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# Self-Initiation of the UV Photopolymerization of Brominated Acrylates

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**ABSTRACT:** Brominated aromatic acrylates were found to polymerize rapidly upon exposure to UV light. Moreover, they are able to initiate the UV-induced polymerization of acrylic formulations that do not contain a conventional photoinitiator. In contrast, the corresponding unbrominated homologues are not effective as initiators. Investigations by real-time FTIR spectroscopy have shown that the addition of only 1 wt % of a brominated acrylate is sufficient for an efficient initiation. Fast photopolymerization is achieved even if irradiation is carried out at  $\lambda > 300$  nm where most acrylates do not absorb. Short-lived transients were studied by laser flash photolysis. The triplet was found to show low sensitivity to oxygen which is because of its very short lifetime. Bromine radicals split off from the acrylates were trapped with bromine ions from tetraethyl ammonium bromide and detected as  $\text{Br}_2^{\cdot-}$ . The resulting quantum yields for the formation of bromine radicals are in the range of up to 0.3. Quantum chemical modeling was carried out to establish a mechanism for the release of bromine radicals. Both bromine and bromophenyl radicals are able to initiate the polymerization reaction. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 4905–4916, 2008

**Keywords:** laser flash photolysis; photopolymerization; quantum chemistry; radical polymerization; real-time FTIR spectroscopy

## INTRODUCTION

The initiation of the UV-induced polymerization of functionalized monomers and oligomers is usually carried out by adding specific photoinitiator compounds, which absorb the incident light and generate the initiating species by cleavage, hydrogen abstraction, electron transfer, etc. Photoinitiators for radical photopolymerization reactions are mostly alkylaryl ketones (cleavable; Norrish type I initiators) or aromatic ketones which are used in combination with an additional coinitiator (Norrish type II systems).

The nature of the photoinitiator and its concentration in the formulation determine the kinetics of the photopolymerization reaction as well as the penetration depth of the UV light into the reactive mixture. In particular, the absorption spectrum has to match to the spectrum of the UV light used for irradiation to achieve an efficient excitation of the initiator. In the past, numerous photoinitiators have been developed which meet the requirements of a wide variety of UV curing applications.<sup>1</sup>

However, the use of photoinitiators results in several disadvantages. Photoinitiators generally degrade during long-term exposure to sunlight, producing a yellowing effect in polymer clear coats. Another drawback is that the depth of cure is limited by the attenuation of UV light by the photoinitiator. Photoinitiator molecules and

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their fragments may migrate within or out of the coating. Moreover, photoinitiators can be toxic and expensive.

Therefore, a growing interest is directed toward photopolymerization reactions, which do not require conventional photoinitiators. A number of different approaches have been reported in the literature including both single and binary systems. Thiol-ene systems follow a successive propagation/chain transfer mechanism resulting in a step-growth radical polymerization.<sup>2,3</sup> Upon UV irradiation, thiyl radicals are formed by the cleavage of the thiol which readily initiate a polymerization. *N*-substituted maleimides and vinyl ethers form donor-acceptor systems which undergo a radical copolymerization upon exposure to UV radiation.<sup>4-6</sup> The light is absorbed by the maleimide. Initiating radicals are formed by electron transfer of the excited maleimide followed by hydrogen abstraction from either one of the two monomers.

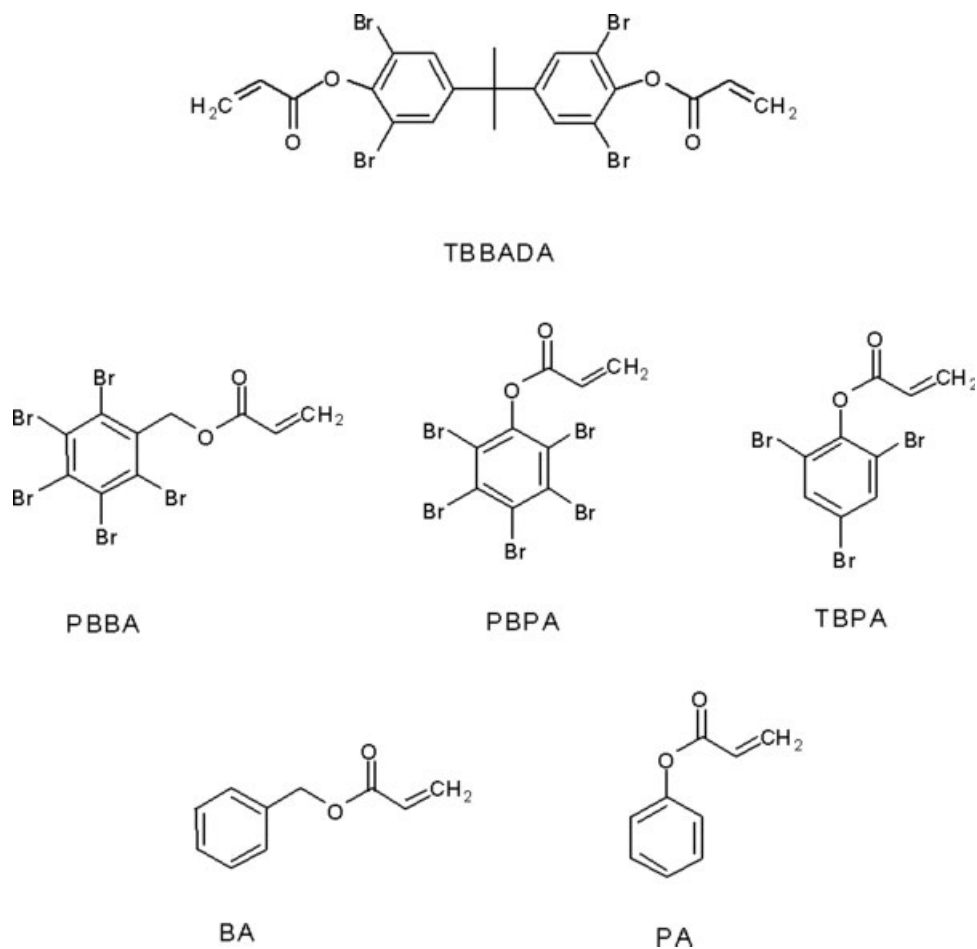
Acrylates and methacrylates can be photopolymerized without traditional photoinitiator as well. Recently, it was shown that thin layers of such monomers can be cured by irradiation with UV light in the UV-C or even VUV range.<sup>7,8</sup> The short-wavelength light leads to a direct excitation of the acrylate, and it was suggested that  $\alpha$ -cleavage from an excited singlet or triplet state is the photolytic start reaction leading to photopolymerization.<sup>9</sup> Because of the rather high extinction coefficients at wavelengths below  $\sim 230$  nm, the polymerization reaction is limited to layers with low thickness.

