Investigations on the Photoinitiator-free Photopolymerization of Acrylates by Vibrational Spectroscopic Methods

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Summary: Photopolymerization of acrylates without photoinitiators was carried out by irradiation with short-wavelength UV light from excimer lamps with an emission at 222 or 172 nm. Basic investigations on the reactivity of various acrylates and on the conditions under which they can be UV-cured were performed by real-time FTIR-ATR spectroscopy. Depending on the molar extinction coefficients of a specific acrylate at the wavelength of irradiation, the absorption of the light within the coating leads to a pronounced intensity gradient which significantly influences polymerization rate and conversion. Accordingly, it limits the maximum thickness of the layer that can be cured (ranging from some hundreds of nanometres up to some micrometers). In addition to the basic studies, thin acrylate coatings were also cured on pilot scale. The actual conversion in the layer after UV irradiation was directly monitored by in-line NIR reflection spectroscopy, and the resulting coatings were characterized by FTIR spectroscopy and hardness measurements.

Keywords: acrylate; photoinitiator-free photopolymerization; real-time FTIR-ATR spectroscopy

Introduction

The photopolymerization of functionalized monomers and oligomers such as acrylates and methacrylates usually requires the addition of one or several photoinitiators to the formulation for the initiation of the polymerization reaction. The light of the widely-used medium pressure mercury arc lamps ($\lambda > 250$ nm) is mainly absorbed by the photoinitiator which leads to an electronic excitation of the molecule, followed by the generation of radicals which start the polymerization reaction. However, excimer lamps and lasers as monochromatic UV sources with intense short-wavelength emission in the UV-C region provide an alternative opportunity for the initiation of the acrylate photo-polymerization. Since acrylates strongly absorb at $\lambda < 230$ nm, they can be directly excited by UV radiation in this spectral range, and self-initiation of the photopolymerization might become possible.

The avoidance of the photoinitiator in the formulation would be beneficial since photoiniators can cause several serious problems in respect of the application properties of a coating such as limited long-term stability (in particular in outdoor applications), unpleasant smell, discolouration (e.g. yellowing), extractability of fragmentation products, etc. Last but not least, photoinitiators contribute significantly to the total costs of a coating formulation. In the past, several UV-curable systems have been introduced which can be photopolymerized without the use of a conventional photoinitiator compound such as specific self-initiating monomers (e.g. vinyl acrylate[1]), thiolene formulations[2,3] or donor-acceptor pairs (e.g. maleimides/vinyl ethers[4,5]). However, all these systems suffer from

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certain limitations such as health or cost aspects.

In this paper, we present results of a study by real-time FTIR-ATR spectroscopy on the direct initiation of the photopolymerization of acrylates without the use of photoinitiators. It deals with the question which acrylates can be cured in this way and which conditions are required. In addition to these basic investigations, pilot-scale curing trials were carried out, and the resulting coatings were characterized by FTIR spectroscopy and hardness measurements. Irradiation was predominantly performed with $KrCl^*$ excimer lamps which have an emission band at 222 nm.[6]

Experimental

Investigations on the kinetics of the photoinitiator-free photopolymerization under various conditions were carried out by real-time FTIR-ATR spectroscopy (time resolution: 21 ms) using a Digilab FTS 6000 spectrometer and a Golden Gate diamond ATR accessory. Acrylate layers on the crystal were prepared by covering a drop of acrylate by a quartz plate with a gap of 4.5 μm in its lower side or by deposition from solution (without quartz cover). UV irradiation was performed with a $KrCl^*$ excimer lamp (222 nm; Heraeus) or with a Xe_2^* excimer lamp (172 nm; Radium), respectively. For comparison, a mercury arc lamp with an interference filter (313 nm) was used. The lamps are directly driven by the spectrometer electronics in order to achieve exact synchronization between UV exposure and FTIR spectroscopy. The intensity on the surface of the diamond was 12 mW/cm^2 (at 222 nm). Irradiation was performed in an inert atmosphere. The concentration of the residual oxygen was determined with an electrochemical sensor (G.E.R.U.S.). A more comprehensive description of this method was given elsewhere.[7,8]

In order to characterize the UV curing of photoinitiator-free coatings in a close-to-pilot-scale, thin layers of acrylate were printed with a coating weight of 5 g/m^2 on a 20 μm polypropylene (PP) foil. They were irradiated on a pilot line consisting of a belt conveyor and a $KrCl^*$ double lamp system which is made up of tubes from Heraeus and a 10 kW RF generator from Hüttinger (irradiance 175 mW cm^{-2}). Subsequently, the conversion of the acrylic double bonds was determined by FTIR-ATR spectroscopy using the acrylate band at 1405 cm^{-1}. In addition, the hardness of the coatings was measured with a Fischerscope H100C microhardness tester.

