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Thermal/Blue Light Induced Cross-Linking of Acrylic Coatings with Diazo Compounds

Felix J. de Zwart, Lukas A. Wolzak, Petrus C. M. Laan, Simon Mathew, Jitte Flapper, Keimpe J. van den Berg, Joost N. H. Reek, and Bas de Bruin*

The thermal curing of industrial coatings (e.g., car painting and metal coil coatings) is accompanied by a substantial energy consumption due to the intrinsically high temperatures required during the curing process. Therefore, the development of new photochemical curing processes—preferably using visible light—is in high demand. This work describes new diazo-based cross-linkers that can be used to photocure acrylic coatings using blue light. This work demonstrates that the structure of the tethered diazo compounds influences the cross-linking efficiency, finding that side reactions are suppressed upon engineering greater molecular flexibility. Importantly, this work shows that these diazo compounds can be employed as either thermal or photochemical cross-linkers, exhibiting identical crosslinking performances. The performance of diazo-cross-linked coatings is evaluated to reveal excellent water resistance and demonstrably similar material properties to UV-cured acrylates. These studies pave the way for further usage of diazo-functionalized cross-linkers in the curing of paints and coatings.

However, many industrial coating processes incur a substantial energy consumption, primarily from the intrinsically high temperatures associated with thermal curing. Thermal curing processes are energy intensive, because in such processes the coated object needs to be heated in full.^[1] This puts a particular pressure on the automotive, coil, and powder coating processes, both from an economic and sustainability viewpoint.^[2] Development of new photochemical curing processes seeks to dramatically reduce the energy footprint of the coating process and is therefore in high demand.^[3] An attractive strategy toward reducing the energy consumption would thus be non-UV photochemical curing that only requires the surface irradiation with safer, nonionizing visible light. Despite the large body of work on visible-light-curing

of acrylates, research toward other visible-light-induced paint curing strategies is still in its infancy, with only a few reported examples thus far.^[4–6]

Carbene-based cross-linkers have seen a large commercial impact in materials chemistry, finding applications as fabric strengtheners,^[7] adhesives^[8] and in mixed plastics recycling.^[9] In particular, diazirine compounds have shown high efficiency in cross-linking polymers bereft of specific functionality (e.g., polypropylene^[10] and polydimethylsiloxane^[11]) through C–H insertion, and functional polymers (e.g., containing hydroxyl and thiol functionalities^[8,12]) through X–H insertion. These diazirines generally require UV-light to activate the diazirine carbene precursor, which next to introducing again a high energy-consumption can cause several selectivity problems. Therefore, alternative carbene precursors are preferred for visible light activation. In synthetic photochemistry, specific diazo compounds have been used as carbene precursors to perform various reactions such as X–H insertion and cyclopropanation under the irradiation of blue light.^[13,14]

Two approaches can be discerned to translate this diazo chemistry to polymer cross-linking. One is the incorporation of the diazo-functionality into the polymer backbone by copolymerization (e.g., acrylate-functionalized diazo compounds) yielding a polymer that demonstrates effective cross-linking via C–H insertion.^[15,16] The complementary approach is to introduce low molecular weight cross-linkers, featuring multiple diazo functionalities, and apply these to existing acrylates used in industrial coatings. This drop-in solution approach has the benefit of

1. Introduction

Coatings protect the materials they are applied on (e.g., wood or metal), thereby prolonging the lifetime of the coated substrate and thus reducing the need for complete object replacement.

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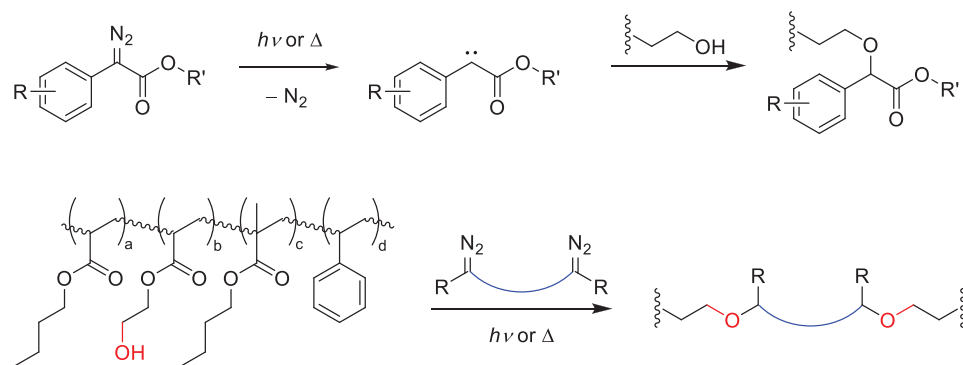


Figure 1. Envisioned strategy toward cross-linking acrylic polyols (APOs) with tethered diazo compounds using blue light.

not requiring re-evaluation of the photobinder-material properties, unlike the use of a new-tailor-made polymer.

