Photoinitiator-free Photopolymerization of Acrylates Using Short-Wavelength Excimer UV Radiation

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Introduction

UV-induced polymerization reactions are usually initiated by one or several photoinitiators which have to be added to the formulation of reactive monomers and oligomers. Irradiation is mostly carried out with medium pressure mercury lamps whose light is mainly absorbed by the photoinitiator. This leads to an electronic excitation of the initiator molecule and subsequently to the generation of radicals which may start the polymerization reaction. However, excimer lamps and lasers as monochromatic UV sources with intense short-wavelength emission provide an alternative opportunity for the initiation of the acrylate photopolymerization by utilizing their high photon energy. Since acrylates strongly absorb at $\lambda < 230$ nm, they can be excited by UV radiation in this spectral range, and direct initiation of the photopolymerization may occur.

The omission of a conventional photoinitiator in the formulation can be beneficial in respect of the application properties of the coatings which are made from it since most photoinitiators may cause a number of serious problems such as extractability of fragmentation products, limited long-term stability, discoloration, unpleasant smell, etc. Last but not least, photoinitiators significantly contribute to the total costs of a coating formulation.

In this paper, we present results of a study by real-time FTIR-ATR (RTIR) spectroscopy on the direct initiation of the photopolymerization of acrylates without the use of photoinitiators. Moreover, a new class of self-initiating monomers will be introduced. Irradiation was performed with the short-wavelength emission of various excimer lamps. The kinetic investigations are complemented by quantum chemical calculations in order to consider possible reaction pathways.

Finally, some pilot-scale curing trials were carried out. Near-infrared (NIR) reflection spectroscopy was used for in-line monitoring of the acrylate conversion during photoinitiator-free photopolymerization on a roll coating machine. The resulting coatings were characterized by FTIR spectroscopy and hardness measurements.

UV Irradiation at 222 nm

The use of 222 nm excimer radiation for photoinitiator-free photopolymerization seems to be promising, since the absorption of most organic substances including acrylates strongly increases below about 230 nm. This means that on the one hand their transmission is still high enough to enable sufficient penetration of radiation into a layer to achieve adequate through cure whereas on the other hand sufficient photons can be absorbed by this layer to initiate a photopolymerization reaction.

For kinetic investigations of such processes by RTIR spectroscopy, a small custom-made KrCl* excimer lamp provided by Heraeus Noblelight was mounted above the diamond ATR unit (Golden Gate; Specac). The intensity at the sample position was 12 mW/cm² which was measured by a SiC diode radiometer (Gerus, Berlin). The lamp was directly driven by the electronics of the FTIR spectrometer (Digilab FTS 6000) in order to achieve exact synchronization between UV exposure and infrared spectroscopy. Irradiation was carried out in an inert atmosphere by flushing the sample compartment with nitrogen. The concentration of residual oxygen was about 200 ppm which was monitored by an electrochemical sensor from Gerus.

Acrylates were applied to the diamond surface and covered by a quartz plate which has a gap of 4.5 µm in its lower side to set the thickness of the layer.[1] Several monomers and oligomers from Sartomer and Cytec Surface Specialties, respectively, were used for investigation. A survey of the acrylates and their molar extinction coefficients at 222 nm is given in Table 1.

Acrylate	Product	M_w [g mol^{-1}]	ε (222 nm) [l mol^{-1} cm^{-1}]
Monomers			
1,6-Hexanediol Diacrylate (HDDA)	Sartomer 238	226	480
Polyethylene Glycol Diacrylate (PE(400)DA)	Sartomer 344	508	630
Tripropylene Glycol Diacrylate (TPGDA)	Cytec	300	740
Oligomers			
Silicone Acrylate	RC 705	500	380
Aliphatic Urethane Diacrylate	Ebecryl 4858	450	680
Aromatic Polyester Tetraacrylate	Ebecryl 800	780	8400
Bisphenol A Epoxy Diacrylate	Ebecryl 600	500	19000
Aromatic Urethane Diacrylate	Ebecryl 210	1500	53000

Table 1 : Molecular weights and molar extinction coefficients at 222 nm of acrylate monomers and oligomers.
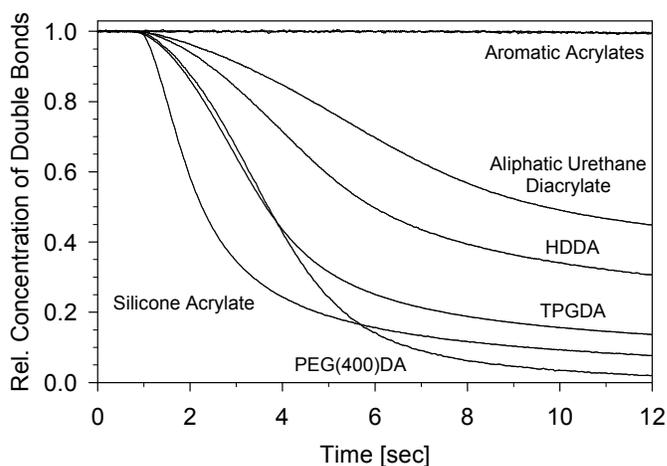
Figure 1 : Photoinitiator-free photopolymerization of various acrylates upon UV irradiation at 222 nm.

