	59.3±2.9	28.38	0.46	>16
BMA10	C12	52	120-160					
EHMA20	C6	63	120-170	99.3±1.2	58.4±2.3	28.34	0.81	>8
EHMA20	C12	56	120-170	96.8±1.7	57.3±1.8	28.45	1.22	>8

Table of content

Novel dynamically crosslinked polyacrylate systems based on Diels-Alder chemistry are presented as transparent, colorless and self-healing coatings for optical applications. These networks combine peculiar properties of common polyacrylates like outstanding transparency, synthetic accessibility and tunability of thermal properties, with thermally-induced remendability, provided by the reversibility of furan/maleimide crosslinks.

Keyword transparent coatings, self-healing polymers, Diels-Alder, acrylates

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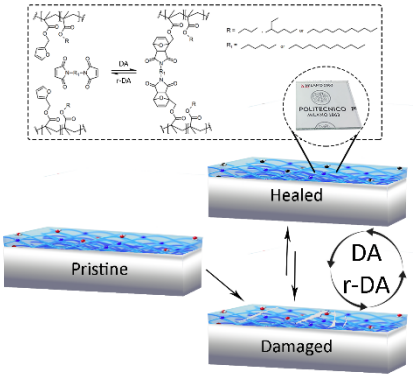

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Supporting Information

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S-II. Thermo-gravimetric analysis

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S-IV. Thermo-mechanical analysis

S-I. Experimental Section

Materials: furfuryl methacrylate (FMA), n-butyl methacrylate (BMA), lauryl methacrylate (LMA), 2-ethylhexyl methacrylate (EHMA), maleic anhydride, 1,6-diaminohexane, 1,12-diaminododecane, acetic anhydride, nickel(II) acetate, triethylamine, sodium sulfate, N,N-dimethylformamide (DMF), were all purchased from Sigma-Aldrich. Acetone, tetrahydrofuran (THF), chloroform and azobisisobutyronitrile (AIBN) were obtained from Fluka.

Synthesis of co-polyacrylates: Linear copolymers bearing furan groups were prepared by free radical polymerization. In a typical synthesis, FMA and a methacrylate comonomer (LMA, EHMA or BMA) were dissolved in chloroform (30 wt%) under inert atmosphere. A solution of AIBN (1 wt% with respect to the monomers) in chloroform was injected and the mixture was stirred for 4h at 80 °C. Products were recovered by two steps of precipitation in cold methanol and re-dissolution in chloroform, which was removed under vacuum.

Synthesis of bismaleimides: 1,6-bismaleimido hexane (C6) and 1,12-bismaleimido dodecane (C12) were synthetized from 1,6-diaminohexane and 1,12-diaminododecane respectively, according to reported procedures [36, 45]. Typically, the diamine (10 mmol) was added to a mixture of maleic anhydride (20 mmol) in DMF (6 mL). The mixture was heated to 100 °C and stirred for 30 min until a yellow solution was obtained. Upon addition of acetic anhydride (40 mmol), nickel(II) acetate (0.1 mmol) and triethylamine (5 mmol) a dark brown solution was obtained and stirring was continued for 30 min at 90 °C. After cooling to 40 °C, the solution was poured into ice water (100 mL) and stirred for 10 min. The brown precipitate was collected by filtration (paper filter on Buchner funnel). The washing and filtering sequence was repeated three times, obtaining light brown solids, which were dissolved in hot acetone (35 mL) and dried with sodium sulfate. The solution was refluxed overnight on carbon black (2 g), which was removed by filtering twice over a Buchner funnel. After recrystallization in acetone and filtration, off-white crystals were obtained. C6: yield ≈ 20%; mp 137 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 6.70 (s, 4H, HC=CH), 3.50 (t, 4H; NCH_2), 1.55 (m, 4H,

$NCH_2C\underline{H}_2$); 1.30 (m, 4H; $NCH_2CH_2C\underline{H}_2$). C12: yield ≈ 40%; mp 112 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 6.60 (s, 4H, $\underline{H}C=C\underline{H}$), 3.50 (t, 4H, $NC\underline{H}_2$), 1.50 ppm (t, 4H, $NCH_2C\underline{H}_2$), 1.20 (m, 16H, CH_2).