Therefore, we sought to explore the ability of bifunctional diazo compounds as cross-linkers, using blue light to generate similar carbene intermediates (Figure 1). These free carbenes can then be used to target the hydroxy functionality in acrylics, introduced by using 2-hydroxyethyl methacrylate as a monomer. This O–H insertion would then create a strong ether linkage that reduces the hydrophilicity of the material, which in turn is expected to improve the water resistance. In this article, we describe our investigations to utilize diazo compounds for blue-light activated paint curing.

2. Results and Discussion

2.1. Synthesis and Characterization

The most commonly used single-component melamine coatings are based on acrylic polyols (APOs) paired with a melamine cross-linker that requires cross-linking at elevated (>120 °C) temperatures.^[17] Alternatively, these APOs can be formulated as two- or three-component coatings with isocyanate cross-linkers.^[18] As we aim to replace such cross-linking motifs, we synthesized a standard APO binder using free-radical polymerization under starved-feed conditions. This APO polymer was synthesized using a mixture of 2-hydroxyethyl methacrylate, butyl methacrylate, butyl acrylate, as main components (91 wt% of dry polymer mass) and methyl acrylate, methacrylic acid, and styrene as minor components (9 wt% of dry polymer mass), as described previously.^[18] After polymerization, the polymer was diluted with butyl acetate (75% solids content) to obtain the appropriate viscosity for film formation. Thereafter the APO coating was characterized by titration and the hydroxyl equivalent weight of the dry polymer was determined to be 410 g mol⁻¹ (4.2 wt% based on solids). A number average molecular weight of 2.3 kD was found by gel permeation chromatography (GPC), translating to each oligomer featuring approximately six hydroxy functionalities. The obtained APO polymer was used as the binder in all formulations and studies presented in this paper.

We synthesized six different tethered diazo compounds based on previous literature reports on cross-linkers (Figure 2). Compounds 1 and 4 have previously been reported to be efficient cross-linkers of unfunctionalized polymers via C–H insertion.^[7]

These bis-diazo compounds allow us to evaluate the influences of side chain (cf. 1 and 3) substitution, main chain (cf. 1 and 4) substitution and electronics (cf. 1 and 2) of the diazo compounds on their cross-linking efficiency. Heptyl-substituted bisdiazole 3 allows the investigation of the effect of softer cross-linkers on the final material properties. Diazo compounds are potentially explosive, therefore it is prudent to first assess the thermochemical decomposition of any diazo compound by differential scanning calorimetry (DSC).^[19] The enthalpy of decomposition in combination with the onset temperature of decomposition can be used as an estimate of the shock (impulse) sensitivity and explosive propagation, using Yoshida's correlations.^[20] From DSC data we found that cross-linkers 1, 3, 4, and 5 are unlikely to be explosive, while cross-linker 2 might have safety issues when applied on large scale (Table S1, Supporting Information). We additionally investigated shock sensitivity by drop hammer testing revealing that compounds 1–5 exhibited no response until at least 20 J impact (Figure S1, Supporting Information), a sufficiently low value to ensure safety upon evaluation of 2 in thermal polymer cross-linking at lab scale. Furthermore, the thermochemical data indicates that a temperature of 120 °C would be sufficient to activate all diazo cross-linkers thermally (Table S1, Supporting Information).

