Photoinitiating Monomers Based on Diacrylamides

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ABSTRACT: Novel monomers with reactive diacrylamide units were developed as alternatives to common acrylate- or acrylamide-based functional groups. By using photo differential scanning calorimetry and ATR-IR spectroscopy, we were able to determine their theoretical polymerization heats and photopolymerization properties. Surprisingly, these new monomers exhibited high polymerization reactivity due to cyclopolymerization and showed self-initiating behavior under irradiation with UV light. As absorption of these photoinitiating monomers tails out at 320 nm, sensitizers were successfully employed to expand the spectral range of sensitivity.

Introduction

Photopolymerization is one of the key techniques to cure coatings in an environmentally friendly way within a fraction of a second. Such formulations are usually based on multifunctional oligomeric acrylates and acrylate-based reactive diluents that can be cured via radical polymerization.[1] In a given monomer composition, the photoinitiator (PI) plays the key role, being responsible for the curing speed, double bond conversion (DBC), and final mechanical properties. Unfortunately, this key component gives rise to several problems during storage of the resin formulation and in application. Thermal decomposition and formation of reactive radicals can lead to limited storage stability. Photoproducts might result in discoloration and odor. Additionally, unreacted PI and photoproducts are able to migrate out of the cured film, which leads to major drawbacks especially for food-packaging applications.

Therefore, coreactive PIs and macromolecular derivatives have been introduced, but limited reactivity has to be accepted.[2] To avoid the usage of PIs, Hoyle, Jönsson, and co-workers have evaluated a series of self-initiating monomers in the past decade. They have found that monomers based on vinyl acrylates (VA and DVM, Figure 1) have remarkable self-initiating behavior.[3] Photocleavage reaction of vinyl acrylate (VA) and radical formation have been confirmed by irradiation experiments in the presence of TEMPO.

Recently, we considered acrylamides as alternatives to classical acrylates for curing of silicone release coatings.[4] Conversion of a simple model amine (*N*-propylamine) with an excess of acryloyl chloride in the presence of triethylamine as a base led to a significant amount of *N*-propyl-*N*-(1-oxo-2-propen-1-yl)-2-propenamide (**1**) as a byproduct. Similarly, reaction of *N*-methoxyacrylamide with 1 equiv of acryloyl chloride delivered *N*-methoxy-*N*-(1-oxo-2-propen-1-yl)-2-propenamide (**2**). Surprisingly, fast photobleaching was found in thin layer chromatography (TLC) after short exposure to the TLC UV lamp. From this experience, we expected decomposition and radical formation similar to those of vinyl acrylate monomers.

Investigations of such di(meth)acrylamide-based monomers focused on the propagation mechanism or polymer properties. Polymerization was carried out in solution, in the bulk,[5−8] or in the presence of comonomers.[9−11] Generally, benzoyl peroxide or azobisisobutyronitrile (AIBN) was used for thermal initiation. Thermal initiation[12] (210 °C) without an initiator or γ-irradiation has also been examined. Sokolova[7] polymerized *N*-propyldimethacrylamide by UV irradiation in the presence of AIBN at 30−35 °C. It has also been described that polymerization of diacrylamides proceeds via cyclopolymerization,[5] which involves intermolecular tail-to-tail propagation alternating with intramolecular head-to-head cyclization as shown in Scheme 1. Also formation of a linear polymer in solution has been found according to the literature.

The degree of cyclization under generation of succinimide units is known to be almost quantitative.[11] The high cyclization tendency to more strained five-membered rings over a wide temperature range[13] suggests a highly favored intramolecular cyclization step which is presumably very fast.

The ability of self-initiation of diacrylamides has not been reported until now. Therefore, we were interested to prepare diacrylamide **1** as a model compound. To facilitate the formation of diacrylamides, electron-withdrawing substituents as in compound **2** might be advantageous. UV−vis absorption behavior was compared with that of typical acrylamides. By photo differential scanning calorimetry (photo-DSC) studies we determined the efficiency to act as a PI in a typical monomer, the reactivity of the monomer in the presence of a PI, and the self-initiation behavior. Last but not least, we were interested to extend the wavelength range of sensitivity by addition of sensitizing compounds.

Experimental Section

Materials. All reagents and monomers *N*-propylacrylamide (PA) and lauryl acrylate (LA) were received from Sigma-Aldrich and were used without further purification. *N*,*N*′-Diethyl-1,3-bis(acrylamido)propane (V 392) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) were received as gifts from Ivoclar Vivadent and Ciba SC, respectively. *N*-Methyl-*N*-propylacrylamide (MPA),[14] dibutylanthracene (DBA),[15] and *N*-methoxyacrylamide[16] were prepared as described in the literature. Analytical data were in agreement with reported data. The solvents were dried and purified by standard laboratory methods. Column chromatography was performed on VWR silica gel 60 (0.040−0.063 mm).

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 FT-NMR spectrometer with $CDCl_3$ as the solvent. ATR-FTIR spectra were recorded on a Biorad FTS 135 spectrophotometer with Golden Gate MkII diamond ATR equipment

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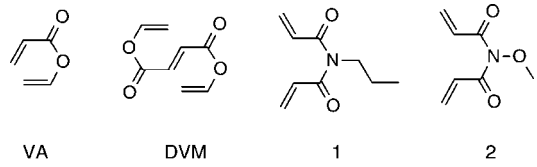
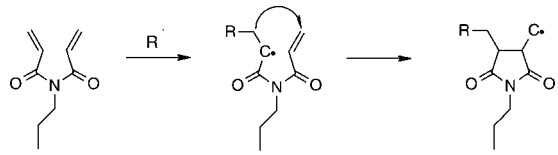


Figure 1. Self-initiating monomers.

