

Hydroxylamine-based Monomers

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Introduction

Radical photopolymerization presents the base of a several hundred million euro industry for films and coatings. The application spectrum covers many important areas of coating technology, for example printing inks, protective coatings, stereolithography, optical devices, dental materials, microelectronics and is also used in the biomedical field.¹ The advantages of photopolymerization are manifold from the point of time-, cost- and energy efficiency, easy handling of the formulations and eco-friendliness. Monomers, that are used, are generally based on acrylates due to their high reactivity. The key component of a given formulation is the photoinitiator (PI), being responsible for the curing speed, the double bond conversion (DBC) and the final properties of the cured material. Unfortunately the use of PIs also results in some disadvantages, as a significant amount of the PI remains unreacted in the final polymer. These, but also some photoproducts can cause discoloration or, if they are more volatile, bad odor. In the worst case migration processes may even lead to contamination of objects, that are in close contact with the polymer. This is of course a major drawback for the use of these PIs in food packaging industry or biomedical applications. With respect to these problems, it was the aim of recent studies to develop new concepts apart from the classical PIs. For example, migration stable PIs based on oligomers were tested, but limited reactivity had to be accepted, as the radicals cannot diffuse easily within the matrix. Also co-polymerizable PIs based on acrylates were examined, but they never reached the market in larger quantities. Another approach was the use of monomers, that are able to induce free radical polymerization upon irradiation with UV light, decomposing into reactive radicals without the need for a PI. Examples from recent studies are maleimide/vinylethers,² vinylacrylate and divinylfumarate derivatives,³ as well as thiol-ene systems.⁴ In our group also the use of diacrylamides as self-initiating monomers has been investigated.⁵ Their key features were the high monomer reactivity and their ability to be sensitized. The purpose of this current study was the further expansion of the diacrylamide concept. By introduction of an O-acrylated moiety on the nitrogen atom, a different type of self-initiating monomers was synthesized, as the homolytic cleavage of the N-O bond in different kinds of O-acyl oxime esters has been described in literature.^{6,7} Also better reaction yield and stability was expected due to the higher negative charge at the oxygen atom. Therefore, we prepared O,N-(acryloyl)-hydroxylamines with different alkyl residues R and also the O,N,N-triacrylated derivative. The structures are shown in Figure 1. Photochemistry of the new monomers was investigated by UV-Vis spectroscopy, photo-differential scanning calorimetry (photo-DSC) and ATR-IR spectroscopy.

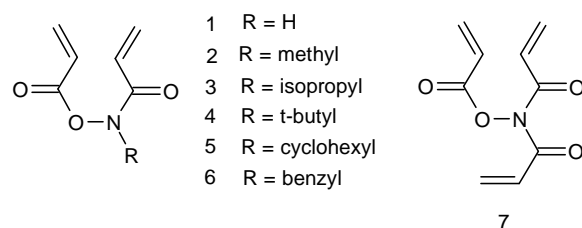
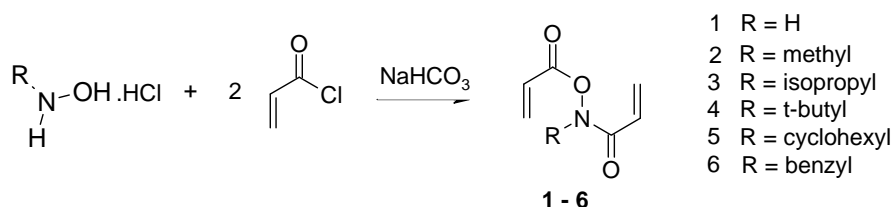


Figure 1. Structures of the self-initiating monomers **1-7**

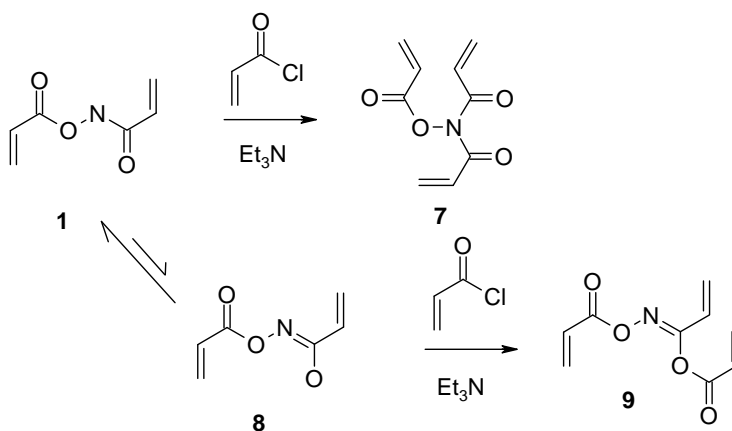
Syntheses

Diacrylated hydroxylamines can be easily synthesized according to Schotten-Baumann conditions by conversion of the corresponding hydroxylamine hydrochloride salts with 2.2 equivalents of acryloyl chloride in an aqueous organic solvent mixture, using sodium bicarbonate as catalyst. The various derivatives **1-6** could be obtained in 58-82% yield after purification by column chromatography (Scheme 1).