An alternative approach is the use of specific self-initiating monomers such as vinyl acrylate.<sup>10,11</sup> Upon irradiation with the light of a medium pressure mercury lamp, the acrylate group in this monomer is consumed rapidly by direct photolysis of the molecule while the reaction rate of the vinyl ester is much slower. Kinetic investigations in combination with modeling calculations have shown that the close proximity of acrylate and vinyl group in the same molecule is essential for an efficient initiation of the polymerization. Initiation most probably proceeds via a biradical resulting from internal cyclization in the triplet state of the vinyl acrylate. Additionally, direct cleavage of the molecule could take place. Possibly, both processes may occur simultaneously. Vinyl acrylate is not only able to initiate its own free radical photopolymerization, but it was also found to be an efficient photoinitiator for the polymerization of other acrylates.

Photochemically induced homolysis reactions of carbon-halogen bonds are known for a long time. They are extensively used in synthesis. Most of this work has been summarized in several review articles.<sup>12-14</sup> In particular, it is well established that upon photolysis many aryl halides undergo homolysis to generate aryl and halogen radicals. Thermodynamic considerations indicate which aryl halides can be expected to undergo the simple homolysis reaction and help to establish an order of reactivity for the various carbon-halogen bonds. They show that the bond strength in bromo- and iodobenzenes is substantially lower than the corresponding aryl-chlorine bond strength. Consequently, bromine and iodine radicals are much more easily released by photoinduced decomposition. So, if bromine or iodine would be used as substituents in suitable monomers such as functionalized derivatives of the corresponding halobenzenes, self-initiation of the UV photopolymerization of these monomers should become possible.

Brominated monomers and polymers are of particular interest because they are widely used as flame retardants in polymeric materials<sup>15-22</sup> and as high refractive index materials.<sup>23,24</sup> The efficiency of bromine and other halogen-containing organic compounds to reduce the flammability of polymers is based on the release of halogen radicals which combine with reactive hydrocarbon radical species produced by the burning polymer which inhibits the combustion.<sup>17</sup> Brominated monomers are superior to other additives since they may be copolymerized. This significantly reduces the adverse effect on the mechanical properties of the material and avoids exudation of the additive from the polymer. Pentabromobenzyl acrylate (PBBA) and pentabromophenyl acrylate (PBPA) as well as acrylated tetrabromobisphenol have been used for this purpose in several studies.<sup>17-22</sup> Because of their high bromine content, they are excellent flame retardants. Moreover, they can be copolymerized by radical polymerization of the acrylic group. The polymerization may be initiated either thermally (e.g., during reactive extrusion<sup>18-21</sup>) or by UV photopolymerization.<sup>17</sup> The UV curing of various brominated acrylic monomers<sup>15-17</sup> was generally initiated by use of a photoinitiator.

In this study, we deal with the question whether the UV photopolymerization of brominated acrylic monomers such as PBBA and PBPA can be actually started by self-initiation, that is, without an additional photoinitiator, and



**Scheme 1.** Molecular structures of the acrylates.

whether this effect could also be used for conventional acrylic formulations which contain only small amounts of a brominated acrylate. These phenomena were studied in detail by real-time FTIR (RTIR) spectroscopy and laser flash photolysis investigations. Supplementary quantum chemical calculations were carried out to assist the interpretation of the experimental data.

## EXPERIMENTAL

### Materials

Pentabromophenyl acrylate (PBPA), 2,4,6-tri-bromophenyl acrylate (TBPA), and 2,2',6,6'-tetra-bromobisphenol A diacrylate (TBBADA) were purchased from ABCR (Karlsruhe, Germany). Pentabromobenzyl acrylate (PBBA) was provided by the Dead Sea Bromine Group (Beer Sheva, Israel). The unbrominated homologues of

PBBA and PBPA were supplied by ABCR (benzyl acrylate; BA) and Alfa Aesar (phenyl acrylate; PA), respectively. The structures of all acrylates are shown in Scheme 1.

To study their ability and efficiency to initiate the photopolymerization of other acrylates, they were added to tripropylene glycol diacrylate (TPGDA; Cytec) used as model system. For comparison, benzildimethyl ketal (BDMK; Irgacure 651, Ciba Specialty Chemicals) was used as a conventional photoinitiator.

### Characterization of the Brominated Acrylates

UV spectra were recorded in acetonitrile ( $[Acr] = 5 \times 10^{-3} \text{ mol L}^{-1}$ ) with a Shimadzu 2101 UV-vis spectrometer. Thermal characterization was carried out with a Perkin-Elmer DSC 7 system. Melting points and the onset of thermal polymerization were determined with 6 mg sample at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

### Real-Time FTIR-ATR Spectroscopy

Investigations on the kinetics of the photopolymerization reactions were carried out by real-time FTIR-ATR (RTIR) spectroscopy using a Digilab FTS 6000 spectrometer and a heatable Golden Gate diamond ATR accessory. The time resolution was set to 120 ms. Acrylate layers on the crystal were prepared by covering a drop of acrylate by a quartz plate with a gap of 4.5  $\mu\text{m}$  in its lower side. Irradiation was carried out with an Osram mercury arc lamp whose irradiance in the focus on the surface of the diamond was 280  $\text{mW cm}^{-2}$ . For some investigations, a 313 nm interference filter (Andover) was used to simulate the emission of a  $\text{XeCl}^*$  lamp (irradiance 13  $\text{mW cm}^{-2}$ ). An electronic shutter (Vincent Associates) which is controlled by the spectrometer computer served for synchronization between UV irradiation and IR spectra recording. Irradiation was performed either in air or in nitrogen (at 313 nm under inert conditions only). A more comprehensive description of the method is given in ref. 25.

### Laser Flash Photolysis

The laser photolysis setup comprised a 308 nm  $\text{XeCl}^*$  excimer laser (MINex, LTB Berlin; pulse width 7 ns, pulse energy up to 4 mJ) as excitation source and a pulsed xenon short-arc lamp (XBO 1000, Osram; equipped with power supply LPS 1200 and lamp pulser MCP 2010, both m-u-t, Wedel, Germany) which supplied the analyzing light. The transient recording electronics consisted of a photomultiplier (R928, Hamamatsu; operated at 850 V, equipped with power supply PS310, Stanford Research Systems) and a 500 MHz digitizing storage oscilloscope (TDS620b, Tektronix; 2.5 GS/s), guaranteeing a time resolution within the limits set by the excitation pulse. All experiments were carried out in flow-through cuvettes with  $5 \times 3 \text{ mm}^2$  cross section. Further details have been published elsewhere.<sup>26,27</sup>

The actinometry was performed by monitoring the yield of the benzophenone triplet at 520 nm ( $\Phi_{\text{T}} = 1$ ,  $\epsilon_{\text{T}} = 6500 \pm 400 \text{ L mol}^{-1} \text{ cm}^{-1}$ )<sup>28</sup> after excitation of benzophenone/acetonitrile solutions, which were carefully adjusted to match the absorbance of the corresponding bromoacrylate solutions at 308 nm.