Scheme 1. Cyclopolymerization of Diacrylamides



(LOT). TLC was performed on silica gel 60 F_{254} aluminum sheets from Merck. UV absorption was measured using a Hitachi U-2001 spectrometer with spectrophotometric grade methanol (MeOH), acetonitrile (MeCN), and cyclohexane as the solvent. HPLC measurements were carried out on a reversed-phase HP-1100 HPLC system with a DAD detector. All separations were carried out on a Waters Xterra MS C_{18} column, particle size 5 μm, 150 × 3.9 mm^2 i.d. A linear gradient with a flow of 0.8 mL/min was formed from 97% water to 97% MeCN over a period of 30 min. Gas chromatography/mass spectrometry was performed on a Hewlett-Packard 5890/5970 B system using a fused silica capillary column (SPB-5, 60 m × 0.25 mm). MS spectra were recorded using electron ionization (EI; 70 eV) and a quadrupole analyzer.

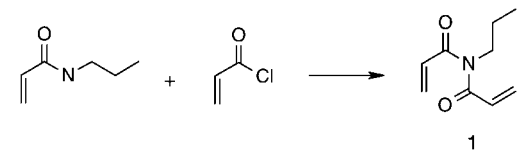
Solution polymerization was carried out in a three-necked round-bottom flask in acetonitrile (50 mL) of 0.32 M solutions of **1** under a nitrogen atmosphere with 2 wt % Darocur 1173 as a PI. Irradiation was carried out for 1 h with EFOS Novacure (250−450 nm, 1000 mW/cm^2) as the irradiation source. Afterward, the solvent was evaporated carefully in vacuo.

Photo-DSC was conducted with a modified Netzsch DSC 204 F1 Phoenix with an autosampler.[17] The compounds were irradiated with filtered UV light (EXFO Omnicure 2001, 280−450 nm) by a light guide attached to the photo-DSC unit. The light intensity at the surface level of the cured samples was measured with an EIT Uvicure high-energy integrating radiometer to be 13 mW/cm^2. The default light intensity at the tip of the light guide was 1000 mW/cm^2. All measurements were carried out in isocratic mode at room temperature under a nitrogen atmosphere. To permit oxygen-free irradiation of the samples, a nitrogen purge (∼50 mL/min) was used for at least 5 min prior to the measurements.

Syntheses. *N-Propyl-N-(1-oxo-2-propen-1-yl)-2-propenamide (**1**).* *N*-Propylacrylamide (4.0 g, 35.3 mmol) and triethylamine (9.8 mL, 70.7 mmol) were dissolved in dry dichloromethane (60 mL) under an inert atmosphere. The reaction mixture was cooled with an ice bath to 0−5 °C, and acryloyl chloride (5.7 mL, 70.7 mmol) dissolved in dry dichloromethane (20 mL) was added within 30 min. The solution was stirred for 24 h at room temperature. The dark brown reaction mixture was extracted with 0.5 N HCl solution (30 mL) and with 0.1 N NaOH solution (30 mL). The organic layer was dried over Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure. The brown oil was purified by column chromatography (PE:EE = 5:1) to give 1.71 g (29%) of **1**. ^{1}H NMR ($CDCl_3$; δ, ppm): 6.66 (dd, 2H, C*H*=CH_2), 6.42 (dd, 2H, *cis*-CH=CH_2), 5.80 (dd, 2H, *trans*-CH=CH_2), 3.77−3.66 (m, 2H, NCH_2), 1.73−1.52 (m, 2H, NCH_2CH_2), 0.92 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$; δ, ppm): 168.58 (C=O), 130.45 (*C*H=CH_2), 129.61 (CH=*C*H_2), 45.89 (NCH_2), 22.20 (NC*C*), 10.99 (CH_3). FT-IR (ATR, cm^{-1}): 2969, 2881,1682, 1660, 1620, 1464, 1402, 1350, 1204, 1111, 1077, 976, 796. Anal. Calcd for $C_9H_{13}NO_2$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.70; H, 7.29; H, 9.07.