Scheme 1. Preparation of diacrylated hydroxylamines **1-6**

The preparation of triacrylated hydroxylamine **7** started with diacrylate **1**, which was converted with excess of acryloyl chloride and triethylamine as acid scavenger. This reaction had to be carried out under water free conditions as the nitrogen atom was far less nucleophile for the second acylation. Due to the formation of tautomer **8** also a side-reaction took place, thus generating by-product **9**. By column chromatography separation of both monomers was possible, delivering **7** in 28% yield and **9** in 16% yield (Scheme 2). Unfortunately, **9** did not exhibit any photoreactivity and will not be discussed any further.



Scheme 2. Preparation of triacrylated hydroxylamine **7**

UV-VIS Spectroscopy

UV-VIS measurements in MeOH of our monomers were carried out to investigate their absorption behaviour. As reference materials lauryl acrylate (**LA**) and dimethyl acrylamide (**DMAA**) were used. The alkylated hydroxylamine monomers exhibited a similar absorption pattern. In Figure 2 the UV spectra of non-alkylated hydroxylamine **1**, alkylated hydroxylamine **5** and triacetylated hydroxylamine derivative **7** are presented. Our hydroxylamine based acrylates showed no clear maxima, only shoulders in the range between 330 and 220 nm. Stronger red-shifted absorption was favoured by an alkyl or an acyl group on the nitrogen atom. The absorption maximum of reference compound **DMAA** was at 226 nm with an extinction coefficient of $4.53 \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$. Detectable absorption for **LA** required a concentration of at least $1 \times 10^{-2} \text{ mol L}^{-1}$.

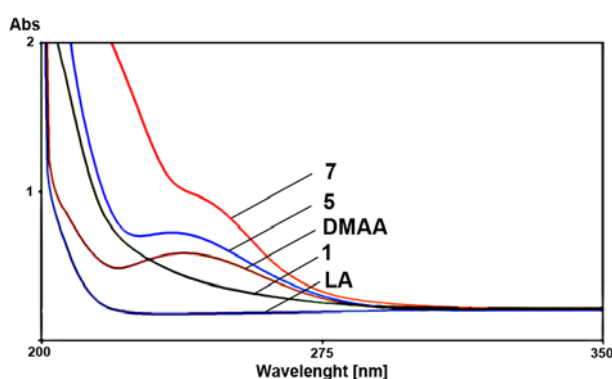


Figure 2. UV-VIS spectrum of **1**, **5**, **7**, **DMAA** and **LA** in MeOH ($1 \times 10^{-4} \text{ mol L}^{-1}$)

ATR-IR Spectroscopy

ATR-IR spectra of our acrylated hydroxylamines **1-7** before and after polymerization without PI by photo-DSC experiments were recorded. By comparison of the C=C bands at $\sim 1660 \text{ cm}^{-1}$ and $\sim 800 \text{ cm}^{-1}$ of monomer and polymer it was possible to calculate the double bond conversion after the UV-curing. The C=O bond at $\sim 1775 \text{ cm}^{-1}$ was used as the internal standard, as it was not influenced by the polymerization process. For better accuracy of the results, the calculation was done using a peak fitting analysis programme (PeakFit V4.12, SSI). Figure 3 shows the PeakFit analysis for compound **3** as example.