### Quantum Chemical Modeling

Calculations were carried out using the program packages Gaussian 03 (Revision B-02, Gaussian,

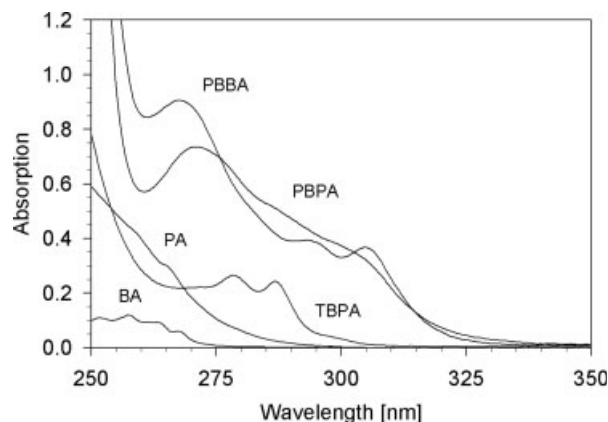
Pittsburgh) and Jaguar (version 6.5, Schrödinger LLC, New York). Geometries were optimized applying the density functional theory (DFT) approach with B3LYP hybrid functional.<sup>29–31</sup> For geometry optimizations, the standard 6-31G(d) and LACVP\* basis sets were used. The LACVP\* basis set uses the standard 6-31G\* basis set for light elements and the LAC pseudopotential<sup>32</sup> for the Br atom. Molecular geometries and energies of all calculated structures were obtained at the same level of theory. The molecular structures and reaction enthalpies were similar with both the 6-31G(d) and the LACVP\* basis sets for all ground state molecules and radicals except for Br radical adducts to the phenyl ring. The reaction enthalpies in the case of weak interaction, calculated with LACVP\* basis set, were systematically underestimated by about 3–5  $\text{kcal mol}^{-1}$  in comparison to those calculated with the 6-31G(d) basis set. This is apparently due to the effective core potential used for the Br atom by the LACVP\* basis set. Nevertheless, the use of LACVP\* basis sets for geometry optimization of large molecules is advisable to reduce the computational time (up to a factor of 20).

The electronic transition spectra of the transients were calculated in vacuum with the time-dependent (TD) DFT B3LYP/6-311G(d,p) method<sup>33</sup> with the molecular geometries being optimized at B3LYP/6-31G(d) level (or B3LYP/LACVP\* in the case of TBBADA).

## RESULTS AND DISCUSSION

### Characterization of Brominated Acrylates

The basic principle of a conventional photoinitiator or the compound which takes its function generally consists of two main steps: (i) the absorption of the incident photons resulting in an electronic excitation of the molecule, and (ii) the generation of initiating species from the excited states. To exploit the incident UV light, the absorption spectrum of the compound which acts as initiator (or, alternatively, that of a sensitizer which may be added) has to match to the emission spectrum of the UV source which is used for irradiation. The UV spectra of the two pentabrominated acrylates and their unbrominated pendants as well as that of the partially brominated TBPA are plotted in Figure 1, whereas the unbrominated acrylates only absorb



**Figure 1.** UV spectra of brominated acrylates and their unbrominated homologues.

below 300 or even 280 nm (which is mainly related to the absorption of the aromatic ring), the absorption of PBBA and PBPA extends to well above 300 nm. Hence, these monomers are able to absorb considerable parts of the emission of the standard medium pressure mercury arc lamp including the intense lines at 297, 302, and 313 nm, and also a XeCl<sup>\*</sup> excimer lamp with an emission line at 308 nm may be used for excitation. In contrast, BA and PA are limited to the short-wavelength part of the spectrum of the mercury arc lamp, and in addition, their extinctions, in particular that of BA, are much lower than those of their brominated counterparts. The UV spectrum of the partially brominated TBPA lies in between those of the pentabrominated and unbrominated acrylates which correspond to its structure. The spectrum of TBBADA is omitted in Figure 1 for clarity. Band positions between 265 and 290 nm resemble those in the spectrum of TBPA, but the absorption in this region is significantly higher.

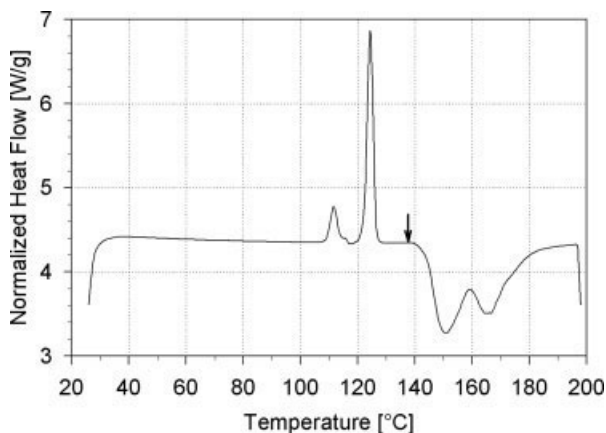
The photopolymerization behavior of the pure brominated acrylates was to be studied in the molten state. Therefore, at first their thermal properties were determined. The DSC trace of PBBA (Fig. 2) shows two endothermic peaks at about 112 and 124 °C which correspond to the melting of two polymorphic crystal modifications. The melting is almost immediately followed by a thermal polymerization process which sets in at about 140 °C. For PBPA also, two melt peaks at 122 and 132 °C were observed whereas polymerization was found to set in beyond 180 °C. TBPA melts at 76 °C showing a single DSC peak only, and a weak polymerization peak appears around 190 °C. TBBADA

shows a single melt peak as well (at 112 °C) and starts to polymerize thermally at about 175 °C.

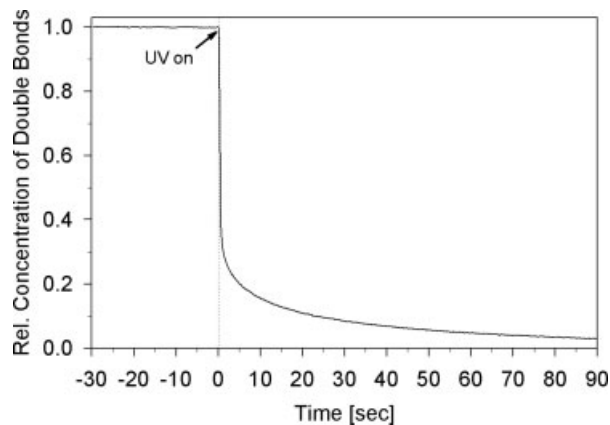
### Photopolymerization with Brominated Acrylates Studied by RTIR Spectroscopy

It is obvious from the results of the thermal analysis, that for PBBA there is only a very small temperature window for studies on the self-initiation of the UV-induced polymerization in the molten state. Accordingly, investigations on pure PBBA were carried out at 138 °C. After melting of the powder on the ATR crystal, the melt was covered with the preheated quartz plate to set the thickness of the layer for UV irradiation. To check the thermal stability of the melt, FTIR spectra were recorded for 2 min before UV irradiation starts. It can be clearly seen from Figure 3 that no thermal polymerization occurs at this temperature. However, when the shutter is opened a fast polymerization reaction occurs. Within only 1 s, a conversion of about 70% is achieved. Finally, the reaction almost approaches completion. This indicates that the UV irradiation activates an efficient self-initiation of the polymerization reaction of PBBA. Similar results were also obtained with the other bromine-containing monomers.