Coating preparation: bismaleimide (C6 or C12) and copolymer (combined on equimolar basis between maleimide and furan groups) were dissolved in THF (15 wt%) and spin coated (1200 rpm, 40 s) on glass slides. Thermal treatment (150 °C, 20 min) followed by slow cooling to rt was performed to ensure complete solvent removal and crosslinking.

Characterization: ^{1}H-NMR (400 MHz) spectra were recorded on a Bruker Avance 400 using $CDCl_3$ as solvent. Differential scanning calorimetry (DSC) analyses were performed with a DSC 823e (Mettler-Toledo) instrument on solid state samples (~10-15 mg) at heating/cooling rates of 10 °C/min or 20 °C/min. Average molecular weights were determined using a gel-permeation chromatography (GPC) apparatus consisting in a Waters 515 HPLC pump (mobile phase: THF; flow rate: 1 mL/min; temperature 35 °C) equipped with three Styragel columns (models HR 4, HR 3 and HR 2) from Waters and a refractive index detector Waters 2410. Samples were dissolved in THF at a concentration of 0.2 wt% and a calibration curve was prepared by using monodispersed fractions of polystyrene. Thermogravimetric analysis (TGA) was performed on a Q500 TGA system (TA Instruments) from ambient temperature to 800 °C at a scan rate of 10 °C/min in air atmosphere. UV–visible spectroscopy analyses were performed at room temperature on an Evolution 600 UV–vis spectrophotometer (Thermo Scientific). Static optical contact angle (OCA) measurements on the coatings were performed with an OCA 20 (DataPhysics) equipped with a CCD photo-camera and with a 500 μL Hamilton syringe to dispense liquid droplets. Water and diiodomethane were used as probe liquids. The surface energy of the coatings was calculated according the Owens-Wendt-Rabel-Kaelble (OWRK) method.[46] Optical micrographs were taken through an Olympus BX-60 reflected-light optical microscope equipped with an Infinity 2 digital camera. The adhesive properties of the coatings on glass substrates were determined through a PosiTest AT-M Manual adhesion pull-off

tester (DeFelsko) by measuring the pulling force needed to detach a 20 mm-diameter aluminium dolly glued to the crosslinked coatings by means of a two-component epoxy adhesive (Araldite 2011, curing cycle: 50 °C, 24 h). Dynamic mechanical analysis (DMA) was conducted on a Mettler Toledo DMA/SDTA861 instrument from 20 °C to 180 °C at a 3 °C/min heating rate.

Table S1. Experimental conditions for the synthesis and characterization of linear co-polyacrylates, namely composition, number average molecular weight (M_n), dispersity ($Đ$) and thermal properties.

Sample	Comonomer	FMA feed [mol%]	FMA [a)] [mol%]	Yield [%]	M_n [b)] [kg/mol]	$Đ$ [b)]	T_g [c)] [°C]
LMA10	LMA	10	8	90	38.6	1.9	-49
EHMA10	EHMA	10	8	90	39.1	1.9	-14
BMA10	BMA	10	8	60	47.6	1.5	36
EHMA20	EHMA	20	20	75	37.2	3.5	7