To further study the utilized cross-linkers, we attempted to investigate the electronics of the diazo groups through assessment of the bond lengths in their respective crystal structures. However, the C_{diazo} – C_{Ar} (avg 1.47 Å), C_{diazo} – C_{ester} (avg 1.46 Å), C–N (avg 1.32 Å) and N–N (avg. 1.12 Å) distances were found to be

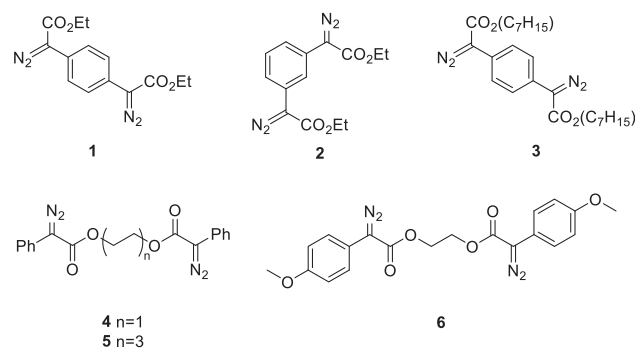


Figure 2. Structures of the diazo compounds utilized in this study.

identical to each other within 0.01 Å. Furthermore, the variation in bond lengths within the asymmetric unit of the crystal structure of cross-linker 4 was found to be larger than between the cross-linkers and therefore we concluded that the bond lengths are a poor descriptor of the electronics of these diazo compounds.

Having synthesized the binder and cross-linkers, we started with thermal cross-linking of the APO binder using diazo compounds 1–6.

2.2. Thermal Cross-linking

To evaluate and compare the performance of the diazo compounds as cross-linkers, we first tested the various compounds in thermal cross-linking of the APO binder up to a 1:1 ratio (w/w) of cross-linker. We then normalized the results for the molecular weight of the utilized diazo compounds and used the above determined hydroxy functionality of 410 g mol⁻¹ to express the data as a molar diazo:hydroxy content ratio. The cross-linkers were added as solids to a vial containing ≈50 mg of APO binder with subsequent heating of the mixture (60 °C for 2 h) to volatilize the remaining butyl acetate. For cross-linkers 2–5 this led to dissolution of the cross-linker in the coating, leading to a clear and orange appearance, whereas cross-linker 1 did not dissolve at loadings above 1.0 N₂/OH. Cross-linker 6 proved to be completely insoluble in the acrylic coating and therefore could not be investigated further in the cross-linking of APO. Finally, the mixtures were heated at elevated temperature (120 °C for 1 h) to activate the diazo moieties and initiate cross-linking.^[7]

To analyze the material properties, the coatings were analyzed by DSC to determine the glass transition temperature (*T_g*). For cross-linkers 1, 2, 4, and 5 the *T_g* increases rapidly with addition of more cross-linker (Figure 3C). Interestingly, the *T_g* of the coatings using high amounts of heptyl-substituted cross-linker 3 plateaus around -3 °C and even decreases slightly above a 1.0 N₂/OH ratio cross-linker doping. The increase in *T_g* as a function of cross-linker doping is influenced by multiple effects. This includes the increase in molecular weight due to cross-linking according to the Flory–Fox equation, chemical functionalization of the hydroxyl groups of the APO, and the interaction of the cross-linker with the polymer chains. For cross-linker 3, the interaction of the heptyl chains with the polymer presumably leads to an increase in the free volume, and thereby a decrease in the glass transition temperature. This shows that 3 operates as an internal plasticizer, which could be interesting for other applications where softer materials are required.^[21]

The insoluble fraction of the coating was analyzed, by determining the gel content by using dichloromethane as washing solvent to remove all solutes. For all cross-linkers, an increase in gel content was observed when using a higher amount of cross-linker doping (Figure 3A). Heptyl-substituted cross-linker 3 achieved a high gel content (>80%) at high cross-linker doping (1.5 N₂/OH) while the maximum gel content starts to plateau at lower cross-linker doping (0.8–1.2 N₂/OH) for the cross-linkers 4 and 5 (Figure 3A). The cross-linking performance is therefore similar for cross-linkers with a comparable main chain structure.

Next, the soluble fractions of the coatings were investigated with GPC to determine the molecular weights of the soluble fraction of the mixtures (Figure 3D). The weight average molecular

weight peaks around 0.3 N₂/OH for cross-linker 4 and 5, and above 0.5 N₂/OH for cross-linkers 1–3, indicating that large insoluble polymer networks start to form after these points. This is in accordance with the results from the gel content and indicates efficient cross-linking of the APO binder.