Brominated acrylates are generally used as functional additives in formulations with other acrylates. Therefore, PBBA and PBPA were added in small amounts to TPGDA to study their efficiency as photoinitiator systematically. Both acrylates were dissolved in TPGDA at concentrations of 1 or 5 wt %, respectively. Analogous mixtures were also prepared with BA and PA. In addition, pure TPGDA as well as a



**Figure 2.** DSC trace of PBBA.

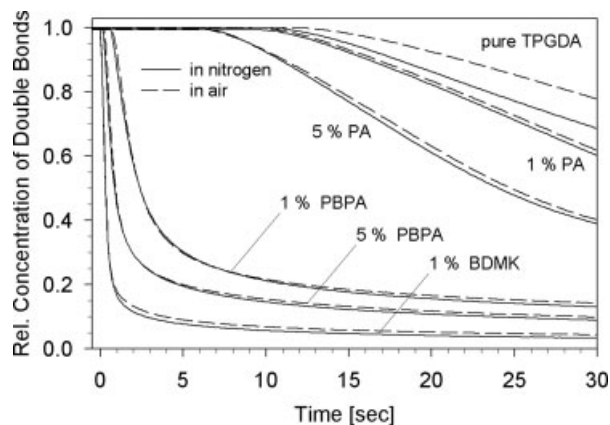


**Figure 3.** UV photo-homopolymerization of PBBA in the melt at 138 °C.

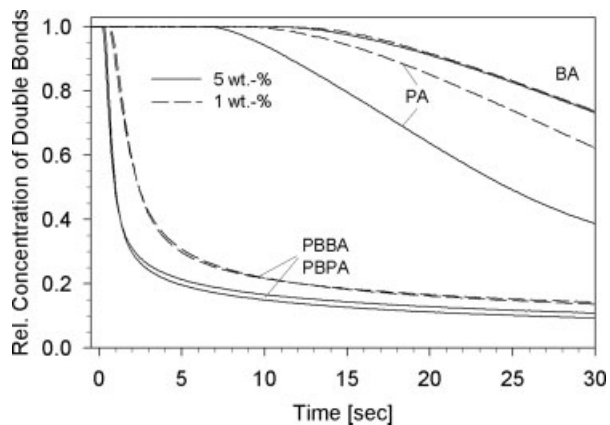
mixture with 1 wt % BDMK as a conventional photoinitiator were selected for comparison.

Figure 4 shows the polymerization profiles of the mixtures with PBPA and PA as well as those of the two reference systems. The results clearly demonstrate that PBPA is a highly efficient photoinitiator for the polymerization of other acrylates although BDMK leads to an even faster reaction as could be expected. In contrast, PA with its poor absorption even below 290 nm is far from being an efficient initiator for the photopolymerization of TPGDA. In fact, the mixtures with PA only react a little faster than pure TPGDA. These results strongly indicate that the ability of PBPA to self-initiation is related to its bromination.

Inertization does not have a significant effect on the kinetics of the photopolymerization



**Figure 4.** Kinetics of the photopolymerization of TPGDA with PBPA or PA in air or nitrogen, respectively. Curves of pure TPGDA and TPGDA with BDMK are given for comparison.

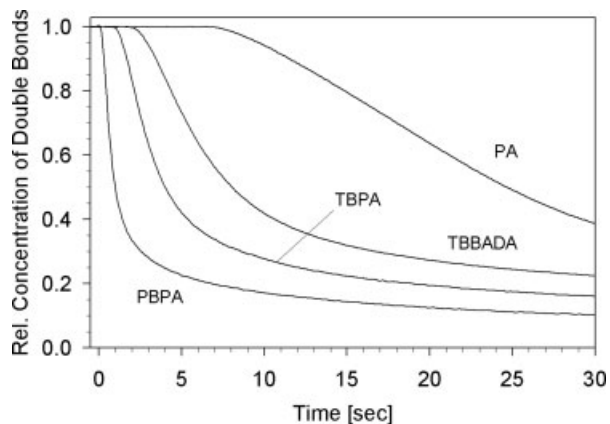


**Figure 5.** Kinetics of the photopolymerization of TPGDA with PBBA, PBPA and their unbrominated pendants.

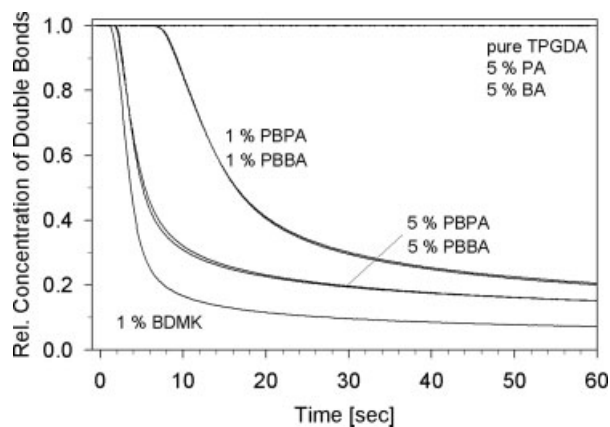
whereas a marked effect of oxygen is usually observed for most other radical photopolymerization reactions.

Figure 5 compares the kinetic behavior of the mixtures with PBPA and PA with those containing PBBA or BA. The two brominated acrylates show identical initiation efficiencies for the polymerization of TPGDA which is related to their quite similar UV spectra. With an addition of only 1 wt %, a fast reaction leading to high conversion is achieved. In contrast, the polymerization reaction with BA is slower than the one with PA which is attributed to its lower absorption.

The kinetic curves of the photopolymerization of the mixture containing the acrylated tetrabromobisphenol as well as those of the three closely related systems with PA, TBPA and PBPA are plotted in Figure 6. It is obvious that both the polymerization rate and conversion in the latter



**Figure 6.** Kinetics of the photopolymerization of TPGDA with 5 wt % TBBADA, PBPA, TBPA, or PA.



**Figure 7.** Kinetics of the photopolymerization of TPGDA with PBBA, PBPA and their unbrominated pendants upon irradiation at 313 nm. Curves of pure TPGDA and TPGDA with BDMK are given for comparison.