Finally, the conversion in photoinitiator-free coatings was directly monitored in a running coating machine using near-infrared (NIR) reflection spectroscopy. NIR spectra were recorded with a process analyzer system which was developed according to the specific requirements of in-line measurements on thin UV-cured acrylate coatings.[9] It consists of a commercial photodiode array spectrometer (Kusta 4004 P from LLA) and a separate tailor-made probe head, interconnected by an optical fibre. The probe head was mounted above the moving web of a roll coating machine at IOM which was equipped with the excimer double lamp system. The conversion was determined from the decrease of the band at 1620 nm which is the first overtone of the C–H stretching vibration of the acrylic double bonds.[10] More details about in-line monitoring of the conversion in UV-cured acrylate coatings were reported in Ref. [11].

Acrylate monomers and oligomers were provided by Cray Valley (Sartomer) and Cytec Surface Specialties (formerly UCB; Ebecryl). They were used as received. Their UV spectra in acetonitrile were recorded with a Shimadzu 2101 UV-VIS spectrometer. An overview over the acrylates used in this study, their molecular weight M_w and their molar extinction coefficient ε at 222 nm are given in Table 1. 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propanone (Darocur 2959; Ciba Specialty Chemicals) was used as photoinitiator.

Table 1.
Molecular weights and molar extinction coefficients at 222 nm of the acrylate monomers and oligomers used in this study.

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
Tetraethylene Glycol Diacrylate (TeEGDA)	Sartomer 268	302	560
Tripropylene Glycol Diacrylate (TPGDA)	Cytec	300	740
Oligomers			
Aliphatic Urethane Diacrylate	Ebecryl 4858	450	680
Aliphatic Polyether Diacrylate	Ebecryl 81	600	2000
Aromatic Polyester Tetra-acrylate	Ebecryl 800	780	8400
Aromatic Urethane Diacrylate	Ebecryl 210	1500	53000

Results

Photopolymerization reactions are usually initiated by irradiation with medium pressure mercury lamps whose main emission lies above 250 nm. Most acrylates are transparent in this spectral region (typically $\varepsilon < 20$ l mol^{-1} cm^{-1}), i.e. they do not significantly absorb light. Moreover, the energy of the photons is not high enough to break chemical bonds such as acrylate double bonds. Consequently, photoinitiators which are tuned to the emission spectrum of the mercury arc lamp are required to provide initiating species which start the polymerization reaction. This is demonstrated in Figure 1 by means of data from real-time FTIR spectroscopy. The irradiation of TPGDA at 313 nm which is one of the most intense lines of the mercury arc lamp leads to a fast polymerization reaction in the presence of an α-hydroxyalkylphenone as photoinitiator despite of its rather low extinction coefficient ($\varepsilon_{313\ nm} = 490$ l mol^{-1} cm^{-1}[12]). In contrast, no reaction at all occurs if no photoinitiator is added.

However, if the irradiation is carried out at 222 nm, a polymerization reaction is observed for both TPGDA with and without added photoinitiator (see Figure 1). In the former case, the consumption of the acrylic double bonds proceeds almost as fast as upon irradiation at 313 nm despite of the lower intensity of the incident light which should be due to the much higher