In an attempt to understand the improved performance of cross-linker 4 (compared to the other cross-linkers), the FTIR spectra of the thermally cured mixtures using cross-linkers 2 and 4 were compared at various loadings of the difunctional diazo compound (Figures S6–S12, Supporting Information). In all coatings, the absence of a diazo signal at 2089 cm⁻¹ indicates full conversion of the diazo moiety. An increase of cross-linker doping leads to a decrease in the broad hydroxyl signal at 3500 cm⁻¹, showing that a significant contribution to the observed cross-linking involves insertion of the generated carbenes into the O–H bonds of the APO binder.^[22] Furthermore, for cross-linker 2 a peak at 1825 cm⁻¹ is observed—and can be assigned to a known side reaction—namely, C–H insertion of the generated carbene into the ethoxy side group, cyclizing to a β-lactone (Figure S6, Supporting Information).^[22] This infrared peak is not detected for cross-linker 4, but a small shoulder on the peak of 1770 cm⁻¹ is suggestive for the formation of a γ-lactone instead (Figure S11, Supporting Information). Whereas these differences are related to any differences in cross-linking efficiency remains unclear.

To confirm the cross-linking of the diazo compounds with the APO to be occurring through O–H insertion of the generated carbene into the hydroxyethyl methacrylate groups of the polymer, we studied the thermal reaction between ethyl diazo(phenyl)acetate 7 and the APO binder at equimolar ratio of diazo to hydroxyl group. As no cross-linking occurs with this monodiazo compound the coating remains soluble, and the results can be analyzed using ¹H DOSY NMR to show only the signals of the polymer (Figure 4). After thermally curing (120 °C for 1 h), we observed new signals in the aromatic region originating from the arene ring of the diazo compound, confirming the incorporation of this moiety into the polymer. Moreover, the newly appearing singlet at δ = 4.93 ppm is indicative of a benzylic proton with geminal ether and ester moieties.^[23] This further confirms that the thermal reaction of the polymer with an aryl-ester substituted diazo leads to carbene insertion into the O–H bonds of the polymer. The singlet at 4.93 ppm does not cleanly integrate in a 5:1 ratio to the additional aromatic protons at 7.4 ppm, indicating that also other pathways such as C–H insertion could be occurring simultaneously. The above identified β-lactone could also be observed with ¹H-NMR spectroscopy, showing a characteristic doublet at δ = 1.72 ppm (Figures S13–S14, Supporting Information). Furthermore, the ¹H-NMR spectrum also displays the product of the reaction of the formed carbene with molecular oxygen, to form ethyl phenylglyoxylate. This is another known side reaction, undesirable during paint curing as does not lead to a cross-link. A rough estimate of the reaction selectivity can be determined by integrating the signals of the benzylic singlet at 4.93 against those of the cyclization β-lactone side product and the ethyl phenylglyoxylate oxidation side products. This indicates 65% O–H insertion, 15% oxidation, and 20% cyclization, assuming that the signals of the acrylic can be accurately integrated against those of small molecules. Release of N₂ during activation of the diazo compounds is expected to suppress reactions with

