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Unique Curing Properties through Living Polymerization in Crosslinking Materials: Polyurethane Photopolymers from Vinyl Ether Building Blocks**

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Abstract: *Photopolymers with unique curing capabilities were produced by combining living cationic polymerization with network formation and restricted polymer motion. A vinyl ether diol was synthesized as a functional building block and reacted with isophorone diisocyanate to form a highly functionalized vinyl ether polyurethane as a model system with high crosslinking ability. When using a cationic photoinitiator, fast polymerization is observed upon short UV irradiation. Curing proceeds in the absence of light and under ambient conditions without oxygen inhibition. Cationic active sites become trapped dormant species upon network-induced vitrification and surprisingly remain living for several days. The polymerization can be reactivated by additional UV irradiation and/or raised temperature. The curing behavior was studied in detail by using UV and FT-NIR coupled rheology and photo-DSC to simultaneously study spectroscopic and mechanical information, as well as thermal effects.*

The desire for novel photopolymers with facile robust curing conditions and highly adjustable mechanical properties has been sparked by the broad availability of energy-efficient light emitting diodes[1] and recent exciting technological developments such as stereolithography,[2] 3D inkjet printing,[3] or nanoimprint lithography.[4] One of the most important classes of photopolymers are polyurethanes carrying terminal (meth)acrylic units, which are designed for UV-initiated radical crosslinking reactions.[5] They can combine various attractive properties, such as chemical and mechanical resistance, fast polymerization, adjustable strength, and an absence of volatile organic contents. This wide range of accessible material properties is generally recognized as a striking feature of polyurethane chemistry and accordingly, various applications can be addressed. However, the radical polymerization mechanism is sensitive towards oxygen inhibition. In particular, thin films with large surface area are prone to termination reactions and defects under ambient conditions.[6]

To overcome this issue, an alternative curing mechanism has to be employed. Since the development of onium salts, the UV-initiated cationic polymerization of epoxides and vinyl ethers has received increasing attention.[7] Although cationic polymerization is sensitive towards a number of functional groups, it provides several advantages over free-radical polymerization, such as propagation without self-termination. Once initiated, the polymerization thus proceeds in the absence of light. This so-called “dark cure” behavior is technologically relevant, for example, for the assembly of nontransparent substrates. Additionally, the absence of oxygen inhibition eliminates the need for nitrogen purging.[8] Unfortunately, the cationic polymerization of epoxides proceeds rather slowly[9] and is not compatible with urethane groups owing to undesired transfer reactions.[10] Furthermore, compared to polyuethane systems, the mechanical properties cannot be tailored over a wide range.

By contrast, the cationic polymerization of vinyl ethers is generally less sensitive towards nucleophilic functional groups and proceeds in the presence of urethanes. Even living polymerization conditions can be achieved owing to mesomeric stabilization of the propagating species.[11] Moreover, the high electron density results in reaction rates similar to those for the free-radical polymerization of acrylates.[12] Unfortunately, the highly exothermic reaction leads to vigorous heat release, which hinders the use of low-molecular-weight vinyl ethers in technical applications. As a consequence, urethane-functionalized or blended vinyl ether systems were investigated.[10,13] It was found that interactions with urethane groups can lead to reduced polymerization rates or yield products with reduced molecular weight and broadened polydispersity, thus indicating that transfer reactions cannot be completely prevented. Vinyl ether terminated urethane prepolymers[9,14] with cationic curing ability were synthesized but they still require blending with multifunctional reactive diluents to obtain higher crosslinking densities and a more distinct mechanical modulus increase upon polymerization. Recently, the first polymer systems bearing vinyl ether moieties along the backbone were reported, prepared as biocompatible polyether[15] and polyphosphorester[16] templates for post-polymerization modification through thiol–ene “click” reactions. In these reports, neither UV-initiated crosslinking nor mechanical material property variations were discussed.