Figure 1 shows the effect of 222 nm UV radiation on the double bonds in various acrylates. It can be clearly seen that a photopolymerization reaction can be initiated at least in some acrylates without adding a conventional photoinitiator component just by irradiation with short-wavelength UV radiation. However, considerable differences with respect to polymerization rate and conversion occur. Moreover, whereas all monomers and oligomers with an aliphatic backbone polymerize more or less rapidly and partly achieve high conversion, there is no reaction observed in the aromatic acrylate oligomers.

The apparently different reactivity of the various acrylates is related to their molar extinction coefficients at 222 nm which causes considerable variation in respect of the penetration of the monochromatic UV light into the layers. Figure 2 shows the intensity gradients within the coatings which were calculated from the extinction coefficients. In the aromatic acrylate oligomers the intensity extremely rapidly drops off until it vanishes in a depth of about 0.5 to 1.5 µm, respectively. Consequently, in these acrylates photopolymerization can occur in a very thin surface layer only. Much better penetration of the light into the coating is achieved for the other acrylates, and hence through cure is achieved for some of them. The intensity at the bottom of a 4.5 µm thick layer roughly correlates with the apparent reactivity of these acrylates as shown in Figure 1.
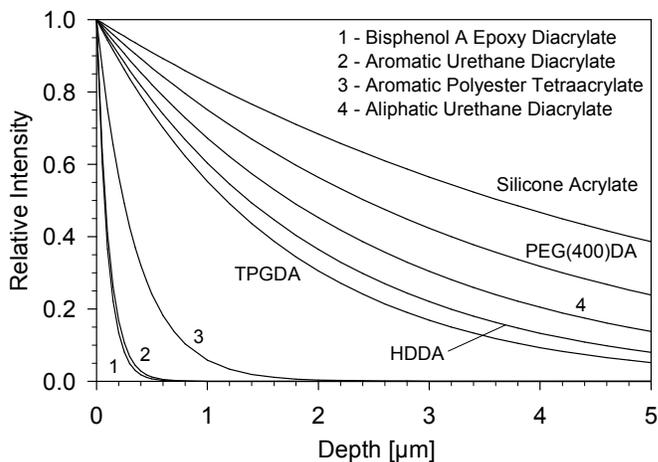
Figure 2 : Decay of the intensity within acrylate layers at a wavelength of 222 nm.

The apparent lack of any reaction in the aromatic acrylates is not only due to the strong decay of the UV intensity within the layer. Likewise, the infrared probe light also penetrates only 1 to 2 μm (depending on the wavelength of investigation) from the ATR crystal into an acrylate coating.[2,3] Hence, the analysis of the conversion is limited to this layer at the bottom of the coating. In 4.5 μm thick coatings from aromatic acrylates no conversion occurs in this depth. However, if much thinner coatings are applied to the diamond surface, the polymerizing layer and the measurement layer will overlap, and detection of the conversion is expected.

Layers of two aromatic acrylate oligomers with a thickness of 300 nm were deposited onto the diamond surface and subsequently irradiated at 222 nm. Figure 3 shows the kinetics of the photopolymerization of these layers in comparison with that of the thicker coatings. It can be clearly seen that substantial conversion can be achieved also in strongly absorbing acrylates when they are studied under adequate conditions.
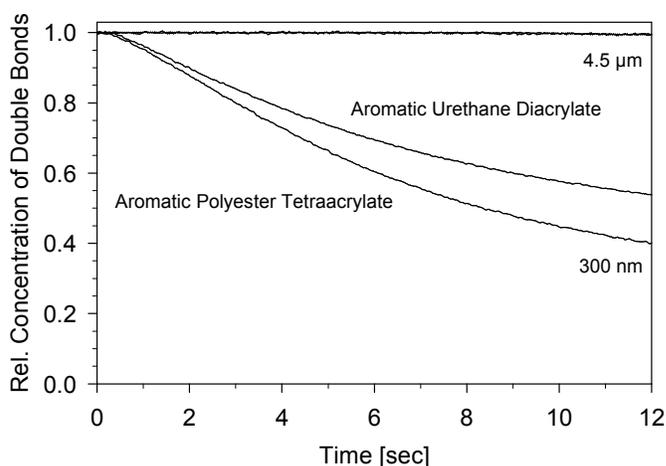
Figure 3 : Effect of the thickness of the layers on the kinetics of the photoinitiator-free photopolymerization of two aromatic acrylate oligomers.