*N-Methoxy-N-(1-oxo-2-propen-1-yl)-2-propenamide (**2**) and N-Methoxyacrylimidic Acid Acrylic Acid Anhydride (**2a**).* *N*-Methoxyacrylamide (2.20 g, 21.8 mmol) and triethylamine (3.6 mL, 26.1 mmol) were dissolved in dry dichloromethane (80 mL) under an inert atmosphere. The reaction mixture was cooled with an ice bath to 0−5 °C, and acryloyl chloride (2.1 mL, 26.1 mmol) dissolved in dry dichloromethane (40 mL) was added within 30 min. The solution was stirred for 3 h at 0 °C, and then the reaction mixture was extracted with 0.5 N HCl solution (3 × 30 mL). The organic layer was dried over Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure at room temperature. The crude oil (96%) consisted of the isomers **2** and **2a** (2:1 by ^{1}H NMR). Purification by column chromatography (PE:EE = 8:1) gave 1.66 g (49%) of **2** and 0.60 g (18%) of **2a** as colorless liquids. The following are data for **2**. ^{1}H NMR ($CDCl_3$; δ, ppm): 6.99 (dd, 2H, C*H*=CH_2), 6.56 (dd, 2H, *cis*-CH=CH_2), 5.91 (dd, 2H, *trans*-CH=CH_2), 3.86 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$; δ, ppm): 164.82 (C=O), 131.74 (CH=*C*H_2), 128.17 (*C*H=CH_2), 64.15 (CH_3). IR (ATR, cm^{-1}): 2989, 2941, 1699, 1617, 1400, 1309, 1240, 1170, 1043, 970, 925, 779. Anal. Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.33; H, 5.84; H, 8.80. The following are data for **2a**. ^{1}H NMR ($CDCl_3$; δ, ppm): 6.61 (dd, 1H, *cis*-COCH=CH_2), 6.43−6.15 (m, 2H, COC*H*=CH_2, N=CC*H*=CH_2), 6.06 (dd, 1H, *trans*-COCH=CH_2), 5.64 (dd, 1H, N=CCH=CH_2), 5.51 (dd, 1H, N=CCH=CH_2), 3.89 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$; δ, ppm): 160.68 (C=O); 147.87 (CN); 133.79, 120.86 (CH=*C*H_2); 126.27, 126.09 (*C*H=CH_2); 62.76 (CH_3). IR (ATR, cm^{-1}): 2948, 1755, 1630, 1586, 1405, 1294, 1218, 1131, 1055, 1032, 982, 930, 880, 795. Anal. Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.26; H, 5.87; H, 8.91.

Scheme 2. Synthesis of Diacrylamide 1



Results and Discussion

Syntheses. The synthesis of diacrylamide **1** was carried out in a way analogous to the method of McCormick[5] by conversion of *N*-propylacrylamide with 2 equiv of acryloyl chloride and triethylamine as an acid scavenger in dichloromethane (Scheme 2). Purification by column chromatography gave **1** as a colorless liquid in 29% yield.

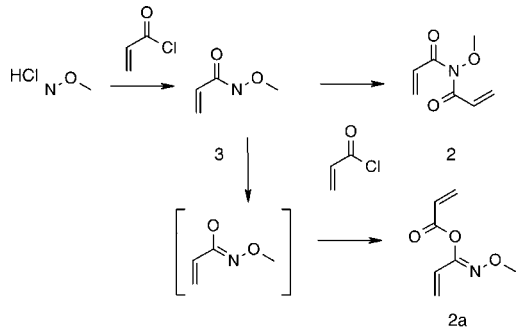
Due to the poor conversion, different solvents and also sodium hydride for deprotonation were examined. Improved yields were observed neither in DMF nor in acetone as the solvent. Especially by using sodium hydride for deprotonation, a large number of side products were detected by TLC. Only the combination of toluene and NaH gave conversion up to 80%, but a significant amount of side reactions had to be accepted. One major side product was the *Michael addition* product 3-(acryloylpropylamino)propionyl chloride.

Preparation of the new monomer **2** was carried out in two steps. *O*-Methylhydroxylamine hydrochloride was reacted with 1 equiv of acryloyl chloride in a procedure modified from that of Epton[17] by using $NaHCO_3$ in dichloromethane and water as the solvents (Scheme 3).

N-Methoxyacrylamide (**3**) was obtained as a colorless solid in 58% yield. The poor yield may be attributed to the good water solubility of the product, which makes extraction difficult. Additionally, excess acryloyl chloride might also improve the yield.

Preparation of the diacrylamide **2** was carried out by conversion of **3** with 1.2 equiv of acryloyl chloride in dichloromethane by using triethylamine as a catalyst. After 3 h, entire conversion and the formation of two products were detected by TLC. Column chromatography gave **2** and **2a** as colorless liquids in 49% and 18% yield, respectively. Formation of **2a**

Scheme 3. Synthesis of Diacrylamide 2



can be explained by the O-acryloylation of a tautomer of **3**. Reduced amounts of side products might be expected by the use of sodium hydride for deprotonation as described by Hopkins[18] and Kornblum.[19] Unfortunately, also in this case the use of NaH forced the formation of a Michael addition side product.

UV−Vis Absorption. UV−vis spectroscopy in acetonitrile (Figure 2) was carried out to investigate the absorption behavior of the diacrylamides **1** and **2**. The wavelength of maximum absorption (λ_{max}) and molar extinction coefficient (ε) are summarized in Table 1. PA and MPA were used as references with amide groups. Introduction of an alkyl residue as in MPA gave a shift of the maximum of about 20 nm to longer wavelength compared to that of PA. Hydrogen bridge formation of the N−H group in PA is responsible for the lower wavelength of absorption. Compound **1** showed an additional shift of about 8 nm to longer wavelength and ε was increased by a factor of 2 compared to those of MPA. Increased electron density on the nitrogen atom in **2** further increased ε but had no influence on λ_{max}. Absorption of our compounds tailed out at 320 nm.