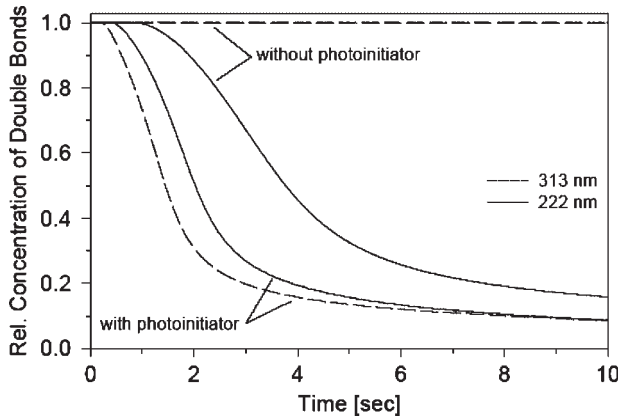

Figure 1.
Consumption of the acrylic double bonds in TPGDA with and without photoinitiator (1 wt.-% α-hydroxyalkylphenone) on irradiation at 313 nm (40 mW/cm^2) or at 222 nm (12 mW/cm^2), respectively.

extinction coefficient of the initiator compound at 222 nm (9400 l mol^{-1} cm^{-1}[12]). But even without photoinitiator, a relatively fast and extensive reaction of the diacrylate occurs upon exposure to the KrCl* excimer lamp. This clearly indicates that the photopolymerization of acrylates can be directly initiated when they are irradiated with UV radiation with a sufficiently short wavelength which is strongly absorbed by the acrylate.

In addition to TPGDA, a number of other acrylate monomers and oligomers (see Table 1) have been investigated by real-time FTIR spectroscopy in respect of their reactivity upon irradiation at 222 nm without a photoinitiator added. Results are summarized in Figure 2.

At first, an inhibition period is observed which is roughly the same for all samples under investigation. Although the sample compartment is flushed with nitrogen, a residual concentration of oxygen remains in the sample which has a marked impact on the initiation of the photopolymerization due to the strong inhibiting effect of oxygen on radical reactions. Moreover, the radical concentration in photoinitiator-free systems is much lower than in conventional radiation-curable formulations containing a photoinitiator. Considerable differences between the various acrylates can be observed with respect to polymerization rate and conversion. Whereas the double bonds in all acrylate monomers and in the oligomers with an aliphatic backbone are converted rapidly, there is no reaction observed in the two aromatic acrylate oligomers.

These differences are correlated with the molar extinction coefficients of the various acrylates at 222 nm. Figure 3 shows the intensity gradients within the coatings as calculated from the data in Table 1. It is obvious that the intensity drops off rapidly in the two aromatic oligomers whereas much better penetration of the light into the coating is achieved for the other acrylates. The maximum penetration depth of the UV light is about 0.5 μm for the urethane diacrylate and 1.5 μm for the polyester tetra-acrylate, respectively. On the other hand, the infrared probe light also penetrates only 1 to 2 μm from the ATR crystal into the 4.5 μm thick coating,[13] i.e. the analysis of the conversion is limited to this layer at the bottom of the coating which is almost completely cut off from the UV light in the aromatic acrylates and where, accordingly, no conversion occurs. Consequently, the conversion of double bonds in coatings from these two acrylates can be detected in much thinner layers only.

Such layers were deposited onto the surface of the diamond from dilute solution. Depending on the acrylate concentration,

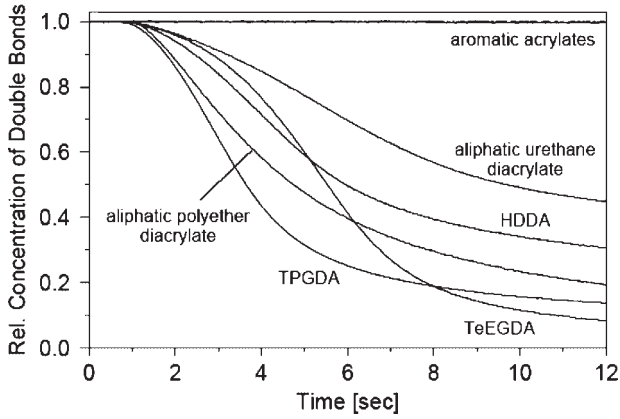

Figure 2.
Photopolymerization of several acrylate monomers and oligomers without photoinitiator by irradiation at 222 nm.