We herein describe the first synthesis of highly functionalized polyurethanes carrying vinyl ether side chains. In contrast to the previous work, we focused on photocuring and

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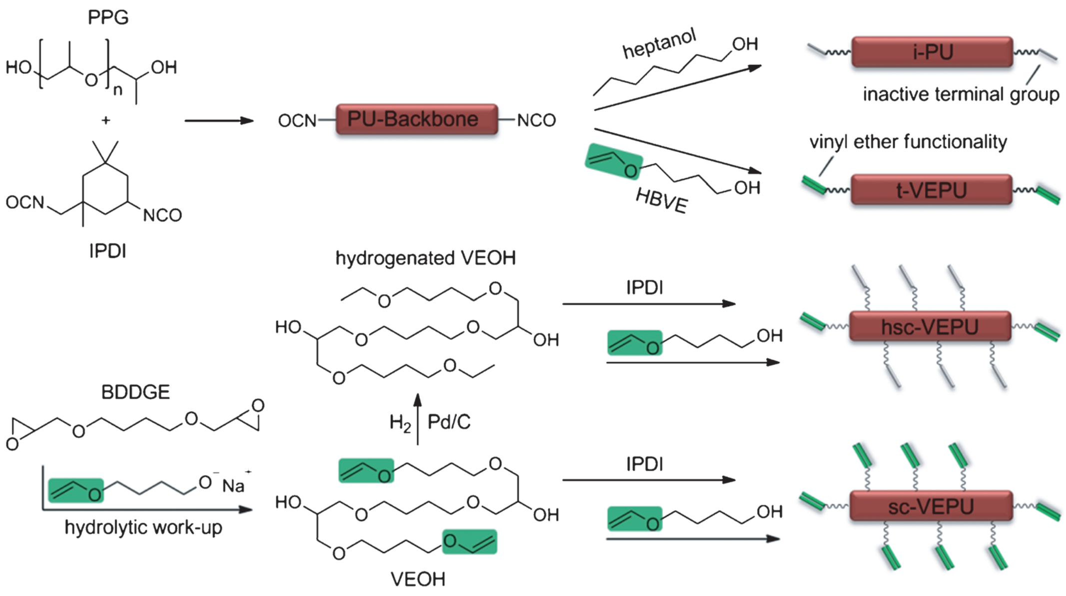

Figure 1. Synthesis of polyurethanes with different vinyl ether functionalities.

mechanical properties and introduce unique curing capabilities. We synthesized a vinyl ether diol (VEOH), which can serve as a functional building block in standard polyurethane synthesis (Figure 1; see the Supporting Information for details). The diol VEOH was then reacted with an excess of isophorone diisocyanate (IPDI) to yield a prepolymer with terminal isocyanate groups, which were subsequently converted with 4-hydroxybutyl vinyl ether (HBVE). The resulting side-chain polyurethane prepolymer (sc-VEPU) was estimated to have a vinyl ether functionality of 16.5 and a number-average molecular weight (M_n) of 5000 g mol^{-1}. For comparison, the VEOH was hydrogenated to obtain a vinyl ether terminated polyurethane with a similar but inactive backbone structure (hsc-VEPU). In addition, vinyl ether and alkyl end-capped polyurethanes (t-VEPU and i-PU) were synthesized from IPDI and polypropylene glycol by using HBVE and 1-heptanol, respectively, as end-capping reagents. The polyurethanes were subsequently formulated with 1 wt % 4,4′-dimethyl-diphenyl iodonium hexafluorophosphate as the cationic photoinitiator. Rheology combined with UV irradiation and NIR spectroscopy[17] was used to simultaneously monitor the evolution of mechanical properties and the conversion of vinyl ether groups upon UV irradiation. Figure 2a illustrates the instrumental setup (see the Supporting Information for details). Figure 2b shows a picture of the cured and highly transparent sc-VEPU on a glass slide. Rheometric plots are provided in Figure 2c. The irradiation time of 10 s is indicated by the section in the diagram marked with a pale purple background.