Additionally, UV absorption spectra were measured in cyclohexane and MeOH (plots not shown). Generally, a blue shift of about 2 nm appeared with increasing polarity. Similar behavior was found for the acrylamide-based reference compounds PA and MPA. Therefore, in agreement with the literature[20] and due to the high extinction coefficient, the shoulders should be assigned to a $\pi-\pi^*$ transition.

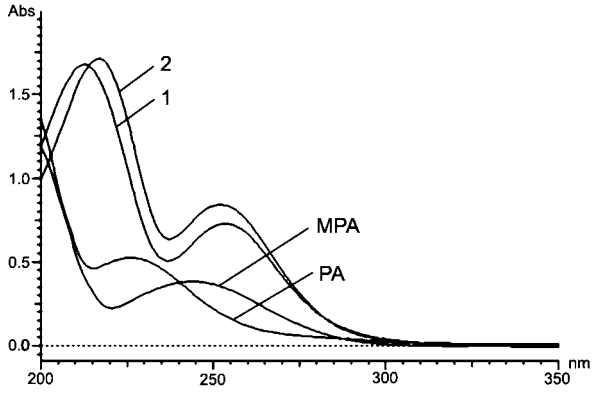


Figure 2. UV spectra of **1**, **2**, PA, and MPA (1×10^{-4} M) in acetonitrile.

Table 1. λ_{max} and ε Values of the Monomers and Reference Initiators in MeCN

compd	λ_{max} (nm)	ε (L mol^{-1} cm^{-1})
1	253	7270
2	252	8400
PA	226	5250
MPA	245	3830
BP	250	17200
	338	124
Darocur1173	243	9260
	280	875
	322	93

As these molecules turned out to be active as PIs during this study, differences in the UV absorption behavior compared to that of commercially available PIs are also of interest. Data for some typical representatives, BP and Darocur 1173, are shown in Table 1. Unlike these reference initiators, there is no maximum from an $n-\pi^*$ transition visible in the important region for UV-curing (>300 nm) for **1** and **2**. The absorption behaviors of these two monomers are very similar in that region, and the extinction coefficients are about 1 order of magnitude smaller ($\varepsilon_{322} \approx 47$ L mol^{-1} cm^{-1} and $\varepsilon_{338} \approx 8$ L mol^{-1} cm^{-1}) than those of the reference initiators.

ATR-FTIR and NMR Analysis. To investigate the photochemistry of our compounds, polymers from solution and bulk polymerization were investigated by ATR-FTIR and ^{1}H NMR spectroscopy. To obtain the theoretical heat of polymerization ($\Delta H_{0,P}$),[21] the actual heat of polymerization (ΔH_P) (photo-DSC) and the DBC (ATR-FTIR) have to be determined from polymer samples obtained in photo-DSC experiments (2 wt % Darocur 1173). Following eq 1, it is possible to calculate $\Delta H_{0,P}$, where M_M is the molecular weight of the compound.

$$\Delta H_{0,P} = \frac{\Delta H_P M_M}{DBC} \quad (1)$$

To evaluate the reactivity of the diacrylamides **1** and **2** and in terms of calculating the $\Delta H_{0,P}$ of our new monomers, we had to find an accurate way to determine the DBC. As polymerization of diacrylamide **1** in solution has been described[13] to deliver a soluble polymer, investigation by ^{1}H NMR and ATR-FTIR is possible. Therefore, the accuracy in the determination of the DBC of our compounds by ATR-FTIR can be revised.

^{1}H NMR spectra of monomer **1** and its polymer received by irradiation in solution (0.32 M, 2 wt % Darocur 1173, 250−450 nm) are shown in Figure 3. As expected, polymerization of **1** caused only small shifts of protons 1−3. Acrylic protons 4−6 gave rise to two new signals due to formation of succinimide units. New signals at 2.5 ppm due to proton 6′ and 1.9 ppm due to proton 4′ + proton 5′ are found to be in good accordance with the required ratio of 2:4 and can be assigned to the backbone of the polymer. Deviations from the expected ratio of methyl group 1′ to protons 6′ and 4′ + 5′, respectively, could be explained by photoreactions of succinimide units of the polymer that give additional signals at 2.8−3.0 and 1.4−1.2 ppm.[22,23] From the ratio of the remaining double bonds to the methyl group, a double bond conversion of about 98% can be estimated.

Figure 4 shows the ATR-FTIR spectra of monomer **1** and the polymers obtained from bulk (photo-DSC, 2 wt % Darocur 1173; cf. the next section) and solution polymerization. The signal at 1772 cm^{-1} in the polymer can be assigned to the five-membered succinimide ring. Compared to the solution polymer, the polymer received from bulk polymerization is not soluble and must therefore be cross-linked to some extent. Surprisingly, both ATR-IR spectra, especially the signal from the five-membered succinimide ring, match almost perfectly. This indicates that polymerization in the bulk proceeds to a very large extent like the linear polymerization in solution.