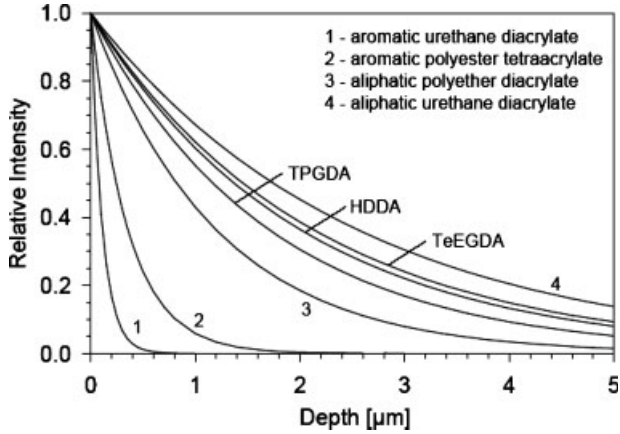

Figure 3.
Intensity gradient within various acrylates at 222 nm.

layers with a thickness between about 250 and 1500 nm were prepared in this way and subsequently irradiated at 222 nm. Figure 4 shows the kinetics of the photopolymerization of 300 nm thick layers of the urethane diacrylate and the polyester tetra-acrylate in comparison with that of the much thicker drawn coatings from Figure 2. It is obvious that the conversion which is achieved in the thin layers is roughly comparable to that in the thicker layers of the other acrylate oligomers. The comparatively low polymerization rate is probably due to the much higher initial viscosity of the two aromatic oligomers.

When the thickness of the deposited acrylate layer on the ATR crystal is further increased stepwise some kind of depth profiling of the polymerization reaction can be carried out. Figure 5 shows the conversion in the polyester tetra-acrylate as a function of 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 layer and the slowing down of the photopolymerization reaction. If the thickness of the layer exceeds about 1.5 µm, no more reaction occurs which is in close correlation with the maximum depth of penetration of

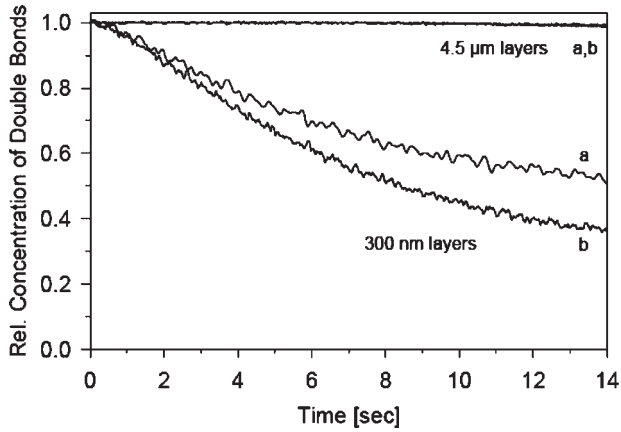

Figure 4.
Photopolymerization of 4.5 µm thick drawn layers and 300 nm thick layers deposited from solution of an aromatic urethane diacrylate (a) and an aromatic polyester tetra-acrylate (b).

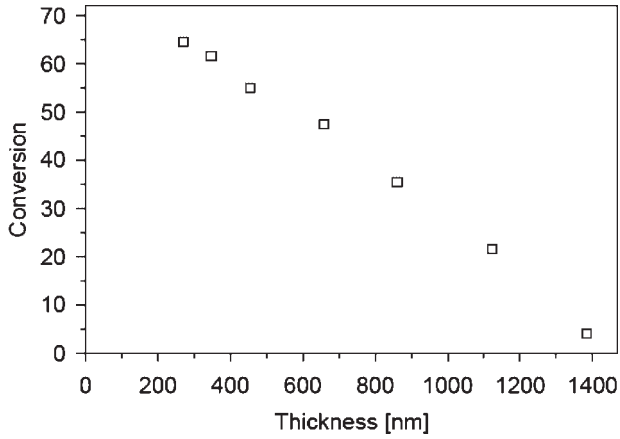

Figure 5.
Conversion in an aromatic polyester tetra-acrylate as a function of the thickness of the layer deposited on the ATR crystal from solution.

222 nm radiation into the polyester tetra-acrylate (see Figure 3). According to this, the photoinitiator-free photopolymerization of acrylates with high extinction coefficient at the wavelength of irradiation is limited to a very thin surface layer since no UV light reaches the deeper-lying layers.