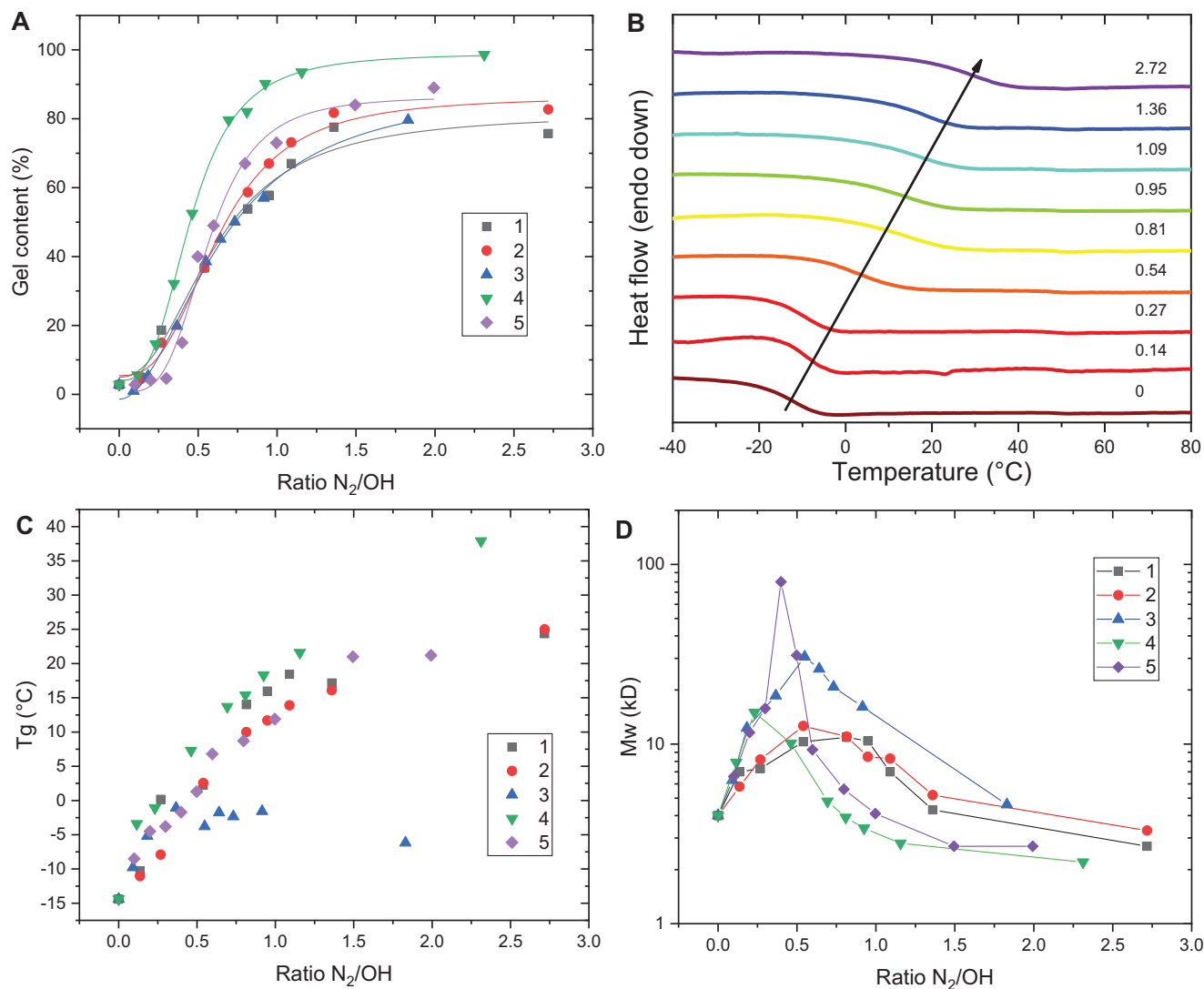


Figure 3. A) Gel content (in CH_2Cl_2) of binder as function of mol ratio cross-linker doping (sigmoidal fit drawn as guide to the eye). B) representative differential scanning calorimetry (DSC) traces of acrylic polyol (APO) with increasing amounts of cross-linker 2. C) Glass transition temperature as a function of cross-linker doping. D) M_w of the soluble fraction, determined by gel permeation chromatography (GPC), as a function of cross-linker doping. See Figures S2–S5 (Supporting Information) for this data as a function of weight ratio.

O_2 from air, but apparently this reaction still occurs to some extent. Carbene oxidation is known to be further suppressed when using more electron-rich carbenes such as cross-linker 6, which is unfortunately not soluble in the acrylic binder.^[10]

2.3. Visible-Light Photochemical Cross-linking

Having established that thermal activation of diazo compounds 1–5 is a suitable method to cross-link the APO binder, we next started studies to explore the photochemical activation of the diazo compounds using blue light. This wavelength is known to be suitable for various push-pull (aryl-ester) type diazo compounds.^[13] To verify, UV–Vis spectra of all cross-linkers in ethyl acetate were measured, confirming the suitability of using blue light for all cross-linkers (Figure S15, Table S2, Support-

ing Information). Thin films of cross-linker 4 containing APO compositions were cast onto a glass substrate using a drawdown bar with a 90×10^{-6} m slit. Thereafter, the films were cured at various intensities of blue light using a 456 nm Kessil LED. The photocuring was performed at $40^{\circ}C$, to stay above the final glass transition temperature of the films allowing them to flow freely and nitrogen bubbles to escape. The need to heat to $40^{\circ}C$ while curing the films with blue light might have some practical limitations, and as such curing at room temperature could be more desirable. However, when implemented in a full practical coating, potential problems associated with release of N_2 gas bubbles can also be solved by applying thinner films or by using antifoaming additives.^[24] The photocuring led to a decrease in both the O–H and diazo signals in the recorded IR spectra (Figure 5A). The photochemical curing was followed by FTIR spectroscopy, by integrating the area of the diazo asymmetric stretch