The IR spectrum of monomer **1** also reveals characteristic C═C bands at 1660 and 795 cm^{-1} that disappear nearly quantitatively in the polymer. The C═O vibration at 1700 cm^{-1} was considered as the reference band. The decrease of the C═C band in the bulk polymer and the solution polymer was calculated using peak deconvolution (PeakFit V4.12, SSI).[24]

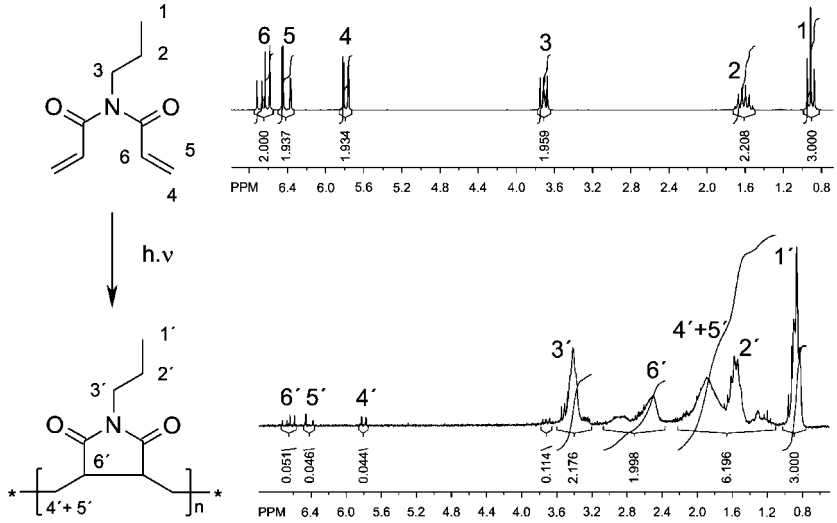


Figure 3. ^{1}H NMR spectra of monomer **1** and its polymer.

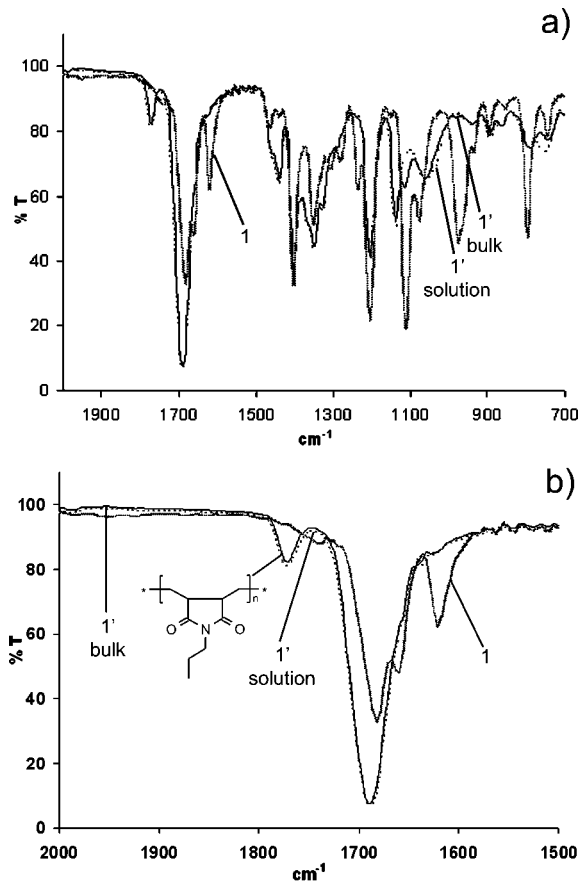


Figure 4. ATR-FTIR spectra of polymers obtained from bulk and solution polymerization, **1′**, compared to monomer diacrylamide **1**.

Both double bond signals gave very similar results (±1%). DBC was calculated to be 82% for the polymer from bulk polymerization and 97% for the solution polymer. The latter value is in perfect agreement with the results from ^{1}H NMR spectroscopy and therefore confirms the suitability of this method.

With this information and the ΔH_P of the same specimen from the photo-DSC experiment, $\Delta H_{0,P}$ was calculated following eq 1 (Table 2). Surprisingly, $\Delta H_{0,P}$ of **1** is significantly higher than values for typical acrylamides (~60 kJ/mol) or acrylates (~80 kJ/mol), which might be assigned to the cyclopolymerization.

Table 2. $\Delta H_{0,P}$ and DBC Values of Diacrylamides 1 and 2

compd	ΔH_P (J/g)	DBC (%)	$\Delta H_{0,P}$(kJ/mol of DB)
1	1130	82	119
2	704	60	65.4

Photopolymerization of **2** in solution led to a spontaneous precipitation of the polymer. Important signals of five-membered rings, C═O and C═C bonds, were only negligibly changed. Therefore, we applied the same procedure in the interpretation of the IR spectrum as for **1**. ATR-FTIR spectra of the polymer showed only a small signal at 1772 cm^{-1}. Therefore, and due to the insolubility of the polymer, cyclopolymerization seems not to be the sole mechanism. Surprisingly, bulk polymerization of **2** similar to **1** gave a $\Delta H_{0,P}$ significantly lower than values for typical diacrylates.