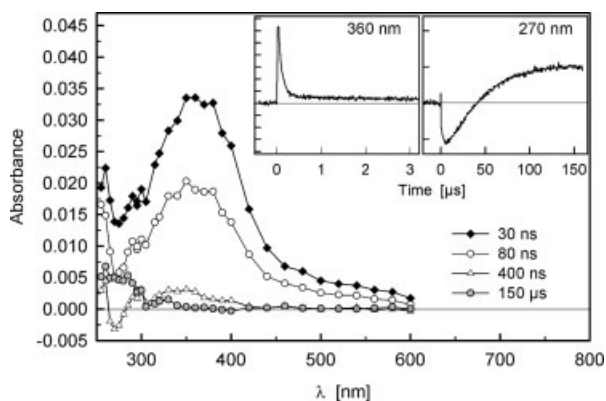
series strongly increase with increasing degree of bromination which once again emphasizes the close relation between bromination and the self-initiation of the polymerization reaction. Even TBBADA with its higher molecular weight was found to be a rather efficient initiator for photopolymerization.

Unbrominated aliphatic acrylates absorb UV radiation with a wavelength shorter than about 280 nm. Below 250 nm, the absorption of all acrylates strongly increases. On the other hand, the emission of standard medium pressure mercury lamps extends to below 250 nm although it is of low intensity. That means that light from the short-wavelength edge may lead to a direct excitation of acrylate molecules and possibly to the initiation of a polymerization reaction.<sup>7</sup> Figure 4 has shown that this way of initiation actually proceeds in the mixtures with BA and PA but also in pure TPGDA. To avoid this excitation path, additional investigations were carried out with monochromatic light with a wavelength of 313 nm. This intense line of the mercury lamp can be easily coupled out by use of an interference filter. Moreover, it is very close to the emission of the XeCl<sup>\*</sup> excimer lamp. Kinetic curves recorded upon irradiation at 313 nm are shown in Figure 7. As expected, no further reaction is observed in pure TPGDA and in the formulations with PA or BA which all do not absorb at this wavelength ( $\epsilon \leq 3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). In contrast, PBBA and PBPA are still efficient photoinitiators for the polymerization of TPGDA which are only excelled by BDMK. Both PBBA

and PBPA distinctly absorb at 313 nm, and their molar extinction coefficients are  $330 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $310 \text{ L mol}^{-1} \text{ cm}^{-1}$ , respectively. These results clearly prove that the efficiency of brominated acrylates to initiate a polymerization reaction is not due to direct excitation of the acrylate group by short-wavelength radiation from the mercury lamp but it is in fact related to the release of bromine species.

### Studies on the Mechanism of Initiation by Laser Flash Photolysis

Laser flash photolysis experiments have been carried out to study the reaction pathways following excitation at 308 nm and to determine the quantum yield of radical formation. In  $\text{N}_2$ -purged PBBA/acetonitrile solutions, a short-lived transient with a band around 360 nm and a shoulder extending to 600 nm is observed immediately after the laser flash (Fig. 8, spectrum  $\blacklozenge$  at 30 ns). Although the spectrum seems to be very similar to the spectrum of  $\text{Br}_2^-$ , especially in the 360 nm region,<sup>34</sup> it cannot be assigned to this species because of a much shorter decay time and the lack of the second characteristic band at 700 nm (see below). The transient decays with a time constant of  $1.2 \times 10^7 \text{ s}^{-1}$  independent of the solute concentration ( $3\text{--}15 \times 10^{-4} \text{ mol L}^{-1}$ ), which indicates that self-quenching is negligible in this concentration range. This short-lived transient is assigned to the PBBA triplet state. As expected for a triplet state, the transient decays faster in the presence



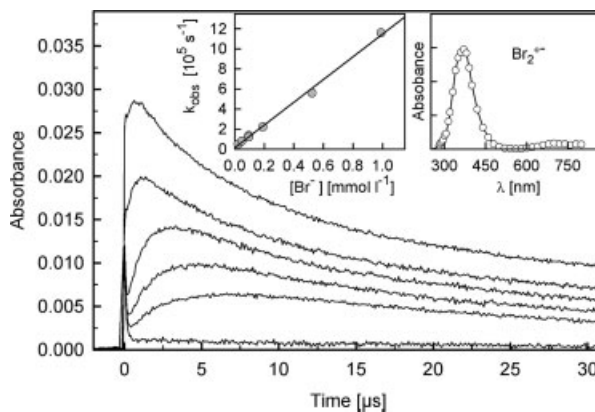
**Figure 8.** Transient optical absorption spectra observed after 308 nm laser flash photolysis of a  $\text{N}_2$ -saturated  $7.5 \times 10^{-4} \text{ mol L}^{-1}$  PBBA/acetonitrile solution (periods after the laser flash as indicated). Insets: time profiles of the absorbance at the given wavelengths.



of oxygen ( $k_q \approx 2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ). Right after the decay of the primary transient only a weak absorbance is observed (Fig. 8, spectrum  $\Delta$  at 400 ns). If fast homolysis of one of the bromine-carbon bonds takes place, this spectrum is expected to correspond to a tetrabromophenyl radical, as the released bromine atom does not show an absorption in the accessible wavelength range. Indeed, TD-DFT calculations of the UV spectra of the phenyl-type radicals of BA, TBPA, and PBBA indicate a significant shift of the main spectral transitions from  $\sim 260 \text{ nm}$  (BA) to  $\sim 300 \text{ nm}$  (TBPA) and  $374 \text{ nm}$  (PBBA). The value calculated for BA agrees fairly well with the known experimental spectrum of the phenyl radical,<sup>35</sup> and thus the values for TBPA and PBBA can be taken as reasonable, at least in a qualitative manner. For the energetically most stable radical in the *para* position of PBBA, transitions are calculated at 331, 374, and 417 nm (oscillator strengths of 0.0010, 0.0031, and 0.0041, respectively), which supports the assignment to the tetrabromophenyl radical. At much longer time-scales, a new band centered around 260–270 nm is formed, which is tentatively assigned to molecular  $\text{Br}_2$  (see Fig. 8, right inset; the bleaching observed just after the pulse is due to the consumption of the PBBA ground state molecules).

The release of bromine atoms can easily be monitored by the addition of bromide to the solution, leading to the fast formation of  $\text{Br}_2^{\cdot-}$  ( $k_{(\text{Br}^\cdot + \text{Br}^-)} = 1.6 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ ).<sup>34</sup> Laser excitation of solutions containing  $(\text{C}_2\text{H}_5)_4\text{NBr}$  leads to strong absorption at 360 nm (and a further weak band at  $\sim 700 \text{ nm}$ ), which is readily characterized as due to  $\text{Br}_2^{\cdot-}$  ( $\epsilon_{360} = 9000 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The spectrum of this intermediate is shown in the right inset of Figure 9. A plot of the observed time constant for the formation of  $\text{Br}_2^{\cdot-}$  against the bromide concentration (Fig. 9, left inset) yields a straight line, and a rate constant of  $1.13 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$  for the reaction of bromide with the bromine atom can be derived, which is quite comparable to the value given above.