[a)] determined from ^{1}H-NMR; [b)] from GPC; [c)] from DSC

S-II. Thermo-gravimetric analysis

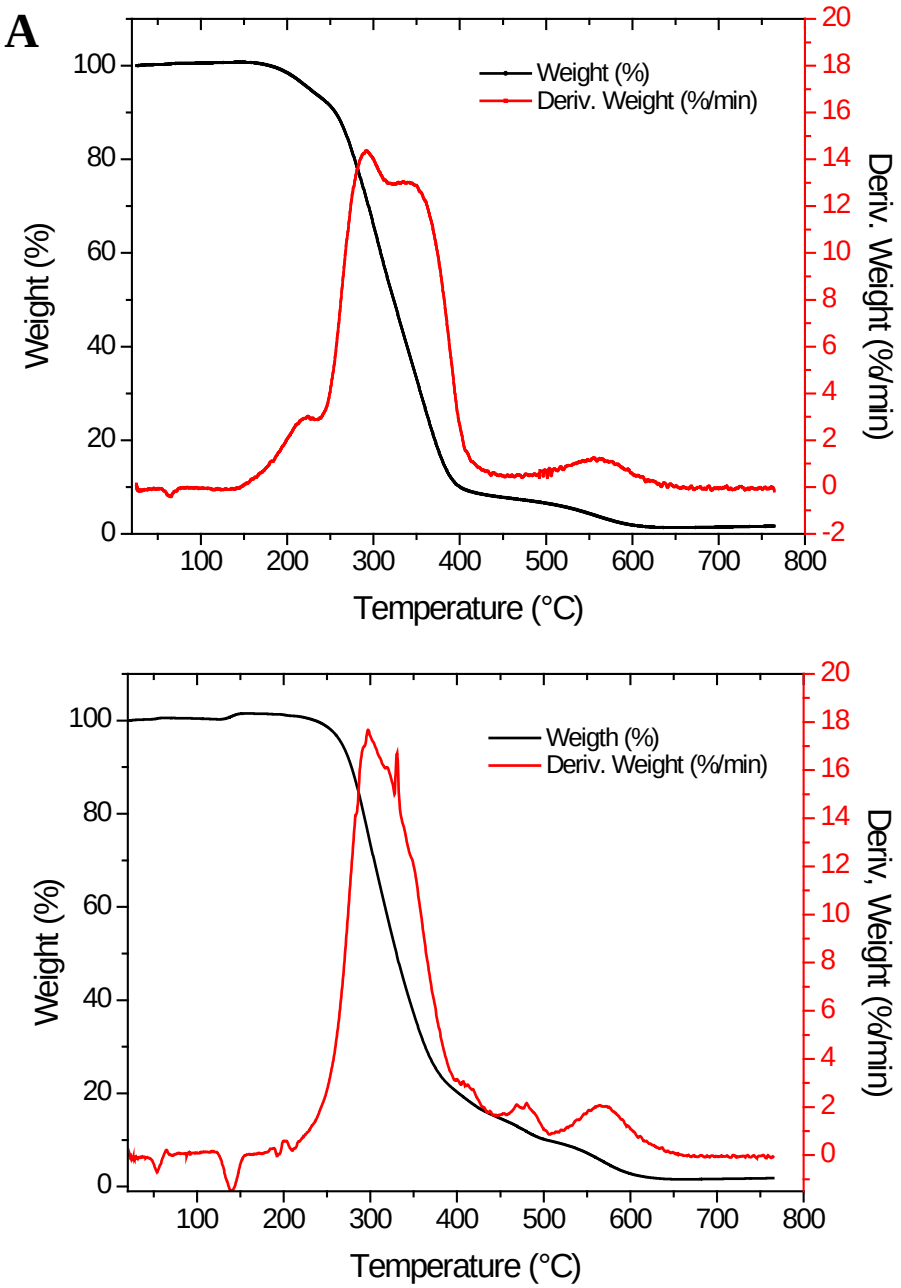

Figure S1. TGA and derivative TGA plots of representative crosslinked formulations EHMA20_C6 (A) and EHMA20_C12 (B). Analyses performed in air.