When the thickness of the layer deposited on the ATR crystal is further increased depth profiling of the polymerization reaction can be carried out. Figure 4 shows the conversion in a polyester tetraacrylate in dependence on the thickness of the irradiated layer. The strong decrease proves the close correlation between the decay of the UV intensity with increasing depth in the
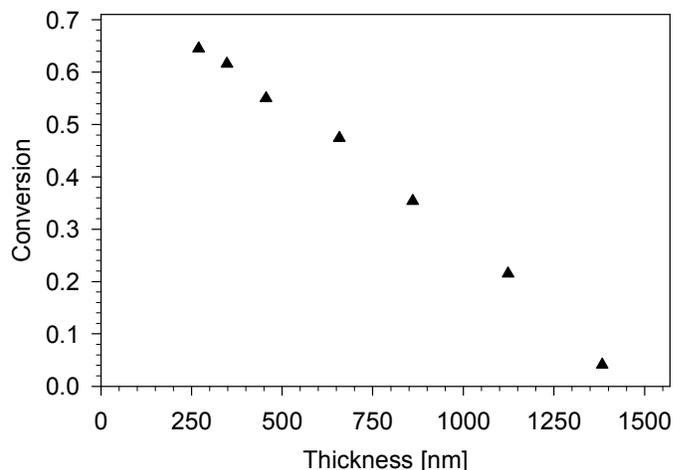
Figure 4 : Dependence of the conversion in an aromatic polyester tetraacrylate on the thickness of the layer

layer and the slowing down of the photopolymerization reaction. If the thickness of the layer exceeds 1.5 µm, no more reaction occurs which is in close correlation with the maximum depth of penetration of 222 nm radiation into the polyester tetraacrylate (see Figure 2).

Generally, photopolymerization reactions proceed faster and achieve higher conversion if the irradiation is carried out in an inert atmosphere since triplet states and radicals are strongly attacked by oxygen leading to quenching and the formation of peroxy radicals, respectively. The detrimental effect of oxygen is well-known from curing processes performed with photoinitiators. In photoinitiator-free systems, the radical concentration is much lower than in those conventional formulations. Consequently, they are even more sensitive to oxygen and require careful inertization. In the present investigation, the concentration of residual oxygen in the sample compartment was about 200 ppm which was controlled by a gas sensor. Nevertheless, a marked inhibition period was observed for all acrylates (see Figure 1) which impressively emphasizes the strong impact of oxygen on the initiation and progression of photopolymerization reactions.

VUV Irradiation at 172 nm

Xe_2^* excimer lamps emit photons with a wavelength of 172 nm which already belongs to the vacuum-UV (VUV) range, i.e. radiation with such a short wavelength is not only strongly absorbed by most organic substances but also by atmospheric oxygen and water vapor. For this reason, Xe_2^* excimer lamps are hardly ever used for UV curing (except for some very special applications such as photochemical matting of acrylate coatings [4]). However, their high photon energy makes them interesting for photoinitiator-free photopolymerization. For such investigations, two basic requirements have to be fulfilled : i) excellent inertization during irradiation is indispensable, and ii) the thickness of the acrylate layers has to be well below 1 micron.

VUV irradiation was carried out with a Xeradex® excimer lamp from Radium. In order to avoid an exceeding absorption of the radiation by atmospheric oxygen, the lamp was directly affixed to the surface of the ATR unit (see Figure 5). After careful sealing, it was continuously flushed with nitrogen. By this means, the oxygen concentration could be reduced to a residual level of 25 ppm which was determined by use of a gas sensor from Zirox (Greifswald). The irradiance on the surface of the diamond was amounting to 15 mW/cm² which had been measured in advance in a similar setup using a VUV radiometer from Epigap (Berlin).

Figure 5 : Xe_2^* excimer lamp attached to the ATR top plate

Thin acrylate layers with a thickness of 500 ± 50 nm were applied to the diamond using a doctor blade. Their thickness was determined from the maximum absorption of the layer in the infrared spectrum. The acrylates studied were largely the same like those in the previous investigation. Molar extinction coefficients at 172 nm have not yet been determined because the VUV region is out of the range of conventional UV spectrometers. The use of synchrotron radiation could be a possible way for such measurements.
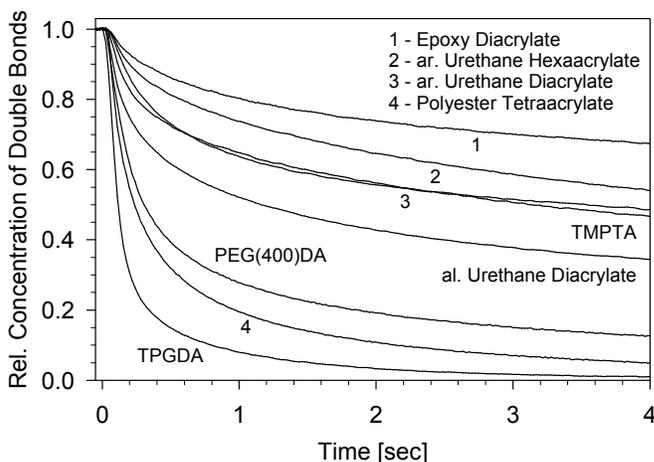
Figure 6 : Photoinitiator-free photopolymerization of various acrylates upon VUV irradiation at 172 nm