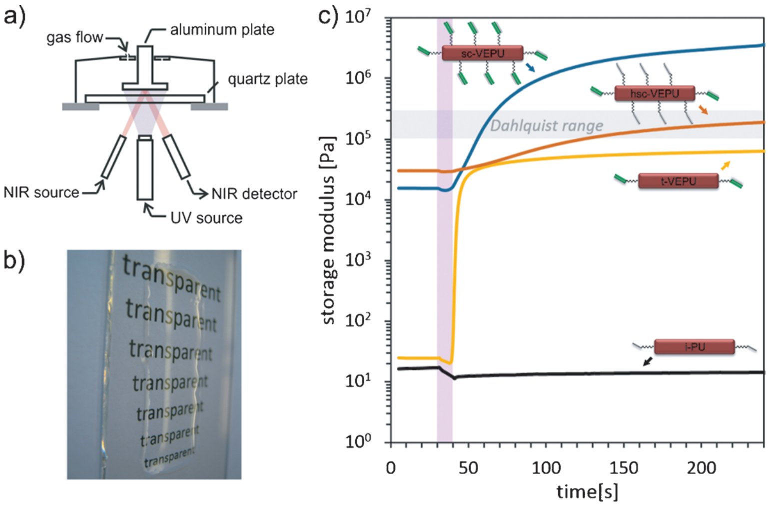

Figure 2. a) Illustration of the rheometer setup. b) Photograph of the sc-VEPU cast onto a glass slide and cured. c) Rheometric plots of the polyurethanes upon 10 s UV irradiation (purple background) at room temperature. The Dahlquist range needs to be exceeded to obtain nontacky films.

As expected, the i-PU does not show any storage modulus increase and instead a slight thermally induced decline in storage modulus can be observed upon irradiation. The t-VEPU shows an inhibition period of 9 s after initial exposure, followed by a rapid increase in the storage modulus. This behavior can be explained by traces of stabilizer impurities, such as potassium hydroxide from HBVE, and is also observed under dry nitrogen atmosphere (Figure S7 in the Supporting Information). Both of the polypropylene glycol based samples (i-PU and t-VEPU) consist of about 82 wt % soft segment and show relatively low initial storage moduli. Therefore, upon UV-curing, the storage modulus of the t-VEPU can increase over several orders of magnitude without exceeding the Dahlquist criterion, which represents the marginal value required to obtain nontacky films.[18] The tackiness of the film indicates that the flexible polymer chains do not have sufficient crosslink density to set solely through terminal reactive sites.

The hsc-VEPU demonstrates the effect of different polyurethane backbones. It has a high content of urethane hard segments as a result of the short polyol structure, which results in stronger intermolecular interactions and increased viscosity (for complex viscosities, see Table S2 in the Supporting Information). Accordingly, the initial storage modulus is significantly increased and, upon UV initiation, evolves at a lower rate. The slower polymerization kinetics are attributed to limited mobility of the functional groups in viscous media, as is described for macromonomers.[19] The results clearly demonstrate the dark cure behavior. Although the cured hsc-VEPU shows a higher storage modulus compared to the t-VEPU, it still remains soft and slightly tacky. In contrast, the highly functionalized sc-VEPU with similar backbone structure cures to a nontacky film and exhibits a superior storage modulus as a direct consequence of the significantly enhanced crosslinking ability.

Figure 3 shows the overlaid storage moduli and vinyl ether conversion plots for the sc-VEPU prepolymer composition at 25 °C, 40 °C, and 60 °C. Increasing polymerization rates and lower initial storage moduli were observed with increasing temperatures. The higher polymerization rates are a consequence of higher mobility of the reactive sites at higher temperatures. Curing at 25 °C and 40 °C resulted in incomplete conversions of about 45 % and 75 %, respectively, after the first exposure to UV. A second exposure further increased the conversion to about 70 % and 90 %, respectively. Isothermal and temperature modulated photo-DSC measurements were also performed (Table 1 and Figure S9, S10 in the Supporting Information).