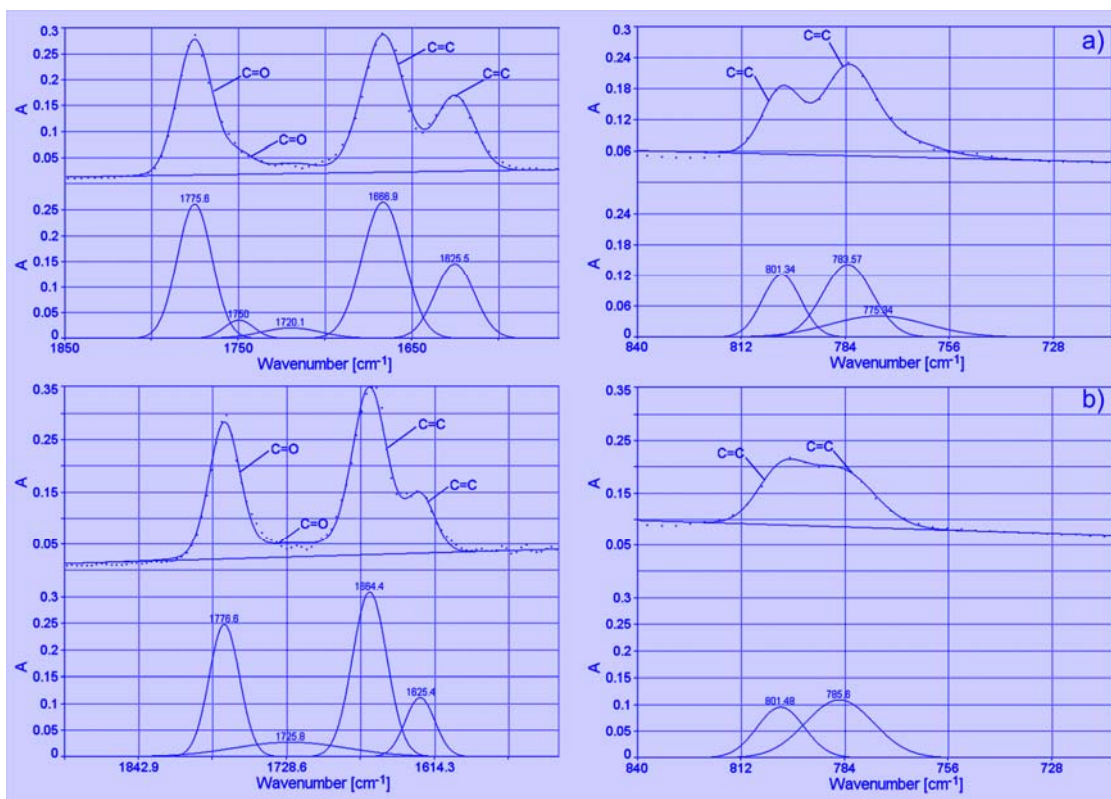


Figure 3. PeakFit analysis for compound **3** as monomer (a) and as polymer (b)

From the DBCs another important characteristic, the theoretical polymerization heat ($\Delta H_{0,P}$, J mol⁻¹) can be derived in combination with photo-DSC experiments, according to equation 1, where M_M (g mol⁻¹) presents the molecular weight of the monomer and ΔH_P (J g⁻¹) the actual heat of polymerization. The DBCs and the values of theoretical heat of polymerization are given in Table 1. The values for the theoretical polymerization heat of our acrylated hydroxylamines are in accordance with the value for a standard acrylate like hexane-1,6-diol diacrylate (**HDDA**, 148 kJ mol⁻¹).⁸

$$\Delta H_{0,P} = \frac{\Delta H_P \times M_M}{DBC} \quad \text{equ. 1}$$

Table 1. Calculated DBC and $\Delta H_{0,P}$ values for compounds 1-7 (PI-free) and HDDA (2wt% Darocur 1173).

Compound	R-	DBC (%) by ATR-IR	$\Delta H_{0,P}$ (J mol ⁻¹)
1	H	31	142700
2	CH ₃	24	132000
3	CH(CH ₂) ₂	34	135600
4	C(CH ₃) ₃	25	120200
5	CH(CH ₂) ₅	40	116700
6	CH ₂ (C ₆ H ₅)	31	127500
7	CO-CH=CH ₂	43	200500
HDDA	-	83	148000

Photoreactivity by Photo-DSC

By photo-DSC the performance of a formulation can be examined easily. From the polymerization exotherm three important parameters are accessible: the time until maximum polymerization heat is reached (t_{max} , s), the height h (mW mg⁻¹) of the exotherm, which delivers also information on the reactivity of a formulation and the actual heat of polymerization ΔH_P (J mol⁻¹), which is related to the double bond conversion. With known theoretical polymerization heat, $\Delta H_{0,P}$ the DBC can be obtained by transformation of equation 1. The rate of polymerization ($R_{p,max}$, mol L⁻¹ s⁻¹) can be calculated according to equation 2, where h is the height of the exotherm (mW mg⁻¹) and ρ (g L⁻¹) is the density of the monomer.

$$R_{p,max} = \frac{h \times \rho}{\Delta H_{0,P}} \quad \text{equ. 2}$$

The photo-DSC experiments were carried out to investigate the photoreactivity of the new monomers. Our studies focussed on the following three topics: monomer reactivity with a Type I photoinitiator (2wt% Darocur 1173), self-initiating behaviour in PI-free formulations and PI reactivity in a standard diacrylate as HDDA (2wt% PI). Irradiation experiments were carried out under nitrogen atmosphere, using an EFOS Novacure with 250-450 nm filter.