S-III. Adhesion strength

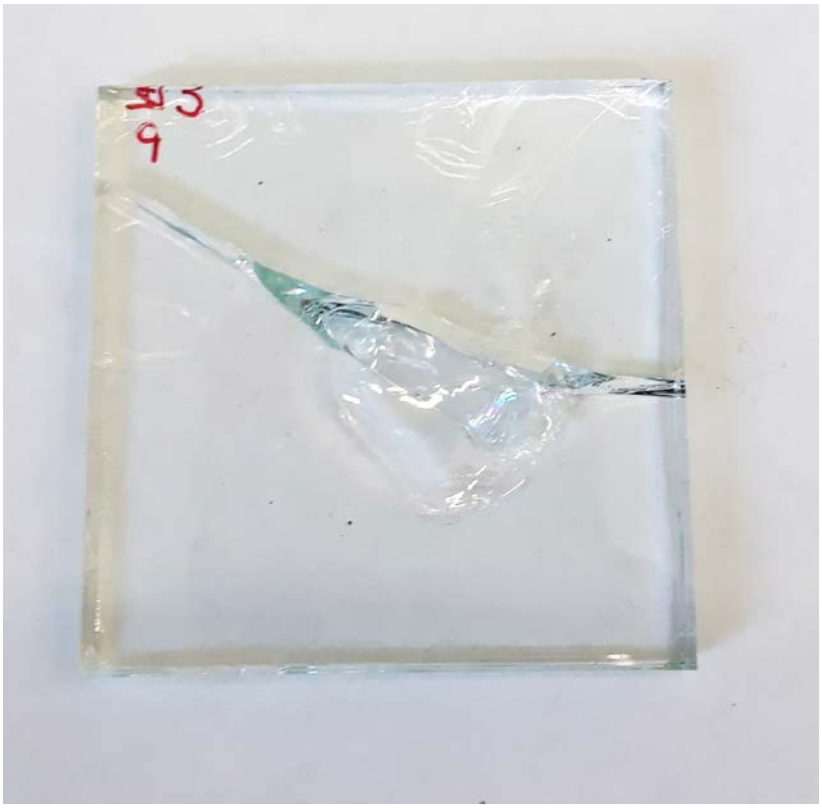

Figure S2. Representative photographic image of failure of the glass substrate after pull-off adhesion test on polyacrylate self-healing coatings.

S-IV. Thermo-mechanical analysis

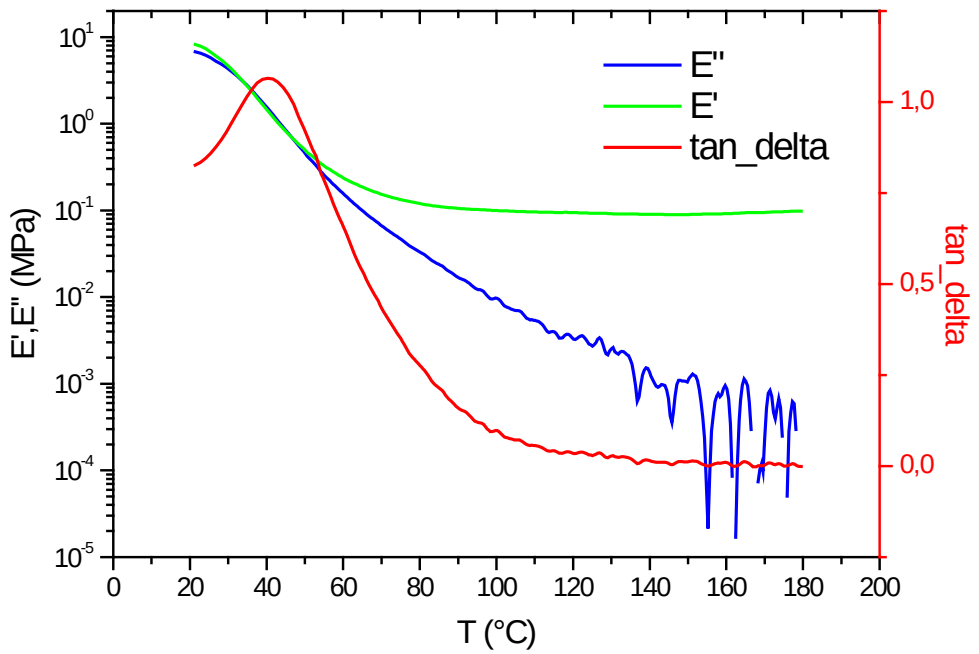

Figure S3. Dynamic mechanical analysis of crosslinked formulation EHMA10_C12.