Table 1: Thermal properties.

	T_{g0}[a] [°C]	T_c[b] [°C]	$\Sigma\Delta H$[c] [J g^{-1}]	T_{g1}[a] [°C]	T_{pc}[d] [°C]	ΔH_{pc}[d] [J g^{-1}]	T_{g2}[a] [°C]
i-PU	−57.9	25	–	−58.0	–	–	−58.1
t-VEPU	−58.5	25	n.d.	−58.7	–	–	−58.3
hsc-VEPU	−12.1	25	n.d.	−5.0	–	–	−4.6
sc-VEPU	−12.0	25	−65	36.9	39.8	−17	64.2
sc-VEPU	−11.1	40	−89	55.0	59.8	−5	77.1
sc-VEPU	−10.9	60	−110	74.7	–	–	85.6

[a] T_{g0}, T_{g1}, T_{g2} are the glass transition temperatures determined before curing and within two consecutive heating runs after curing. [b] T_c is the curing temperature. [c] $\Sigma\Delta H$ is the entire reaction enthalpy over several irradiations. [d] T_{pc} is the onset temperature of the post-curing reaction and ΔH_{pc} is the corresponding reaction enthalpy.

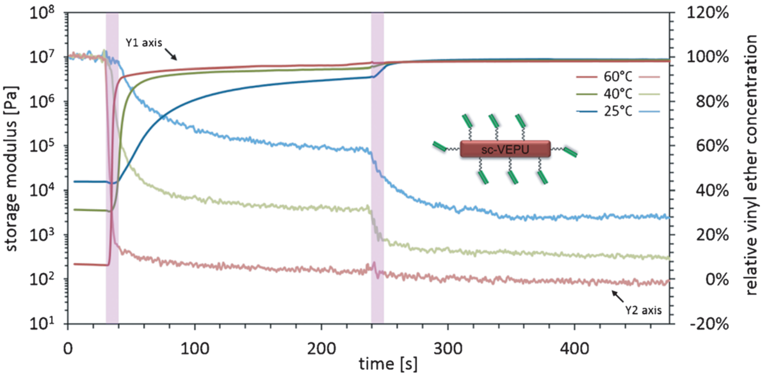

Figure 3. Photoinitiation (purple background) and dark cure of the side chain functionalized polyurethane (sc-VEPU) at different temperatures. The evolution of mechanical properties (intense lines) and vinyl ether consumption (pale lines) were recorded simultaneously.

The glass transition temperatures after polymerization (T_{g1}) reveal that the polymer vitrifies when the increasing T_g of the curing photopolymer exceeds the curing temperature (T_c). Mechanistically, the active chain ends become trapped in crosslinked vitrified regions and are inaccessible to residual vinyl ether groups. A subsequent exposure to UV generates new, mobile polymerizing species (and heat), which further increases the conversion. In general, the concentration of carbocations is rather low and difficult to quantify. The vitrification of the living polymerization is induced by tight network formation and is hence only possible in systems with high crosslinking capability. The reactivation of the living but otherwise dormant cationic sites by simple thermal treatment represents a novel and unique mechanism of post-curing. Onset temperatures and enthalpies of the thermally induced post-curing are plotted as a function of the time since initial curing in Figure 4. These results demonstrate that the trapped cationic species remain active for days.