Monomer Reactivity with Darocur 1173 as PI. As reference monomers **HDDA**, **LA** and 2-(2-ethoxy ethoxy) ethyl acrylate (**EEEA**) were used. Highest DBC values could be found for monoacrylates like **LA** and **EEEA** due to the lack of crosslinking reactions. Also compared to the diacrylate **HDDA**, our diacrylates showed lower reactivity. The low DBC values might be caused by high crosslinking density combined with inhibition of the polymerization by microgelation and trapping of monomer.⁹ Furthermore, with increasing bulkiness of the residue R on the nitrogen atom, the reactivity decreased. Surprisingly, triacrylate **7** performed well for a trifunctional monomer. The reason might be some kind of cyclopolymerization of the diacrylamide unit as described by McCormick et al.,¹⁰ although we did not find confirmative signals in the ATR-IR spectrum of the polymer of **7**. Besides, UV-induced N-O bond cleavage in the polymer chains might also result in less crosslinked networks. Table 2 shows the photo-DSC data for compounds **1-7** and the references **HDDA**, **EEEA** and **LA**.

Table 2. Photo-DSC data for monomers 1-7 and the reference compounds HDDA, EEEA and LA with Darocur 1173 as PI (2wt%)

Compound	R-	DBC (%) by ATR-IR	t_{\max} (s)	$R_{P,\max} \times 10^3$ (mol L ⁻¹ s ⁻¹)
1	H	66	7	225
2	CH ₃	62	7	269
3	CH(CH ₂) ₂	61	7	169
4	C(CH ₃) ₃	67	7	116
5	CH(CH ₂) ₅	71	7	101
6	CH ₂ (C ₆ H ₅)	66	12	81
7	CO-CH=CH ₂	79	7	176
HDDA	-	83	5	288
EEEA	-	89	12	237
LA	-	98	10	182

Self-initiation behaviour. To investigate the reactivity of our monomers in PI-free formulations, photo-DSC experiments without PI were performed. As references **LA** and **DMAA** were used, also in PI-free formulations. As expected, reference formulations showed no reactivity without a photoinitiator (Figure 4). The alkylated hydroxylamine-based monomers exhibited comparable reactivities. t_{\max} was reached within 30-40 s, but the exothermic polymerization reaction proceeded for about 5 min under these conditions. The highest self-initiating activity was displayed by triacrylate **7**, expressed by DBC and $R_{P,\max}$ (Table 3). Compared to the experiments with PI, Darocur 1173 (Table 2), the lower DBC values could be improved by light sources with higher intensities as lower reactivity might be due to limited absorption behaviour up to 320 nm.

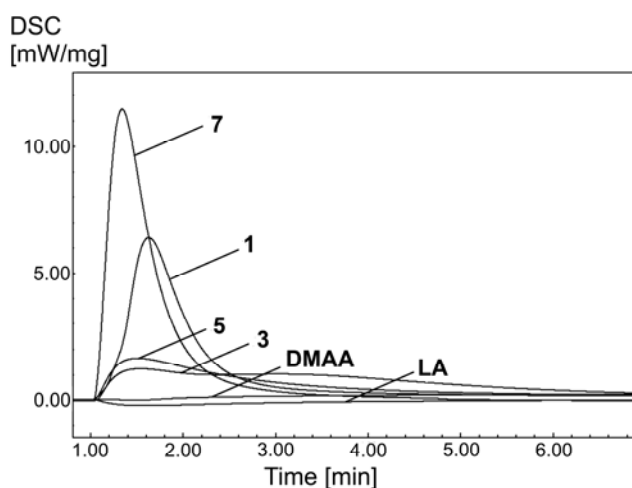


Figure 4. Photo-DSC plots for compounds **1**, **3**, **5**, **7** and references **LA** and **DMAA** in PI-free experiments.