Figure 6 shows the kinetics of the photopolymerization of a number of acrylate monomers and oligomers upon irradiation at 172 nm. Although no photoinitiators were used for initiation, some of the acylates show a remarkable reactivity. In particular, the low-viscosity diacrylate monomers TPGDA and PEG(400)DA exhibit fast reaction and achieve high conversion which surprisingly also applies to the polyester tetraacrylate. In contrast, the polymerization of the other oligomers proceeds much slower. Due to the lack of extinction coefficients, the reactivity of the various acrylates cannot be explicitly correlated with the penetration depth of the VUV radiation into the layer. However, it might be expected that acrylates with an aromatic backbone should have stronger absorption which leads to a concentration gradient within the layer. But, the thickness of the layers used here is much lower than those in the previous study with irradiation at 222 nm. Consequently, FTIR-ATR measurements cover the total profile of the coating, and the above results represent the average conversion across the layer.

The comparatively slow reaction of the aromatic epoxy and urethane acrylates in Figure 6 is mainly due to the extremely high viscosity of these systems at room temperature. When the temperature is increased to 60°C, the viscosity decreases to about 3 to 4 Pa s. If the VUV irradiation is carried out at this temperature, both polymerization rate and conversion strongly increase (Figure 7). The same effect is achieved by dilution with a low-viscosity monomer such as TPGDA. An exceptionally distinct influence is observed for the aromatic urethane diacrylate which achieves very high conversion at 60°C. This can be attributed to its low glass transition temperature (T_g = -6° C).
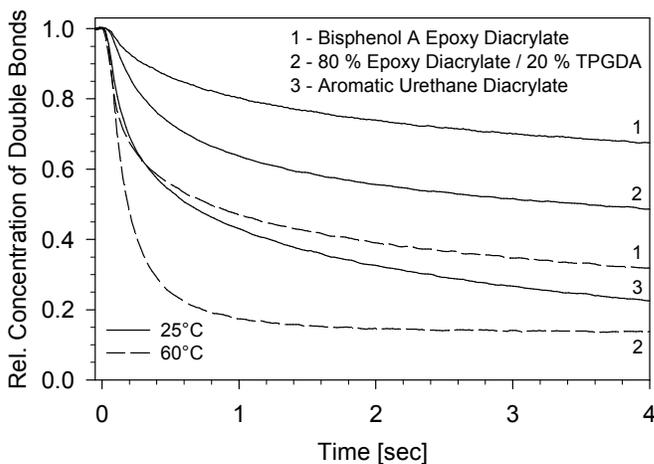
Figure 7 : Effect of temperature and dilution on the kinetics of the photopolymerization of two highly viscous acrylate oligomers upon VUV irradiation at 172 nm
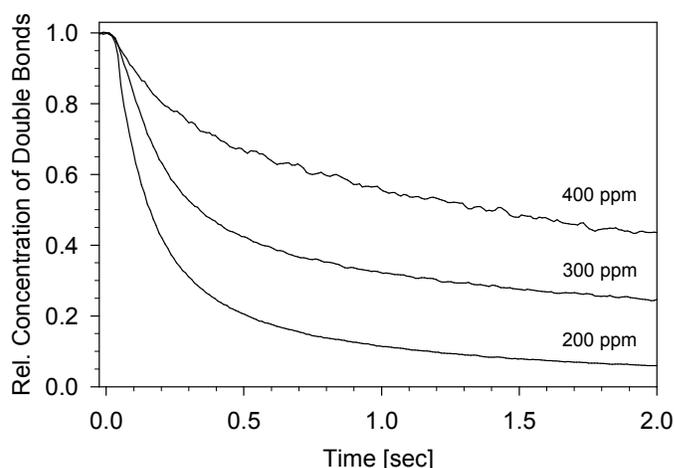
Figure 8 : Effect of the residual oxygen concentration on the kinetics of the photoinitiator-free photopolymerization of a 50/50 mixture of an aliphatic urethane triacrylate and TPGDA upon UV irradiation at 172 nm

In order to demonstrate the strong impact which oxygen has on the kinetics of the photoinitiator-free photopolymerization in particular upon exposure to VUV radiation, thin layers of an acrylate formulation were irradiated at 172 nm, and the concentration of residual oxygen was stepwise increased. Results are shown in Figure 8. It is obvious that both polymerization rate and conversion rapidly decrease even when the oxygen content is only slightly increased. The combined effect of the lower irradiance of the VUV radiation in consequence of its increased absorption by atmospheric oxygen and the scavenging of the formed radicals by dissolved oxygen lead to a substantial suppression of the polymerization reaction : whereas the former causes a lower rate of radical generation, the latter simultaneously leads to their stronger consumption.