Under conditions where quantitative trapping of bromine atoms occurs, the yield of  $\text{Br}_2^{\cdot-}$  should be identical to the photochemical yield of bromine atoms. Using the triplet state of benzophenone as actinometer,<sup>28</sup> a quantum yield of 0.31 was determined for the formation of bromine atoms from PBBA. An error of  $\sim 25\%$  has to be taken into account reflecting some system-



**Figure 9.** Time profiles of the absorbance at 360 nm observed after 308 nm laser flash photolysis of  $\text{N}_2$ -saturated  $3.8 \times 10^{-4} \text{ mol L}^{-1}$  PBBA/acetonitrile solutions containing  $(\text{C}_2\text{H}_5)_4\text{NBr}$  as scavenger for Br atoms. Concentration of  $\text{Br}^-$  [ $10^{-5} \text{ mol L}^{-1}$ ]: 0, 2.4, 4.7, 9.5, 19, and 52. Left inset: Plot of  $k_{\text{obs}}$  versus  $\text{Br}^-$ . Right inset: spectrum of  $\text{Br}_2^{\cdot-}$ .

atic influences which may have been introduced due to the errors in the extinction coefficients of  $\text{Br}_2^{\cdot-}$  and the benzophenone triplet state. At  $\text{Br}^-$  concentrations higher than  $5 \text{ mmol L}^{-1}$ , the observed rate constant  $k_{\text{obs}}$  for the formation of the  $\text{Br}_2^{\cdot-}$  levels off to a value comparable to that of the decay of the primary transient ( $\sim 10^7 \text{ s}^{-1}$ ). This points to the fact that the rate determining step at high concentrations is the decay of the precursor, that is, the homolytic scission of the short-lived triplet state.

In the case of PBPA, very similar results were obtained for both transient spectra and kinetic data, which shows that the additional methylene group in PBBA does not influence the photochemistry of the compound. A quantum yield of 0.34 was determined, which compares well with the value of 0.31 for PBBA within the experimental error.

Laser flash photolysis experiments were also performed on TBPA. Because of the much lower absorption coefficient at 308 nm ( $15 \text{ L mol}^{-1} \text{ cm}^{-1}$  in comparison to 650 and  $520 \text{ L mol}^{-1} \text{ cm}^{-1}$  for PBBA and PBPA, respectively), a 20-fold higher concentration of TBPA had to be used which restricted the measurement window to  $\lambda > 295 \text{ nm}$  because of the self-absorption of the sample. After the laser flash, no short-lived transients due to any triplet state could be observed in the wavelength range above 295 nm. If the triplet energy is expected to be higher than those of PBBA and PBPA, the triplet should absorb at lower wavelength. In fact,

**Table 1.** Results of Quantum Chemical Calculations

Acrylate	$\lambda_{\text{exp}}$ [nm]	$\lambda_{\text{calc}}$ [nm]	$E_{\text{T}}$ [eV]	$E_{\text{Diss}}$ [eV]	$E_{\text{Diss}}$ [kcal mol <sup>-1</sup> ]	$\Delta H_{\text{T}}$ [kcal mol <sup>-1</sup> ]
PA	265	273 (0.0001)	3.53	–	–	–
	258	258 (0.0001)				
	<250	251 (0.0001)				
TBPA	288	288 (0.004)	3.41	2.82	65	–14
	277	261 (0.006)				
	<250					
PBPA	300	291 (0.007)	3.24	2.78	64	–11
	285	278 (0.001)				
	272	274 (0.007)				
BA	267	267 (0.003)	3.54	–	–	–
	264	259 (0.001)				
	257	253 (0.009)				
	252	253 (0.001)				
	<230	250 (0.073)				
PBBA	305	307 (0.006)	3.24	2.52	58	–18
	293	285 (0.004)				
	270	278 (0.002)				
	~250	256 (0.003)				
TBBADA	305	284 (0.004)	3.40	2.69	62	–16
	283	270 (0.001)				
	260	260 (0.006)				
		258 (0.001)				
	<230	257 (0.002)				

Measured ( $\lambda_{\text{exp}}$ ) and calculated ( $\lambda_{\text{calc}}$ ) wavelengths of absorption bands in the UV spectra, triplet energies ( $E_{\text{T}}$ ) of the unrelaxed triplet state, bond dissociation energies ( $E_{\text{Diss}}$ ) of the C–Br bond, and reaction enthalpies ( $\Delta H_{\text{T}}$ ) for Br<sup>•</sup> formation from the triplet state

quantum chemical calculations predict an unrelaxed triplet energy of 3.41 eV (see Table 1) which compares better to phenyl and butyl acrylate (3.53 and 3.54 eV, respectively) than to PBBA and PBPA (both 3.24 eV).

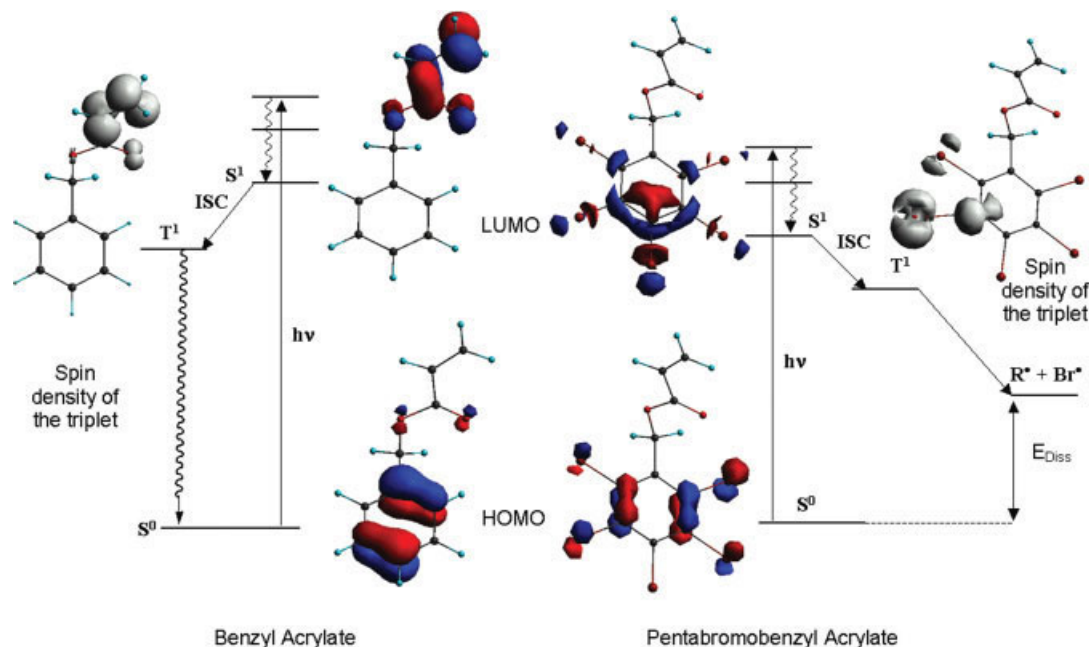
However, the addition of bromide ((C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr) to the solution also leads to the formation of the characteristic Br<sub>2</sub><sup>•-</sup> spectrum, which shows that homolytic cleavage of a phenyl-bromine bond takes place in the case of TBPA as well. Applying the same procedure as described earlier, a quantum yield of only 0.11 is derived for Br<sup>•</sup> formation. This value is considerable lower than the values for PBBA and PBPA and may reflect the reduced number of bromine atoms on the phenyl ring.