Table 3. Photo-DSC Data for compounds 1-7, DMAA and LA in PI-free experiments

Compound	R-	DBC (%) by ATR-IR	t_{\max} (s)	$R_{P,\max} \times 10^3$ (mol L ⁻¹ s ⁻¹)
1	H	31	38	440
2	CH ₃	24	30	111
3	CH(CH ₂) ₂	34	32	81.2
4	C(CH ₃) ₃	25	34	61.3
5	CH(CH ₂) ₅	40	31	89.2
6	CH ₂ (C ₆ H ₅)	31	22	67.1
7	CO-CH=CH ₂	43	20	629
DMAA	-	-	-	-
LA	-	-	-	-

Photoinitiator activity in HDDA. After examination of monomer reactivity and self-initiation behaviour, we were also interested, if our compounds could be used as PIs in standard acrylates like **HDDA**. As reference photoinitiator system, industrially applied Type II PI benzophenone/triethanolamine (**BP/TEA**) was employed. The concentration of the PI was 100 $\mu\text{mol g}^{-1}$ **HDDA**. All diacrylated derivatives, except compounds **2** and **1**, had almost the same reactivity. Poor reactivity of **2** could not be clarified yet. Surprisingly, triacrylate **7** showed similar reactivity as **BP/TEA**, although it can absorb only a fraction of the light, in contrast to BP (Figure 5).

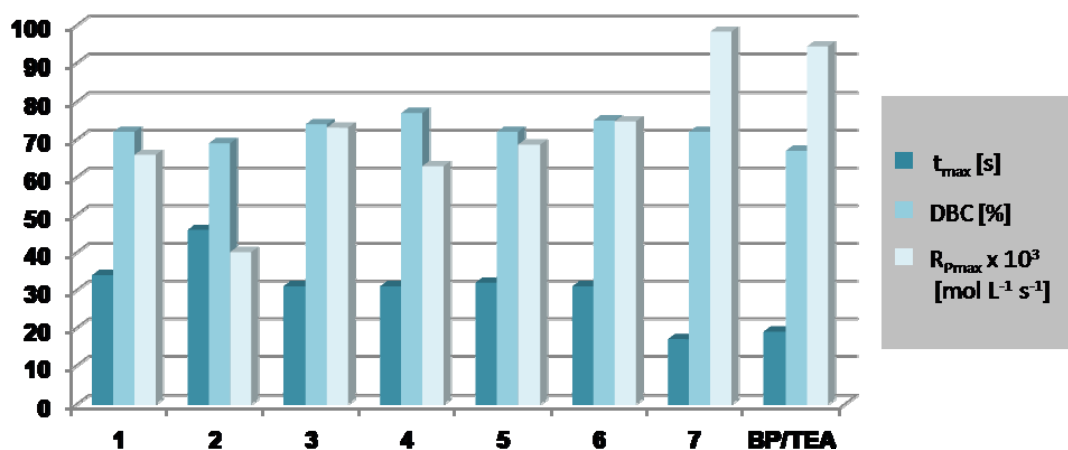


Figure 5. Photo-DSC data of **HDDA** containing 100 $\mu\text{mol g}^{-1}$ of compounds **1-7** and **BP/TEA** as PI

To enhance the PI reactivity of our hydroxylamines, a classical set of photo-sensitizers, that react by energy-transfer and/or electron transfer was selected. 11 $\mu\text{mol g}^{-1}$ of photo-sensitizer (benzophenone, isopropylthioxanthone and dibutyl anthracene) were used. However, no significant synergism could be seen. Benzophenone and isopropylthioxanthone might fail as they are triplet sensitizers, whereas the cleavage of our compounds might occur from the excited

singlet state, similar to Barton – esters.¹¹ Furthermore, dibutyl anthracene is a typical singlet sensitizer,⁵ but might mismatch the excited state energy levels of the acrylated hydroxylamines.

Summary

During this study the self-initiation behavior of di- and triacrylated hydroxylamines was described. The theoretical polymerization heat of our new monomers was determined by ATR-IR spectroscopy and PeakFit analysis of the monomers and the polymers obtained from photo-DSC experiments. Investigations on the reactivity of the acrylated hydroxylamines as monomers with Type I PI Darocur 1173, in PI-free formulation and as PIs for standard diacrylate **HDDA** was investigated by photo-DSC. The photoinitiating ability of triacrylate **7** in **HDDA** exceeded the difunctional derivatives by far and was comparable to industrially used PI system **BP/TEA** although it can absorb only a fraction of the light as benzophenone can, as could be seen from UV-Vis spectroscopy. Monomer reactivity in combination with a Type I PI like Darocur 1173 showed good results for triacrylate **7** and some of the diacrylated monomers. The performance of the PI-free formulations was far from comparable as if a photoinitiator was used, but nevertheless they might be a potential model system for a new generation of copolymerizable PIs. Further studies will focus on the photochemistry and photophysics of these interesting compounds.

Acknowledgment

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