The penetration depth of short-wavelength UV radiation does not only depend on the molar extinction coefficient of a specific acrylate but also on its molecular weight (corresponding to the molar concentration). Figure 6 shows kinetic curves of a homologous series of ethylene glycol diacrylates (supplied by Sartomer) with chain lengths from 2 to 14 ethoxy units. Their molar extinction coefficients are almost independent of the molecular weight and lie in the range between 560 and 650 l mol^{-1} cm^{-1}. Nevertheless, both polymerization rate and conversion strongly increase with the number of ethoxy units in the molecule. This behaviour is

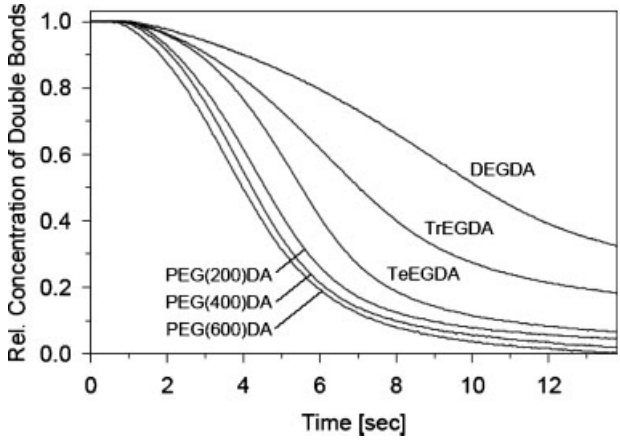

Figure 6.
Effect of chain length on the kinetics of the photopolymerization of various ethylene glycol diacrylates. (DEGDA – diethylene glycol diacrylate; TrEGDA – triethylene glycol diacrylate; TeEGDA – tetraethylene glycol diacrylate; PEG(x)DA – polyethylene glycol diacrylates of different molecular weight).

linked to the deeper penetration of 222 nm radiation into the coatings with increasing chain length of the acrylates because of their decreasing molar concentration. In respect of the polymerization rate, these results are in contrast to the reactivities of the same series of acrylates when the irradiation is carried out with a mercury arc lamp in the presence of a conventional photoinitiator.[14] In that case, the reverse order is found since the polymerization rate strongly increases with the molar concentration of double bonds whereas the absorption of the incident UV light by the acrylate does not play a role. Additionally, the increasing viscosity with increasing molecular weight leads to a decrease of the reaction rate. For the conversion, however, similar results were found in both studies, i.e. the conversion increases with chain length, and almost complete conversion is achieved in the polyethylene glycol diacrylates. This is attributed to the enhanced molecular mobility and the decrease of the glass transition temperatures. In particular, the glass temperatures of DEGDA and TrEGDA are much higher than room temperature (100 and 61 °C, respectively), and accordingly these two acrylates do not attain complete conversion of double bonds at ambient temperature (see Figure 6).

Instead of the KrCl* excimer lamp with its emission at 222 nm, UV light with an even shorter wavelength such as 193 nm from an ArF* excimer laser, 185 nm from a line of a low pressure mercury arc lamp, or 172 nm from a Xe_2^* excimer lamp can be used for the direct initiation of the photopolymerization. However, the UV absorption in organic matter strongly increases with decreasing wavelength. The resulting drop of the penetration depth of the light into the coating more and more limits the thickness of the acrylate layer which can be polymerized. But this is not the only limitation. When the wavelength of irradiation is decreased to below 200 nm, i.e. into the vacuum-UV (VUV) region, the absorption of light by atmospheric oxygen starts to play a role which rapidly increases with further decreasing wavelength (see Figure 7). Depending on the distance between light source and sample this leads to a marked reduction of the irradiance on the surface of the coating to be cured.