### Quantum Chemical Modeling of the Initiation

To summarize the previous experimental results and to establish a probable mechanism for the self-initiation of the photopolymerization reaction of the brominated acrylates, quantum chemical calculations were carried out. At first,

the equilibrium geometries of the monomer molecules were optimized which was followed by the calculation of the electronic structures of major transients such as triplet states and neutral radicals. Finally, position and intensity of the absorption bands in the UV–vis spectra were estimated.

At first, it is worth to consider the behavior of the unbrominated acrylates, BA and PA, for comparison (see BA as example in Scheme 2). In the singlet ground state, which has a coplanar geometry, the HOMO orbital is located at the aromatic ring. Upon excitation by UV light and subsequent intersystem crossing (ISC), the spin density of the T<sup>1</sup> state will now be localized at the carbon–carbon double bond. The electrons in the LUMO orbitals have antibonding character, which leads to a weakening of the former double bond followed by a rotation of the CH<sub>2</sub> group by 90° during energetical optimization of the molecular geometry in the triplet state. Nearly identical results were obtained recently for the excitation of simple aliphatic acrylates,<sup>9</sup> and hence one may conclude that unbrominated aromatic acrylates behave similarly despite their better



**Scheme 2.** Excitation scheme of benzyl acrylate and PBBA compiled from quantum chemical calculations.

excitation probability at  $\lambda \sim 250$  nm because of their aromatic ring.

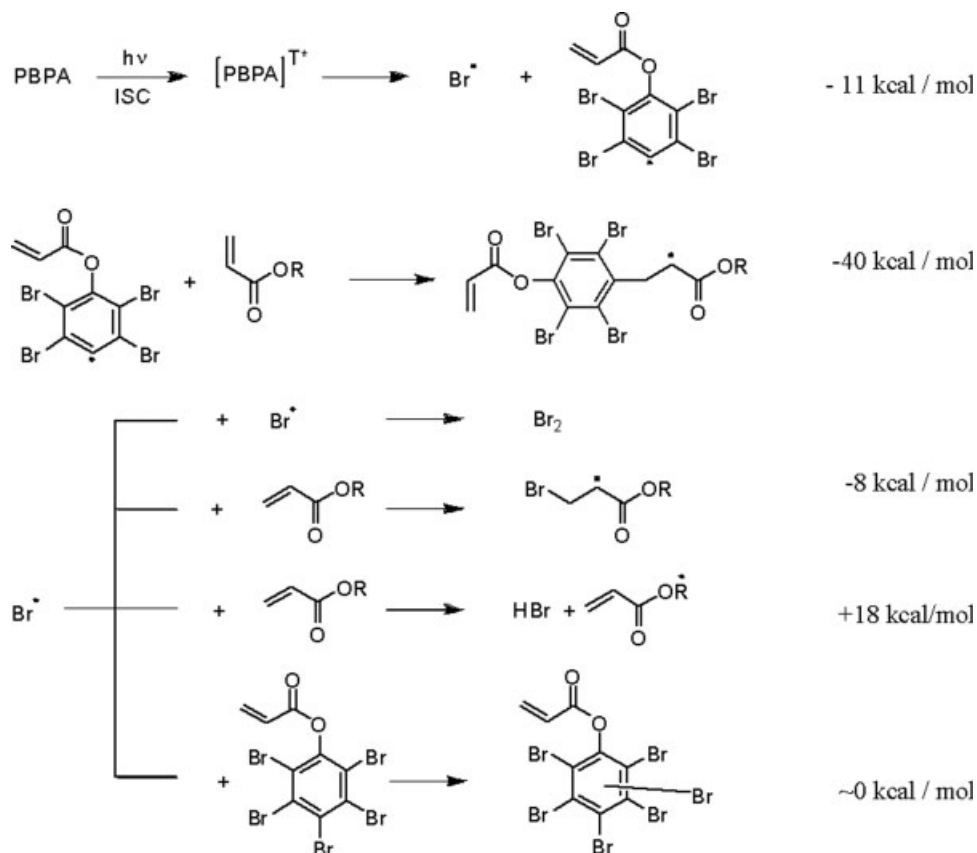
In the brominated acrylates, the acrylate group stands nearly perpendicular to the aromatic ring, which is probably a steric effect because of the bulky bromine substituents at the ring. This leads to an electronic coupling between both groups resulting in lower energy levels in comparison to coplanar geometries. Table 1 summarizes experimental ( $\lambda_{\text{exp}}$ ) and calculated ( $\lambda_{\text{calc}}$ ) wavelengths of the UV spectra as measure of the excitation energy as well as triplet energies  $E_T$  of the unrelaxed triplet state (i.e., triplet energy calculated at singlet geometry; the calculation of  $E_T$  in the relaxed state fails due to immediate release of a bromine atom) of all systems under study. Basically, the triplet energies of pentabrominated acrylates were found to be significantly lower than those of unbrominated systems, with TBPA being in between (see earlier).

Comparing singlet ground states of unbrominated and brominated acrylates, the HOMO orbitals are localized in both cases at the benzene ring. After excitation and ISC, some rearrangement of the electron distribution occurs in PBBA (see Scheme 2), 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 one of

the bromine atoms substantially increase from 1.89 to 2.72 nm which finally leads to the release of a bromine radical. Bond dissociation energies ( $E_{\text{Diss}}$ ) of the aryl-bromine bond and the resulting reaction enthalpies  $\Delta H_T$  for the cleavage from the (unrelaxed) triplet state were calculated (see Table 1). The bond dissociation energies of the brominated acrylates were found to be slightly lower than that reported by Davidson et al.,<sup>13</sup> who quotes a typical value of 79.2 kcal mol<sup>-1</sup> for the general structure Ph-Br. Nevertheless, it is obvious that for all brominated acrylates the bond dissociation energy is less than the energy of the respective triplet state rendering the bond homolysis possible.

The calculation of the spin density distributions for the triplet states indicate that in PBBA splitting should preferentially occur in the *meta* position whereas in PBPA and TBPA *para* and *ortho* position, respectively, are the most probable sites for bond cleavage. However, all bromine atoms at the aromatic ring are rather loosely bound, and the energetical difference for the release of a bromine radical from one of the various positions is only 2–3 kcal mol<sup>-1</sup>; thus, it is debatable whether this small energy difference plays a significant role in determining the site of bromine release.