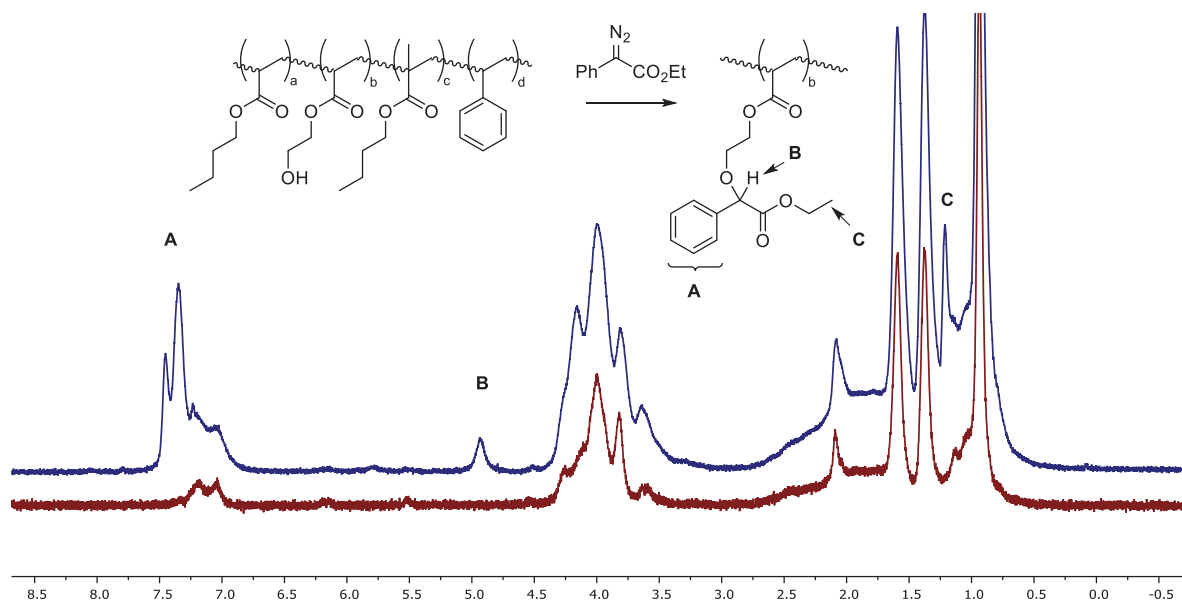


Figure 4. ^1H 1D-DOSY NMR spectra of acrylic polyol (APO) (red) and APO thermally reacted with 1:1 N_2/OH ethyl diazo(phenyl)acetate (blue) at 80% gradient strength in CDCl_3 .