Photoreactivity by Photo-DSC. Photo-DSC is a simple and accurate tool to determine the performance of a formulation. The reactivity can be derived from the time which is needed to reach the maximum polymerization heat (t_{max}, s). The DBC and the rate of polymerization ($R_{p,max}$, mol L^{-1} s^{-1}) calculated from the height of the peak maximum, h (mW/mg), give additional information on the performance of a system. The DBC in the individual experiments can be obtained according to eq 1 with $\Delta H_{0,P}$ calculated in the previous section. $R_{p,max}$ was calculated from the height of the peak maximum, h (mW/mg), and the density of the monomer, ρ (g L^{-1}), following eq 2.

$$R_{p,max} = \frac{h\rho}{\Delta H_{0,P}} \quad (2)$$

The present photo-DSC study (250−450 nm, N_2) was carried out to investigate the so far unknown photoreactivity of the diacrylamides **1** and **2**. Our interest focused on the following characteristics: (1) reactivity as a monomer in the presence of Darocur 1173 as a type I PI, (2) activity of **1** and **2** as PIs in HDDA, a typical acrylate-based reactive diluent, (3) self-initiation of **1** and **2** in the absence of any PI. Finally, as the absorption of these photoinitiating monomers tails out at 320 nm, various photosensitizers should be used to extend the range of spectral sensitivity.

Monomer Reactivity with a Type I Photoinitiator. Photo-DSC measurements with a type I PI, Darocur 1173 (2 wt %), were carried out to investigate the monomer reactivity of the diacrylamides **1** and **2**. PA, MPA, LA, and V392 were used as acrylate- and acrylamide-based reference systems giving linear or cross-linked polymers. Values for $\Delta H_{0,P}$ of the reference

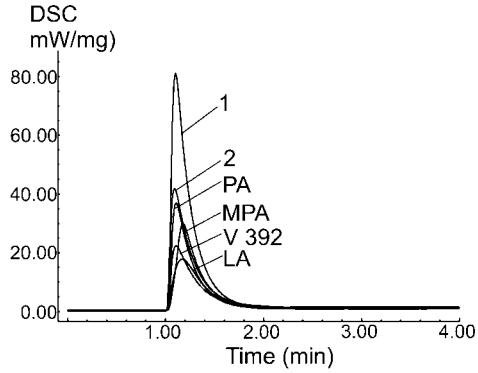


Figure 5. Photo-DSC measurements with 2 wt % PI (Darocur 1173) for **1** and **2** in comparison with PA, MPA, V 392, and LA.

Table 3. Photo-DSC of 1 and 2 in Comparison with PA, MPA, V 392, and LA with 2 wt % PI (Darocur 1173)

monomer	t_{max}(s)	$\Delta H_{0,P}$ (kJ/mol of DB)	DBC (%)	$R_{p,max} \times 10^2$(mol of DB L^{-1} s^{-1})
1	6	119	79.5	67.9
2	6	65.4	82.8	62.9
PA	6.6	59.9	98.5	60.1
MPA	10.8	65.9	94.6	43.8
V 392	6.6	63.9	78.2	33.6
LA	10.2	80.8	97.3	17.9

monomers were determined as discussed previously. $\Delta H_{0,P}$ values of about 60 kJ/mol for acrylamides are in good agreement with values given in the literature.[25]

The photo-DSC plots in Figure 5 show that the final conversion was reached within 1 min in all cases. As expected, monoacrylates PA, MPA, and LA gave the highest t_{max} and DBC due to the absence of cross-linking reactions (Table 3). The good values for PA might be assigned to some kind of preorganization due to intermolecular hydrogen bridges between N−H and C═O groups. As a well-known fact and also proved in our experiments, $R_{p,max}$ values of acrylate-based monomers are significantly lower than those of acrylamides. Although only slightly cross-linked polymers are formed, our monomers gave t_{max} and DBC similar to those of highly reactive diacrylamide V392. The unusually high exotherm of **1** can be assigned to the formation of less sterically hindered radicals in cyclopolymerization (Scheme 1) and, therefore, to a high heat of polymerization. $R_{p,max}$ values of **1** and **2** are of the same order of magnitude as that of the highly reactive PA.

PI Activity in HDDA. As there was some indication that diacrylamides are also able to act as PIs, the PI activity of these compounds (2 wt % in HDDA) was compared to that of an established type II PI system, an equimolar mixture of benzophenone (BP; 2 wt%) and triethanolamine (TEA).

This reference initiator system was chosen as it is widely used and from the viewpoint of reactivity of the same order of magnitude as those of our compounds. Darocur 1173 is about 3 times more reactive. $\Delta H_{0,P}$ of HDDA was reinvestigated with the above-mentioned method and was found to be 81.7 kJ mol^{-1}, which is in good agreement with the values found in the literature[24] for typical acrylates.

As expected, by irradiation of HDDA without PI no photoinitiated polymerization occurred (Figure 6). Indeed, both of our compounds showed some remarkable photoinitiation activity. Especially with diacrylamide **2** a DBC nearly identical to that of the reference system was obtained, although more than 2 times the amount of time was required to achieve the final DBC (Table 4). Nevertheless, these results are very promising as only a small fraction of the light was used compared to that of the BP/amine system.

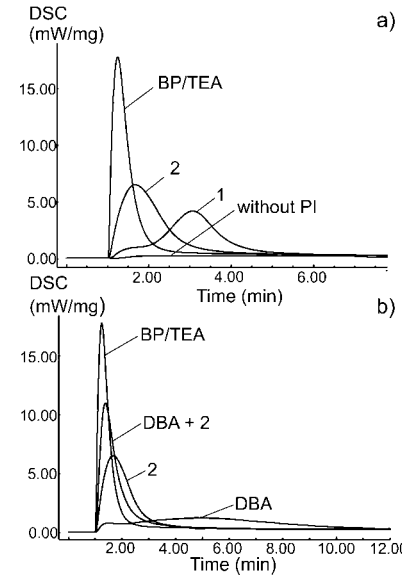


Figure 6. Photo-DSC plots for (a) the initiation behavior of 2 wt % **1**, **2**, and BP/TEA in HDDA and (b) the effect of 0.2 wt % sensitizer DBA on **2** (2 wt %) as a PI in HDDA.