Figure 8 shows the effect of the concentration of residual oxygen on the kinetics of the photoinitiator-free photopolymerization of an acrylic clear coat upon irradiation with the 172 nm emission of a Xe_2^* excimer lamp. With regard to the absorption of the acrylates in this spectral region, thin layers with a thickness of 400 nm were deposited onto the ATR diamond from solution. A rather fast polymerization reaction leading to high

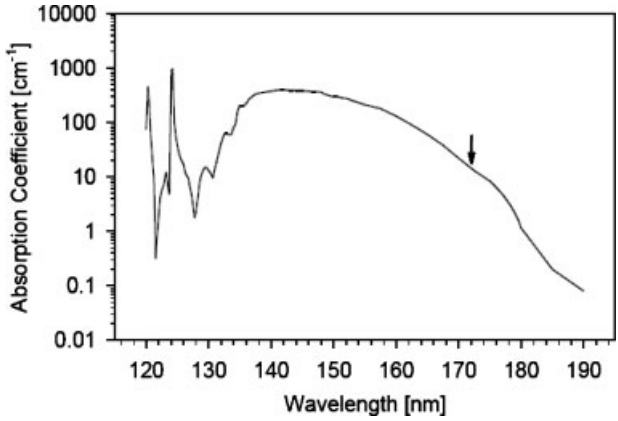

Figure 7.
Absorption coefficient of molecular oxygen in the VUV region (according to [15,16]).

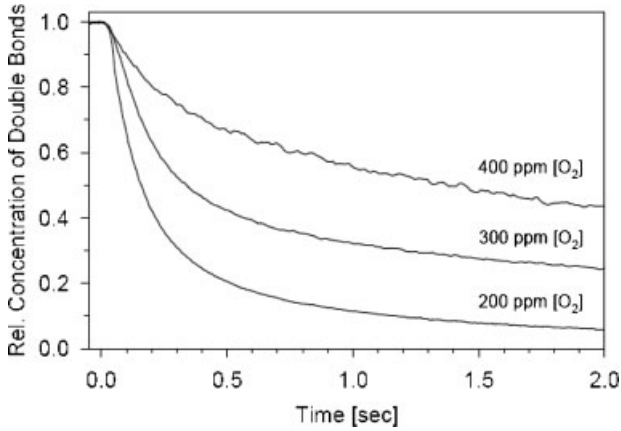

Figure 8.
Irradiation of 400 nm thick layers of a 50/50 mixture of an aliphatic urethane triacrylate and TPGDA with a Xe_2^* excimer lamp (172 nm, 7 mW/cm^2) at various oxygen concentrations.

conversion is observed when the oxygen concentration is below 200 ppm. However, even when the oxygen content only slightly increases, both polymerization rate and conversion rapidly decrease which is attributed to the combined effect of the lower intensity of the UV radiation impinging on top of the layer and the scavenging of the formed radicals by oxygen. The former causes a lower rate of radical generation, while the latter simultaneously leads to their stronger consumption. So, if direct excitation of acrylates is carried out by irradiation in the VUV an even better inertization is implicitly required. But aside from this, the poor penetration of VUV light into acrylate coatings strongly limits its usability for both photoinitiator-free and conventionally initiated photopolymerization.

In addition to the basic investigations by real-time FTIR spectroscopy, a number of curing trials were carried out on a pilot-scale curing station. An acrylic clear coat made up of TPGDA and various aliphatic urethane acrylates, with a well-defined extinction of its components at 222 nm and the viscosity of the formulation, was printed on PP foil at 5 g/m^2 and irradiated with a KrCl* double lamp system at various speeds of the conveyor belt. Figure 9 shows the conversion of double bonds and the microhardness of the coatings in dependence on the line speed recorded after 24 h.

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

In further trials, it was attempted to improve the conversion (or the maximum line speed, respectively) by increasing the number of excimer lamps, variation of the lamp distance and by optimizing the geometry of irradiation. Moreover, other lacquer formulations were tested. Nevertheless, a speed of about 30 m/min seems to be the upper limit under the experimental conditions used here, i.e. with the intensity of the KrCl* lamp as the limiting factor.