Investigations on the Photochemistry of the Photoinitiator-free Polymerization of Acrylates

Since only little is known about the possible mechanism of the initiation of the photoinitiator-free photopolymerization of acrylates a number of basic investigations were carried out. At first, laser flash photolysis was used to characterize short-lived transients, and quantum chemical calculations were performed to assist the interpretation of the photolysis data. Results of the investigations have already been published elsewhere.[5] In all acrylates studied, a transient with an absorption around 280 nm and a lifetime of 10 µs was observed immediately after the laser pulse which was assigned to the acrylate triplet. Further investigations militated in favor of an addition reaction of this triplet instead of H-abstraction.

In order to substantiate this assumption, a product study has been carried out by GC/MS to analyze stable products which were formed after steady-state photolysis of acrylate solutions.[6] The main product after the photolysis of *n*-butyl acrylate was found to be *n*-butanol. This was somewhat unexpected since the α-cleavage of the triplet state leading to a butoxyl radical seems to be energetically unfavorable. However, quantum chemical modeling has shown that this reaction may readily proceed from an excited singlet or triplet state. Further proof of the cleavage reaction can be drawn from the detection of the products formed by addition of both fragments to another acrylate molecule. Though not yet quantified the results indicate that α-cleavage seems to be a main reaction channel. However, a complete reaction scheme could not yet be established. Hence, further investigations will be necessary for a deeper understanding of the photochemistry of acrylates upon irradiation with short-wavelength UV radiation.

Self-Initiation of Brominated Acrylates

In the past, self-initiation of specific monomers such as vinyl acrylate has been reported,[7] which can be photopolymerized without the use of a conventional photoinitiator compound by irradiation with the light of an usual medium pressure mercury lamp. Moreover, vinyl acrylate not only self-initiates its own free radical photopolymerization, but may also act as an efficient photoinitiator for the polymerization of other acrylates.[8]

Brominated polymers are typically used as efficient flame retardants and high refractive index materials. The corresponding monomers can be used for the development of special coatings with such properties.[9] During the development of such coatings it was observed that pentabromophenyl acrylate (PBBA) polymerizes upon UV irradiation even without addition of a photoinitator.[10] This interesting phenomenon was studied in more detail by RTIR spectroscopy and supplementary quantum chemical calculations. First results of these investigations will be reported in this section.

PBBA was purchased from the Dead Sea Bromine Group (Beer Sheva, Israel). Its UV spectrum recorded in acetonitrile with a Shimadzu 2101 UV-VIS spectrometer is plotted in Figure 9. In addition, the spectrum of unbrominated phenyl acrylate (Alfa Aesar) is shown which has a similar structure like PBBA. The most striking feature is the strong absorption of PBBA up to well above 300 nm which is different from the spectrum of phenyl acrylate. This enables the absorption of considerable parts of the emission of the mercury arc lamp, and even the use of a XeCl* excimer lamp with an emission line at 308 nm seems to be possible for initiation.
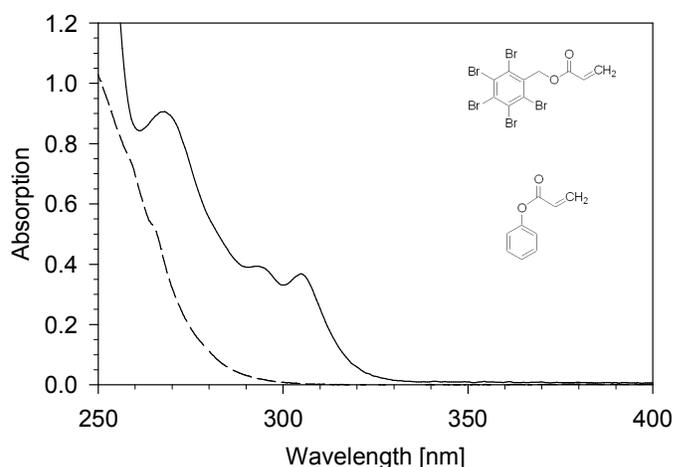
Figure 9 : UV spectra of PBBA (—) and phenyl acrylate (- - -) ([Acr] = 5 × 10^{-3} M in acetontrile)

For kinetic investigations with RTIR spectroscopy, samples were applied to the ATR crystal and covered by the quartz plate setting the thickness to 4.5 μm. Irradiation was carried out with an Osram mercury arc lamp whose irradiance in the focus on the diamond was 280 mW/cm². For some investigations, a 313 nm interference filter was used in order to simulate a XeCl* lamp (irradiance at 313 nm : 13 mW/ m²). An electronic shutter which is controlled by the spectrometer computer serves for synchronization between UV irradiation and IR spectra recording. Irradiation was performed either in air or in nitrogen.