Table 4. Photo-DSC Data of HDDA with 2 wt % PI (BP/TEA, 1, 2), with 0.2 wt % PS (DBA), and with DBA/2 as the PI/PS System

PI (2 wt %)	PS (0.2 wt %)	t_{max} (s)	DBC (%)	$R_{p,max} \times 10^2$ (mol of DB L^{-1} s^{-1})
BP/TEA		15.0	71.2	21.3
1		124.2	53.2	4.8
2		39.6	70.8	7.8
2	DBA	22.8	78.5	13.4
	DBA	244	69.2	1.4

To overcome this limitation and to improve the reactivity of our new initiators, we also performed studies on the addition of different photosensitizing agents. As there is little known about the photochemistry and photophysics of this class of compounds, we used a set of classical sensitizers that are able to act by energy transfer and/or electron transfer. Therefore, BP, DBA, and isopropylthioxanthone (ITX) were applied in a concentration of 0.2 wt % for photo-DSC measurements of **1** and **2** (2 wt %) in HDDA. To ensure that there is no significant direct interaction of the photosensitizer with the monomers, HDDA and sensitizer combinations were also measured alone.

As expected, BP and ITX alone in the monomer already gave some photoinitiation activity, but in combination with **1** and **2** only an accumulative effect and no synergistic effect was obvious (data not shown). By using DBA as a sensitizer for **1** in HDDA, no significant change in the polymerization exotherm was achieved compared to that of **1** in HDDA without a photosensitizer. Only by the combination of DBA with **2** was some significant effect observed (Figure 6). It has been found that t_{max} was nearly half that for **2** without a photosensitizer (Table 4) and therefore comes quite close to the value of the BP/amine system. The DBC was significantly improved and exceeds the performance of the reference system.

PI-Free Photopolymerization. In the studies above, both compounds presented themselves as highly reactive monomers. Especially **1** turned out to undergo fast polymerization with high DBC due to cyclopolymerization. Both compounds are also able to act as PIs. In this case, **2** is the better PI and can also be sensitized with DBA efficiently. Therefore, in the following studies we were interested to see the combined effect of high monomer reactivity and the ability to act as a PI by photo-DSC experiments of the pure compounds **1** and **2**. For good

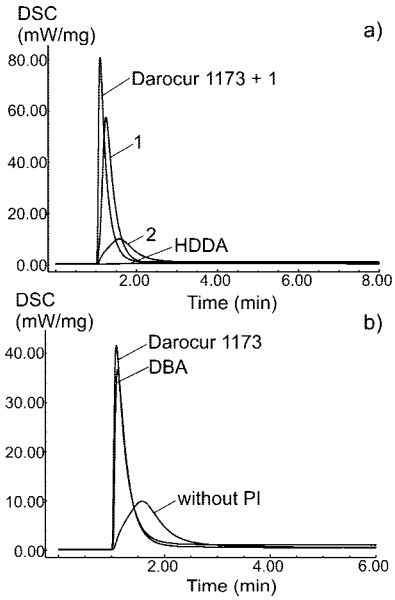


Figure 7. Photo-DSC plots of (a) the self-initiating behavior of **1, 2**, and HDDA compared to **1** with 2 wt % Darocur 1173 as a PI and (b) **2** with and without Darocur 1173 (2 wt %) as a PI compared to **2** with 0.2 wt % DBA as a sensitizer.

Table 5. Photo-DSC Data of the Self-Initiating Behavior of 1, 2, and HDDA

monomer	PI (2 wt %)	PS (0.2 wt %)	t_{max} (s)	DBC (%)	$R_{p,max} \times 10^3$(mol of DB L^{-1} s^{-1})
1			15	82	48.2
1	Darocur 1173		6	79.5	67.9
2	Darocur 1173		6	82.8	62.9
2		DBA	7.2	81.4	55.8
2			34.8	60	14.6

comparison with previous studies, we have also added the plot of the highly reactive formulation of **1** with Darocur 1173. Furthermore, the photo-DSC plot of HDDA without an additional PI is shown as a reference in Figure 7. As expected, this reference system displayed no activity. Self-initiation was observed with both compounds **1** and **2**; especially compound **1** had a remarkable reactivity. For **1**, nearly the same exotherm compared to that of **1** with 2 wt % Darocur 1173 can be seen. The overall DBC is nearly the same in both systems. Only t_{max} differs by a factor of 2.5 (Table 5).

Similar to the studies on the effect of photosensitizers above, we also added 0.2 wt % BP, DBA, or ITX to our compounds **1** and **2**. Again, only in the combination of **2** with DBA was a significant effect achieved. For comparison, in Figure 7 the plot of **2** with 2 wt % Darocur 1173 is also added. Surprisingly, 0.2 wt % DBA were as active as 2 wt % Darocur 1173. t_{max} and DBC were nearly identical; only $R_{p,max}$ was about 10% lower.