At 60 °C, the sc-VEPU prepolymer composition cures rapidly to essentially complete conversion and does not show thermally induced post-curing. Despite thermal treatment of all of the samples, higher final glass transition temperature (T_{g2}) values are observed for samples cured at higher temperature within just a few irradiations. At lower temperatures, when the samples are subjected to additional UV exposure to increase conversion, higher quantities of the photoinitiator

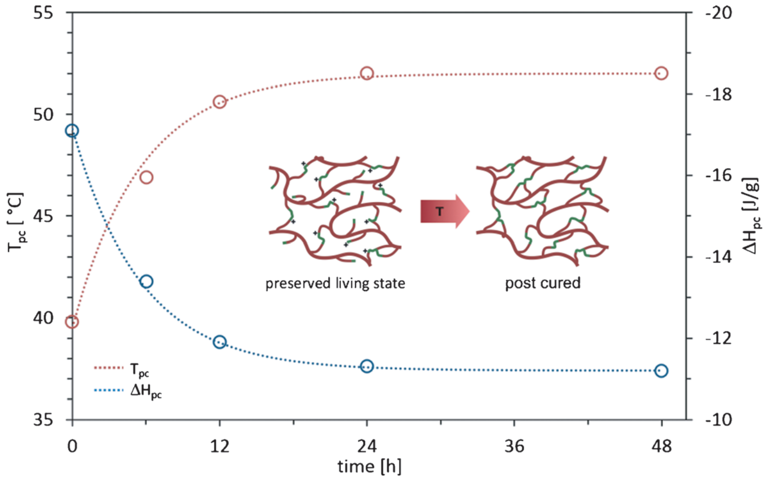

Figure 4. Durability of the post-curing capability of the sc-VEPU pre-cured at 25 °C.

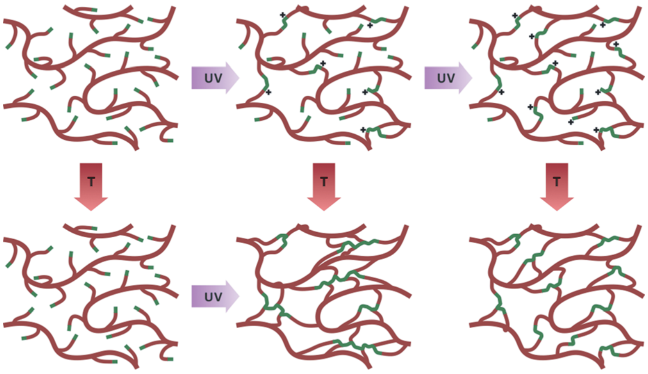

Figure 5. Schematic illustrating curing and post-curing.

are decomposed. Additional propagating species are then generated, which leads on average to shorter kinetic chain lengths and correspondingly reduced crosslinking densities (Figure 5). This behavior can explain the variations in T_{g2} through altered network structures.

The polyurethane model system chosen for this study resulted in a material with a comparatively high starting storage modulus and viscosity. However, polyurethane chemistry is highly modular and VEOH can be utilized as a functional building block to create various different photopolymer structures with adjustable properties. Furthermore, vinyl ethers are highly reactive in thiol–ene "click" reactions because of their high electron density and the absence of radical homopolymerization.[20] Such systems could be adapted as an alternative curing mechanism to the cationic system described in this work.

In summary, we present the first synthesis of vinyl ether polyols and highly functionalized vinyl ether polyurethanes and demonstrate their use as a novel class of photopolymers with unique and adjustable curing capabilities. Our modular synthetic approach is compatible with standard polyaddition and polycondensation reactions and therefore enables the production of a wide range of new photopolymers with tunable mechanical properties. Originating from living cationic polymerization, curing proceeds in the absence of light and is not inhibited by oxygen. Depending on the polymerization conditions, material systems with high crosslinking capability can deliver trapped, vitrified active sites which remain living but dormant owing to restricted mobility. Simple heating and/or repeated UV initiation leads to the reactivation of the polymerization reaction and hence allows numerous new engineering solutions and processes. The overall material and curing characteristics, including capability for thermal- and/or UV-induced post-curing, can be customized for various needs and this is expected to stimulate the development of new applications and existing technologies.

Keywords: curing · living crosslinking · photochemistry · polymerization · vinyl ethers

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