Recently, it was shown that NIR reflection spectroscopy can be used as an efficient tool to monitor the conversion in radiation-cured (meth)acrylate coatings directly in a running coating line.[9,11] Despite the low

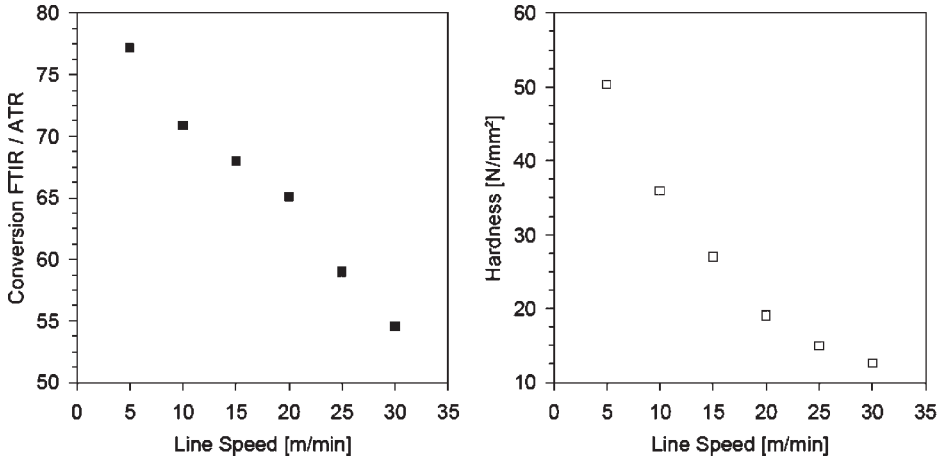

Figure 9.
Conversion of double bonds from FTIR-ATR spectroscopy (left) and Martens hardness (right) of photoinitiator-free acrylate coatings (coating weight 5 g/m^2) on 20 μm PP foil after irradiation at 222 nm (175 mW/cm^2) as a function of the line speed.

extinction coefficients in the near infrared and the generally low thickness of such coatings in the range of about some tens of micrometers, spectra with adequate signal-to-noise ratio were recorded. In the present study, this method was applied to the photoinitiator-free photopolymerization of acrylates, where the typical thickness of the cured layers is even lower, i.e. a few microns only.

Curing trials were carried out on a roll coating machine equipped with the KrCl* double lamp system. Figure 10 shows the in-line monitoring of the conversion in an acrylate layer with a coating weight of only 4 g/m^2. Again, the lacquer formulation was based on multifunctional aliphatic urethane acrylate oligomers which were diluted with TPGDA. UV irradiation was carried out under inert conditions. As expected, a stronger scattering of the conversion data than in records of typical UV coatings with a thickness in the range of 10 to 20 g/m^2 is observed.[11] Nevertheless, NIR reflection

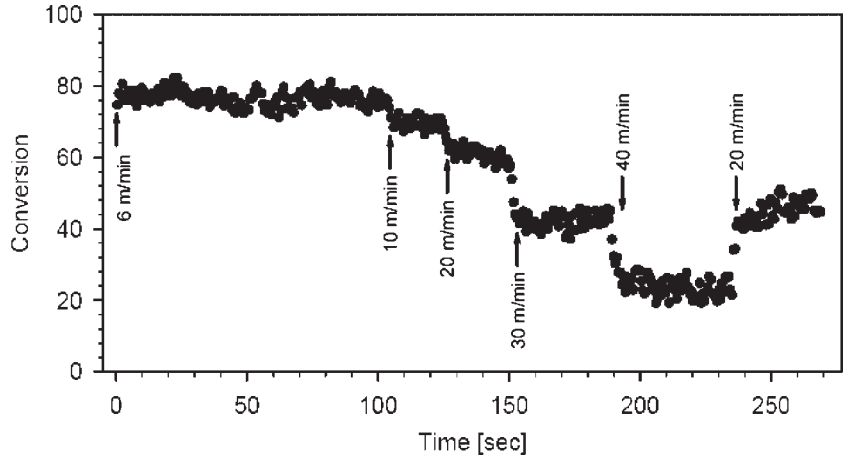

Figure 10.
In-line monitoring of the conversion in a photoinitiator-free acrylate coating (coating weight 4 g/m^2) on 20 μm PP foil after irradiation at 222 nm (175 mW/cm^2) using NIR reflection spectroscopy.

spectroscopy is able to supply quantitative data with a time resolution of about 2 spectra per second even from the much thinner coatings studied here. 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 to 25 % at 40 m/min. These results are in close correlation with the off-line experiments and thus confirm 30 m/min as the maximum speed which can be achieved up to now.