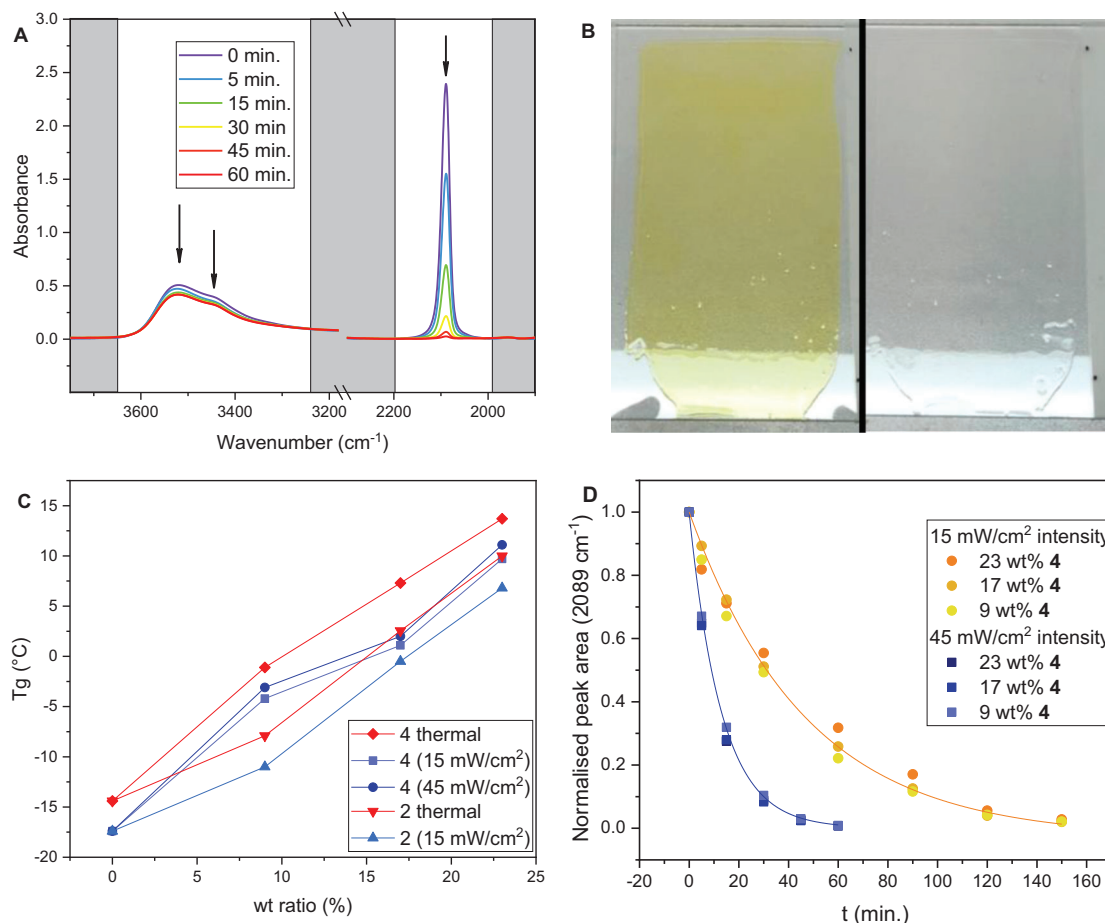


Figure 5. Blue-light photochemical curing of acrylic coating. A) Cutout of IR spectra of the curing of **4** at 45 mW cm^{-2} light intensity, 23 wt% showing a decrease in diazo signal at 2089 cm^{-1} . B) Film containing 17 wt% of cross-linker **4** prior to (left) and after photocuring (right). C) Glass transition temperatures of cured coatings as measured by differential scanning calorimetry (DSC). D) Decrease in signal at 2089 cm^{-1} during photocuring using cross-linker **4** at various wt% and light intensities (see also Figures S20–S25, Supporting Information).

Table 1. Acrylic polyol (APO) coating using cross-linker **4** and mechanical properties.

Mol ratio N_2/OH	Weight ratio diazo/APO	Gel content	T_g [°C]	Water resistance (0–5)	MEK resistance (0–5)	Hardness (oscillations)
0.5	0.13	53%	7.3	5	0	60 ± 3
1	0.30	91%	20.4	5	2	215 ± 12

Films were cast using doctor blading resulting in a film thickness of 58×10^{-6} m. Coatings were cured thermally and thereafter aged for 3 days.

vibration at 2089 cm^{-1} . As shown in Figure 5D, at a light intensity of 45 mW cm^{-2} the photochemical curing completes within 1 h, which is not affected by the weight loading. Using 440 nm light at the same light intensity only slightly decreases the curing time, as this presumably irradiates the same band (Figure S16, Supporting Information). The films displayed no significant bubble formation, even though the photolytic generation of the carbenes releases dinitrogen (Figure S17, Supporting Information). Furthermore, the yellow color of the diazo compounds is lost after photolysis, leading to an optically clear and colorless film (Figure 5B).

We then used the kinetics of gas evolution from the film to determine the relation between light intensity and rate and found a first order dependence on light intensity (Figures S18–S19, Supporting Information), indicating that curing times can be adjusted simply by tuning the light intensity. Using the rate dependence on light intensity, we determined the exposure total required for 90% diazo conversion to be 160 J cm^{-2} .