Conclusions

On the basis of the demands for photoinitiator-free formulations in radical photopolymerization, we have prepared diacrylamide-based monomers by reaction of acrylamides with acryloyl chloride using triethylamine as a catalyst. UV absorption spectra of compounds **1** and **2** tailed out above 320 nm and showed therefore a significant red shift and higher extinction coefficient compared to those of typical acrylamides. For our compounds, theoretical heats of polymerization were determined from the DBC obtained by ATR-FTIR of specimens from photo-DSC experiments with their corresponding heat of polymerization. The unusually high heat of polymerization of **1** can be explained by cyclopolymerization. Photo-DSC experiments of the new monomers in the presence of Darocur 1173 as a PI showed extremely high $R_{p,max}$, which can be explained by the formation of less sterically hindered radicals. If the new molecules are used as PIs for HDDA, remarkable photoinitiating activity is found, although only a fraction of light can be consumed compared to that of the BP/amine reference PI. Addition of a small amount of DBA as a sensitizer gave a higher DBC than the well-established PI system consisting of BP/TEA. Finally, experiments on the self-initiating behavior of **1** showed nearly the same reactivity as those of **1** with 2 wt % Darocur 1173 as a PI. Furthermore, 0.2 wt % DBA as a sensitizer for **2** gave nearly the same exotherm compared to measurements with 2 wt % Darocur 1173 as a PI for **2**. Currently, detailed studies are being carried out to explore the initiation and sensitizing mechanism.

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References and Notes

(1) Fouassier, J. P. *Photoinitiation, Photopolymerization and Photocuring*; Hanser Publishers: Munich, 1995; pp 1−7.
(2) Dietliker, K. *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints Vol. 3; Photoinitiators for Free Radical, Cationic & Anionic Polymerisation*, 2nd ed.; SITA Technology Ltd.: London, 1998.
(3) Joensson, E. S.; Lee, T. Y.; Viswanathan, K.; Hoyle, C. E.; Roper, T. M.; Guymon, C. A.; Nason, C.; Khudyakov, I. V. *Prog. Org. Coat.* **2005**, *52* (1), 63–72.
(4) Kopeinig, S.; Gruber, H.; Hummer-Koppendorfer, E.; Liska, R. Photopolymerization of Silicone Acrylamides and Acrylates. *RadTech Europe 2007 Conference Proceedings*, Vienna, Austria, Nov 13−15, 2007; Vincentz Network: Hannover, Germany, 2007; p 7S.
(5) McCormick, C. L.; Zhang, Z. B.; erson, K. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*, 364–365.
(6) Götzen, F.; Schröder, G. *Makromol. Chem.* **1965**, *88*, 133–148.
(7) Sokolova, T. A.; Rudkovskaya, G. D. *J. Polym. Sci.: Part C: Polym. Symp.* **1967**, *16*, 1157–1166.
(8) Kodaira, T.; Aoyama, F. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 897–910.
(9) Lundmark, S.; Kobayashi, S. *Makromol. Chem., Macromol. Symp.* **1992**, *54*, 107–112.
(10) Kadokawa, J. I.; Matsumura, Y.; Kobayashi, S. *Macromol. Chem. Phys.* **1994**, *195*, 3689–3698.
(11) Musha, Y.; Aoki, N.; Sato, Y.; Daigaku, N.; Kogakubu, K.; Bunrui, S. *Kogaku Hen* **1989**, *30*, 209–225.
(12) Alder, A. Patent EP 317.506, **1989**.
(13) Kodaira, T.; Kitagawa, N.; Aoyagi, K. *Kobunshi Ronbunshu* **1989**, *46*, 507–514.
(14) Corminboeuf, O.; Renaud, P. *Org. Lett.* **2002**, *4*, 1731–1733.
(15) Höfer, M.; Moszner, N.; Liska, R. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6916–6927.
(16) Epton, R.; Marr, G.; Shackley, A. T. *Polym. Rep.* **1981**, *22*, 553–557.
(17) Liska, R.; Herzog, D. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 752–764.
(18) Hopkins, G. C.; Jonak, J. P.; Minnemeyer, H. J.; Tieckelmann, H. *J. Org. Chem.* **1967**, *32*, 4040–4044.
(19) Kornblum, N.; Smiley, R. A.; Blackwood, R. K.; Iffland, D. C. *J. Am. Chem. Soc.* **1955**, *77*, 6269–6280.
(20) Banwell, C. N. *Fundamentals of Molecular Spectroscopy*; McGraw Hill Book Co. Ltd.: London, 1966.
(21) Roper, T. M.; Hoyle, C. E.; Magers, D. H. In *Photochemistry and UV-Curing New Trends*; Fouassier, J. P., Ed.; Research Signpost: Kerula, India, 2006; Vol. *25*, pp 3−264.
(22) Musha, Y.; Aoki, N.; Hori, Y.; Sato, Y.; Katayama, M.; Bunrui, A. *Kogaku Hen* **1988**, *29*, 293–302.
(23) Kanaoka, Y.; Hatanaka, Y. *J. Org. Chem.* **1976**, *41*, 400–401.
(24) Lemon, M. T.; Jones, M. S.; Stansbury, J. W. *J. Biomed. Mater. Res., Part A* **2007**, *83A* (3), 734–746.
(25) Ullrich, G.; Ganster, B.; Salz, U.; Moszner, N.; Liska, R. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1686–1700.

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