Due to its melting point of 115°C, the photoinitiator-free polymerization of pure PBBA was studied at a temperature of 160°C where the monomer still forms a rather viscous melt. Nevertheless, it reacts quite rapidly upon irradiation and achieves a conversion of more than 95 %.

Subsequently, it was used as photoinitiator for the polymerization of a conventional acrylate. It was dissolved in TPGDA at concentrations of 1 or 5 wt.-%, respectively. In addition, mixtures of TPGDA and phenyl acrylate were studied in order to show that the outstanding reactivity of PBBA is due to its bromination. Finally, pure TPGDA as well as a mixture with benzildimethyl ketal (BDMK; Irgacure 651) as a conventional photoinitiator were investigated for comparison. At first, irradiation was carried out with the mercury arc lamp. Results are summarized in Figure 10.
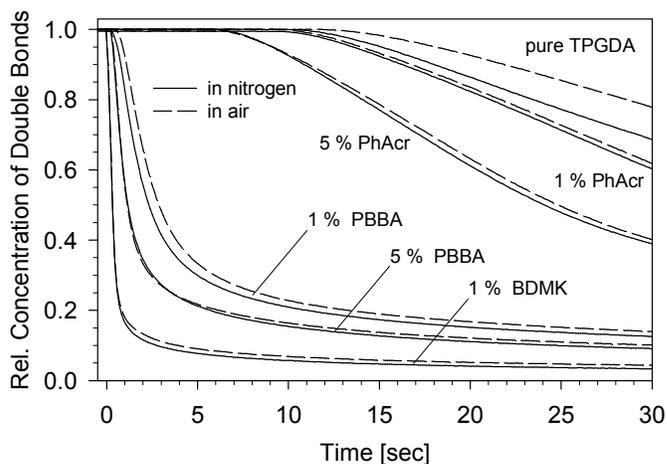
Figure 10 : Photoinitiator-free photopolymerization of TPGDA / PBBA and TPGDA / phenyl acrylate (PhAcr) mixtures upon irradiation with a mercury arc lamp. Curves of TPGDA with BDMK and of pure TPGDA are given for comparison.

The kinetic curves of the various systems clearly demonstrate that PBBA is a highly efficient photoinitiator for the polymerization of other acrylates although BDMK has an even higher performance as could be expected. In contrast, phenyl acrylate which due to its aromatic structure significantly absorbs UV light with a wavelength below 290 nm is far from being an efficient initiator for the photopolymerization of TPGDA. In fact, the mixtures with phenyl acrylate do not react much faster than pure TPGDA which slightly absorbs light from the short-wavelength end of the emission of the mercury arc lamp. These results strongly indicated that the self-initiation properties of PBBA are related to its bromination.

Additionally, analogous investigations were carried out with irradiation at 313 nm (Figure 11). Results are quite similar to those in Figure 10, i.e. PBBA is still an efficient photoinitiator for the polymerization of TPGDA which is only excelled by BDMK. No reaction is observed in
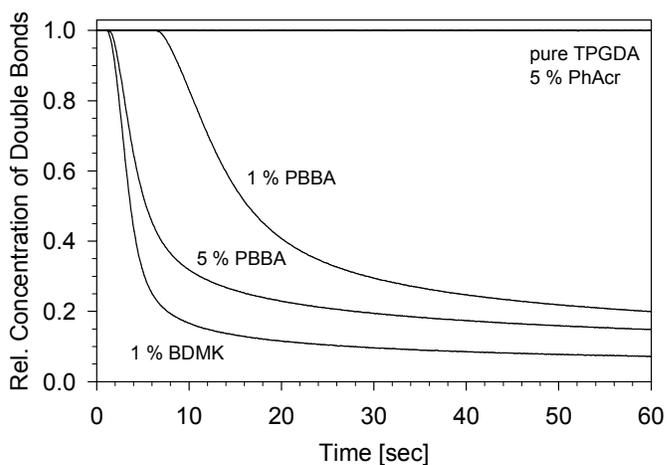
Figure 11 : Photoinitiator-free photopolymerization of TPGDA / PBBA and TPGDA / phenyl acrylate (PhAcr) mixtures upon irradiation at 313 nm in an inert atmosphere. Curves of TPGDA with a BDMK and of pure TPGDA are given for comparison.

pure TPGDA and in the formulation with phenyl acrylate. These results are not surprising since they are related to the molar extinction coefficients : it is obvious from Fig. 9, that PBBA strongly absorbs at 313 nm ($\varepsilon = 333$ l mol^{-1} cm^{-1}), whereas TPGDA and phenyl acrylate do not absorb at this wavelength ($\varepsilon \leq 3$ l mol^{-1} cm^{-1}).

In order to elucidate a possible mechanism for the self-initiation of the photopolymerization reaction of PBBA, quantum chemical calculations were carried out. Investigations were based on the density functional theory (DFT) Hybrid B3LYP method with standard 6-31G(d) basis set (Gaussian 03 program). At first, the equilibrium geometries were optimized without any restriction which was followed by calculation of the energy of the systems and the electronic structures for the triplet states and neutral radicals. Finally, UV-VIS stick spectra were calculated using the unrestricted time-dependent (UTD) approach at the B3LYP / 6-31 + G(d,p) level.