Conclusions

In this paper it was shown that very thin layers of acrylates can be cured without photoinitiator by irradiation with short-wavelength UV radiation. The maximum thickness of the layer which can be cured strongly depends on the wavelength of irradiation and the molar extinction coefficient of the specific acrylate and is in the range of a few micrometers at most. Multifunctional aliphatic acrylate oligomers as well as typical monomers were found to be most suitable. Due to the low concentration of radicals formed in this way, polymerization must be performed under inert conditions to avoid complete inhibition. This applies to irradiation in the VUV region as the absorption of the light by atmospheric oxygen additionally leads to attenuation of the irradiance. Moreover, it was shown that the photoinitiator-free photopolymerization of acrylates can be carried out in pilot scale on a roll coating machine. Under the conditions in this study, a maximum line speed of 30 m/min was attained.

First investigations were also carried out in order to establish at least a tentative mechanism of the initiation of the polymerization reaction. Laser photolysis experiments were performed to characterise short-lived transients.[17] Stable products formed after steady-state photolysis were analyzed by GC-MS.[18] The results indicate that α-cleavage seems to be the main reaction channel. Complementary quantum chemical modelling suggests that this reaction proceeds from an excited singlet or triplet state but not from a relaxed triplet state for energetic reasons. However, further investigations will be necessary for a deeper understanding of the photochemistry of acrylates upon irradiation with short-wavelength UV radiation.

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[1] T. Y. Lee, T. M. Roper, E. S. Jönsson, I. Kudyakov, K. Viswanathan, C. Nason, C. A. Guymon, C. E. Hoyle, *Polymer* **2003**, *44*, 2859.
[2] N. B. Cramer, J. P. Scott, C. N. Bowman, *Macromolecules* **2002**, *35*, 5361.
[3] C. E. Hoyle, M. Cole, M. Bachemin, W. Kuang, V. Kalyanaraman, S. Jönsson, in: *Photoinitiated Polymerization*, K. D. Belfield, J. V. Crivello, Eds., ACS Symp. Ser., Vol. *847*, Am. Chem. Soc., Washington **2003**, p. 52.
[4] C. E. Hoyle, S. Jönsson, M. Shimose, J. Owens, P. E. Sundell, in: *Photopolymerization*, A. B. Scranton, C. N. Bowman, R. W. Pfeiffer, Eds., ACS Symp. Ser., Vol. *673*, Am. Chem. Soc., Washington **1997**, p. 133.
[5] F. Morel, C. Decker, S. Jönsson, S. C. Clark, C. E. Hoyle, *Polymer* **1999**, *40*, 2447.
[6] U. Kogelschatz, *Appl. Surf. Sci.* **1992**, *54*, 410.
[7] T. Scherzer, U. Decker, *Vibr. Spectrosc.* **1999**, *19*, 385.
[8] T. Scherzer, *Macromol. Symp.* **2002**, *184*, 79.
[9] T. Scherzer, R. Mehnert, H. Lucht, *Macromol. Symp.* **2004**, *205*, 151.
[10] L. G. Weyer, *Appl. Spectrosc. Rev.* **1985**, *21*, 1.
[11] T. Scherzer, S. Müller, R. Mehnert, A. Volland, H. Lucht, *Polymer*, in press.
[12] T. Scherzer, U. Decker, *Nucl. Instr. Meth. B* **1999**, *151*, 306.
[13] T. Scherzer, *Appl. Spectrosc.* **2002**, *56*, 1403.
[14] D. L. Kurdikar, N. A. Peppas, *Polymer* **1994**, *35*, 1004.
[15] K. Watanabe, E. C. Y. Inn, M. Zelikoff, *J. Chem. Phys.* **1952**, *20*, 1969.
[16] K. Watanabe, E. C. Y. Inn, M. Zelikoff, *J. Chem. Phys.* **1953**, *21*, 1026.
[17] W. Knolle, T. Scherzer, S. Naumov, R. Mehnert, *Rad. Phys. Chem.* **2003**, *67*, 341.
[18] W. Knolle, S. Naumov, M. Madani, C. von Sonntag, *Nucl. Instr. Meth. B* **2005**, *236*, 195.