Thereafter, we investigated the material properties of the photo-cured films using cross-linkers **2** and **4** by DSC (Figure 5C). Only small differences were found between the T_g of the films cured at 15 and at 45 mW cm^{-2} indicating that light intensity, and thereby curing time, has no significant effect on the cross-linking performance. When comparing the glass transition temperature of the photochemically (Figure 5C, blue) and thermally (Figure 5C, red) cured coatings, for both cross-linker **2** and **4** a difference of approximately $3 \text{ }^\circ\text{C}$ in the T_g was found at all cross-linker weight dopings. However, this difference is already observed when the pure APO is subjected to the photochemical or thermal cross-linking procedures without any cross-linker present (Figure 5C, 0 wt%). The thermal APO self-curing was studied by repeated heating to $120 \text{ }^\circ\text{C}$ in 15-min increments in the DSC, which indeed showed a small stepwise increase in the glass transition temperature from $-17.4 \text{ }^\circ\text{C}$ to $-14.4 \text{ }^\circ\text{C}$ in line with the observed $3 \text{ }^\circ\text{C}$ difference in the T_g when comparing the photochemical and thermal curing procedures (Figure S26, Supporting Information). This process presumably occurs through esterification with methacrylic acid functionalities in the binder. Therefore, we conclude that cross-linkers **2** and **4** operate equally well under photochemical and thermal conditions, and thus provide a novel way for the blue light photocuring of APO binders.

Next, we evaluated the hardness of the films with cross-linker **4** using the pendulum hardness. The Persoz hardness is directly related to the Young's modulus of a coating, and is the preferred method in industry due to its ease of use compared to tensile testing.^[25,26] The composition containing 0.5 equivalents diazo relative to the hydroxyl functionality of the acrylic remains soft with a pendulum hardness of 60 oscillations (Table 1). When using 1 equivalent of cross-linker (molar ratio $N_2/OH = 1$), the hardness increases dramatically to 215 oscillations, which is comparable to UV-curing acrylics such as the ones developed by the

group of Feringa.^[27] More importantly, this hardness is also comparable to scratch-resistant melamine curing paints used for automotive applications.^[28] Therefore, we conclude that tethered diazo compounds can be used to cross-link acrylic coatings providing material properties similar to currently applied systems. The water resistance was shown to be excellent, but the resistance to methyl ethyl ketone (MEK) solvent is not as good as melamine curing paints (Figure S27, Supporting Information). We attribute this to the side reactions that can occur when using free carbenes as cross-linker, such as cyclization to a lactone and oxidation with molecular oxygen which may lead to small molecule impurities in the film that presumably dissolve in MEK.

As the photochemical activation of the diazo group provides spatial control over cross-linking, providing opportunities for photo-patterning, we also performed the cross-linking using a 3D-printed photomask (Figure 6). As such, since activation of the diazo compound occurs only at the illuminated section, disappearance of the yellow color is clearly visible at the exposed section kept uncovered by the photomask (Figure 6B). This shows that the herein developed diazo cross-linker can be used for photopatterning, which might have interesting applications.

3. Summary and Conclusions

We synthesized and characterized various diazo compounds and evaluated them in the thermal and visible-light photochemical cross-linking of an APO binder. We show that depending on the molecular structure of the cross-linker the cross-linking efficiency changes, and the final material properties of the films can be tuned. Furthermore, we also show that the cross-linker structure has an influence on the side reactions that occur, with cross-linker **2** reacting partially with itself to form a β -lactone whereas cross-linker **4** does not. Thereafter, we showed that these diazo compounds can also be cured photochemically using blue light, without a difference in cross-linking efficiency when compared to thermal cross-linking. The best cross-linker was shown to

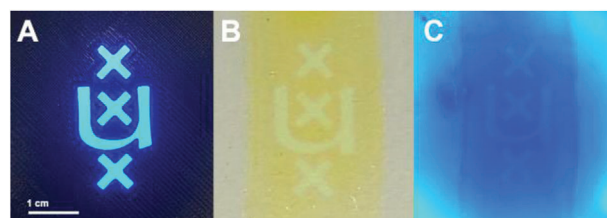


Figure 6. Photopatterning on acrylic polyol (APO) containing 0.5 equiv. diazo **4**. A) Photomask with the UvA logo. B) Image of the photopatterned film, C) photopatterned film with blue LED as backlighting (contrast adjusted for visibility).

provide a hardness similar to the currently utilized melamine curing systems, and films with excellent water resistance. These studies pave the way for further usage of diazo functionalized cross-linkers in the curing of paints and coatings. Currently, studies are ongoing to improve the solvent resistance of the herein developed diazo curing system.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

coatings, cross-linking, diazo compounds, photochemistry, polymers

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