Initially, benzyl acrylate which is the unbrominated homologue of PBBA is considered. In the singlet state, the electron of the HOMO orbital is located at the aromatic ring. Upon excitation by UV light and subsequent inter-system crossing (ISC), the spin density is now localized at the carbon-carbon double bond. The orbitals are distorted by 90° against each other, i.e. they are antibonding and form a triplet. This complies with the usual behavior of acrylates upon excitation.[6]

In PBBA, the HOMO electrons in the ground state are likewise localized at the benzene ring. After excitation and ISC, some rearrangement of the electron distribution occurs. However, the spin density is still localized at the ring structure. The orbitals become antibonding, and the bond distances between the carbon atoms in the ring and the bromine atoms substantially increase from 1.89 nm to 2.72 nm which finally leads to the release of one bromine radical. The calculation of the spin density indicates that the splitting should occur in meta position. The energy levels of the excited singlet and triplet states of PBBA are rather low which makes the release of the bromine radical very favorable from an energetical point of view. Both the bromine radical and the 4-bromobenzyl radical may initiate the polymerization reaction.
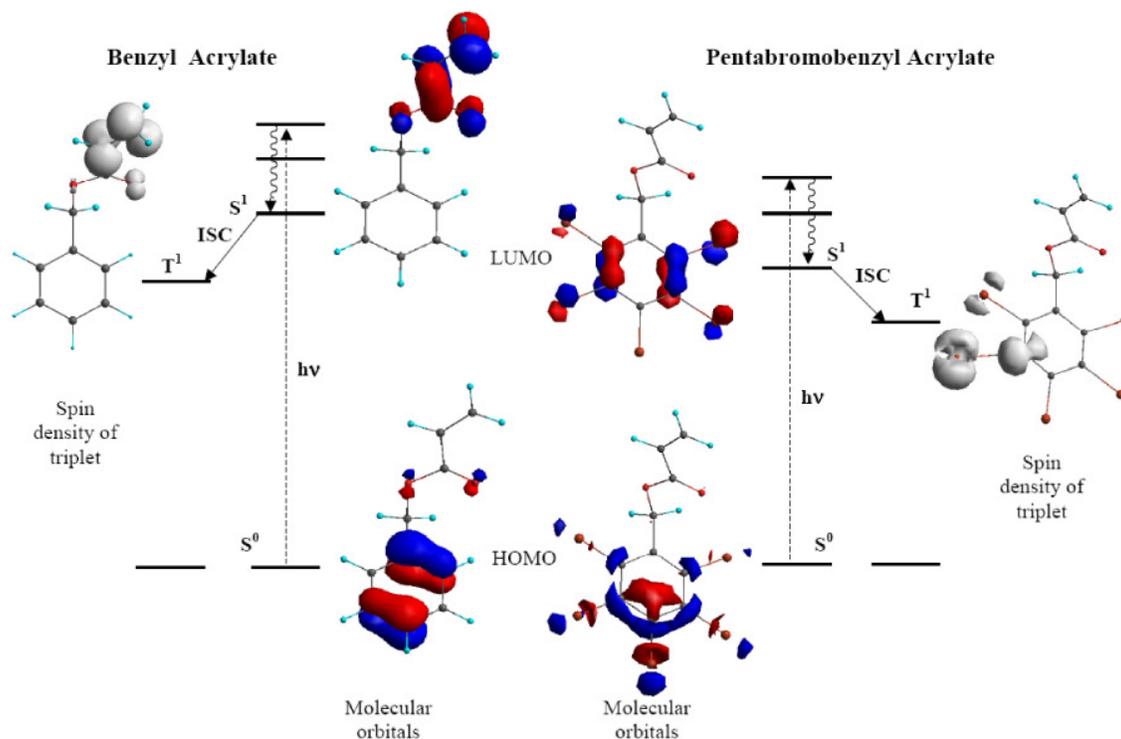
Photoinitiator-free UV Curing in Pilot Scale

In addition to the basic investigations, some preliminary curing trials were carried out in pilot-scale. A clear formulation made up of two aliphatic urethane acrylates and TPGDA was printed on 20 µm polypropylene foil with a grammage of 5 g/m². These layers were irradiated at various line speeds using a KrCl* double lamp system which is made up of tubes from Heraeus Noblelight and a 10 kW RF generator from Hüttinger (222 nm, irradiance 175 mW/ cm²). Subsequently, the conversion of the acrylic double bonds was determined by FTIR-ATR spectroscopy using the acrylate band at 1405 cm^{-1}, and the hardness of the coatings was measured with a Fischerscope H100C microhardness tester. Results are summarized in Figure 12.
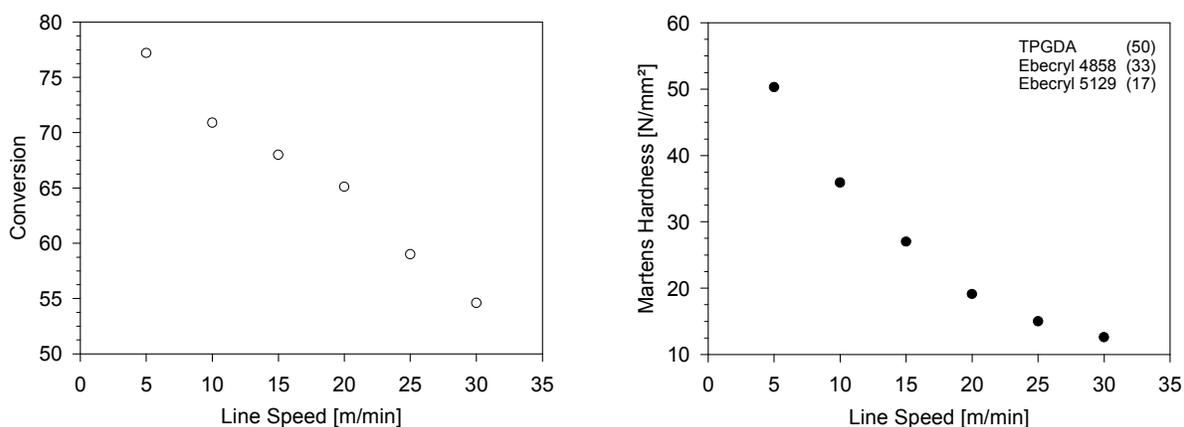
Figure 12 : Conversion (left) and hardness (right) of photoinitiator-free acrylate coatings on polypropylene foil after irradiation at 222 nm in dependence on the line speed.

Both conversion and microhardness uniformly drop down with increasing line speed which is due to the decreasing irradiation dose. At line speeds higher than 30 m/min, only the top layer of the coating is reasonably cured whereas it is still liquid at the bottom causing a lack of adhesion. Due to the gradient of the light intensity within the sample, the dose which is absorbed at the bottom of the layer during passage under the UV lamp is too low to achieve sufficient conversion.

Recently, it was shown that near-infrared (NIR) reflection spectroscopy can be used as an efficient tool to monitor the conversion in radiation-cured acrylate coatings directly in a running coating line.[11,12] In the present study, this method was applied to the photoinitiator-free photopolymerization of acrylates. Curing trials were carried out on a roll coating machine equipped with the KrCl* double lamp system. NIR spectra were recorded with a process analyzer which was developed according to the specific requirements of in-line measurements on thin UV-cured acrylate coatings.[11] It consists of a commercial photodiode array spectrometer (Kusta 4004 P from LLA, Berlin) and a separate tailor-made probe head which was mounted above the moving web. The conversion was determined from the decrease of the overtone band at 1620 nm. Figure 13 shows the in-line monitoring of the conversion in a photoinitiator-free acrylate layer with a coating weight of only 4 g/m². The lacquer formulation was based on multifunctional aliphatic urethane acrylate oligomers which were diluted with TPGDA. UV irradiation was carried out under inert conditions.
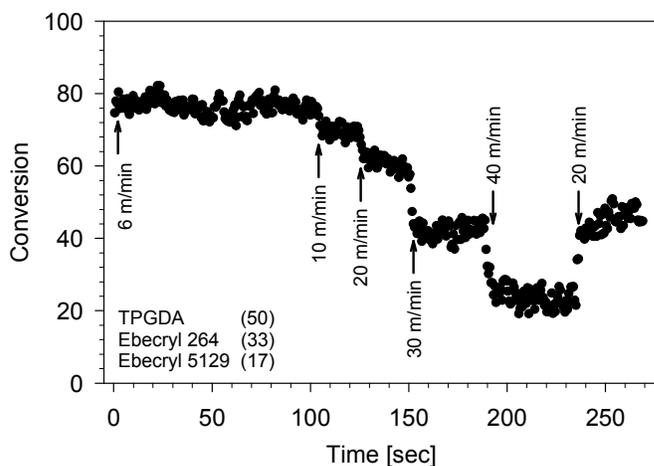
Figure 13 : In-line monitoring of the conversion in a photoinitiator-free acrylate coating on 20 μm polypropylene foil after irradiation at 222 nm using NIR reflection spectroscopy

Despite of the low thickness of the layer, NIR reflection spectroscopy is able to supply quantitative data with a time resolution of about 2 spectra per second. Initially, i.e. at a web speed of 6 m/min, an acrylate conversion of more than 75 % is achieved. With increasing line speed it decreases until it is only 25 % at 40 m/min. These results are in close correlation with the off-line experiments, i.e. they confirm that 30 m/min is the current maximum speed which can be achieved.

Acknowledgements

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