Both the bromine radical and the tetrabromophenyl radical—or the respective radical in the



**Scheme 3.** Possible reaction pathways of the radicals and calculated reaction enthalpies.

other acrylates—may afterwards initiate the polymerization reaction. Calculations of the reaction enthalpies for the addition of both radicals to another ground state molecule yielded values of  $-8.2$  and  $-39.4 \text{ kcal mol}^{-1}$  (B3LYP/LACVPd\*), respectively, indicating that the bromobenzyl radical should be more efficient in initiation. On the other hand, bromine atoms are known to be nonreactive toward oxygen, thus oxygen inhibition of the polymerization reaction is expected to be reduced, which was observed indeed.

Considering other possible reaction pathways (see Scheme 3) of the bromine atom (besides addition and self-termination to  $\text{Br}_2$ ), complexation to the aromatic ring and hydrogen abstraction (in particular, when bromoacrylates are used to initiate the polymerization of simple aliphatic acrylates) have to be taken into account. Complexation of Br was found to occur with mono- and disubstituted aromatics, especially in benzene solution,<sup>36,37</sup> with dimethylsulfoxid in cyclohexane solution,<sup>38</sup> and even with the parent compounds in neat bromoalkanes, if other complexing agents are absent.<sup>38</sup> However, it was

not observed experimentally in the present case since no intense absorption band in the visible region ( $\sim 540\text{--}560 \text{ nm}$ ) due to the formation of a bromine complex<sup>36,39</sup> could be found. Quantum chemical calculations predicted a small reaction enthalpy only ( $\sim 0$  or  $-5 \text{ kcal mol}^{-1}$  by B3LYP/LACVPd\* or B3LYP/6-31G(d), respectively). They show, that a complex is less likely due to an electrostatic repulsion between the bulky bromine atoms, which is not the case with a less substituted aromatic system. On the other hand, H abstraction can only be expected to play a role if easily accessible H atoms are available,<sup>40</sup> for example, from an aliphatic side chain. Using butyl acrylate as a model H donor, the formation of HBr was calculated to be highly endothermic ( $+18 \text{ kcal mol}^{-1}$ ) and can therefore be excluded as well.

## CONCLUSIONS

Brominated acrylate oligomers were found to be able to self-initiate free radical photopolymerization

reactions upon exposure to UV radiation. An addition of only 1 wt % is sufficient to trigger the polymerization of unbrominated acrylates. The high efficiency of brominated acrylates is due to an appropriate extinction extending to well above 300 nm and the fast cleavage of a bromine-phenyl bond which occurs with a rather high quantum yield of up to  $\sim 0.3$ . The fast unimolecular reaction of the triplet state considerably reduces the possibility of physical quenching of the triplet state by oxygen. Additionally, the bromine atom released does not react with residual oxygen and can still initiate the polymerization. Both findings explain the reduced oxygen sensitivity, which is observed if brominated acrylates are used as photoinitiators for conventional acrylic formulations

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## REFERENCES AND NOTES

1. Crivello, J. V.; Dietliker, K. *Photoinitiators for Free Radical, Cationic & Anionic Photopolymerization*, 2nd ed.; Wiley-SITA: London, 1998.
2. Cramer, N. B.; Scott, J. P.; Bowman, C. N. *Macromolecules* 2002, 35, 5361–5365.
3. Hoyle, C. E.; Cole, M.; Bachemin, M.; Kuang, W.; Kalyanaraman, V.; Jönsson, S. In *Photoinitiated Polymerization*; Belfield, K. D., Crivello, J. V., Eds.; American Chemical Society: Washington, 2003; p 52. ACS Symposium Series 847.
4. Hoyle, C. E.; Jönsson, S.; Shimose, M.; Owens, J.; Sundell, P. E. In *Photopolymerization*; Scranton, A. B., Bowman, C. N., Pfeiffer, R. W., Eds.; American Chemical Society: Washington, 1997; p 133. ACS Symposium Series 673.
5. Morel, F.; Decker, C.; Jönsson, S.; Clark, S. C.; Hoyle, C. E. *Polymer* 1999, 40, 2447–2454.
6. von Sonntag, J.; Knolle, W. *J Photochem Photobiol A* 2000, 136, 133–139.
7. Scherzer, T. *J Polym Sci: Polym Chem* 2004, 42, 894–901.
8. Scherzer, T.; Knolle, W.; Naumov, S.; Prager, L. *Macromol Symp* 2005, 230, 173–182.
9. Knolle, W.; Naumov, S.; Madani, M.; von Sonntag, C. *Nucl Instrum Methods Phys Res B* 2005, 236, 195–200.
10. Lee, T. Y.; Roper, T. M.; Jönsson, E. S.; Kudyakov, I.; Viswanathan, K.; Nason, C.; Guymon, C. A.; Hoyle, C. E. *Polymer* 2003, 44, 2859–2865.
11. Jönsson, E. S.; Lee, T. Y.; Viswanathan, K.; Hoyle, C. E.; Roper, T. M.; Guymon, C. A.; Nason, C.; Kudyakov, I. V. *Prog Org Coat* 2005, 52, 63–72.
12. Grimshaw, J.; da Silva, A. P. *Chem Soc Rev* 1981, 10, 181–203.
13. Davidson, R. S.; Goodin, J. W.; Kemp, G. *Adv Phys Org Chem* 1984, 20, 191–233.
14. Košmrlj, B.; Šket, B. *J Org Chem* 2000, 65, 6890–6896.
15. Eren, T.; Küseföglü, S. H. *J Appl Polym Sci* 2004, 91, 2700–2710.
16. Guo, W. J. *J Polym Sci: Polym Chem* 1992, 30, 819–827.
17. Imamoglu, T.; Yagci, Y. *J Appl Polym Sci* 2002, 83, 1181–1189.
18. Gutman, E.; Utevski, L.; Scheinker, M.; Kozlovsky, A.; Michler, G. H. *J Macromol Sci Phys* 1999, B38, 1081–1093.
19. Ferry, L.; Cuesta, J. M. L.; Chivas, C.; Mac Way Hoy G.; Dvir, H. *Polym Degrad Stab* 2001, 74, 449–456.
20. Dvir, H.; Goldraich, M.; Gottlieb, M.; Daren, S.; Lopez Cuesta. *J Polym Degrad Stab* 2001, 74, 465–474.
21. Dvir, H.; Gottlieb, M.; Daren, S.; Tartakovsky, E. *Compos Sci Technol* 2003, 63, 1865–1875.
22. Janovic, Z. *Polym Degrad Stab* 1999, 64, 479–487.
23. Minns, R. A.; Gaudiana, R. A. *J Macromol Sci: Pure Appl Chem* 1992, 29, 19–30.
24. Davis, T. P.; Gallagher, M. J.; Ranasinghe, M. G.; Zammit M. D. *J Mater Chem* 1994, 4, 1359–1363.
25. Scherzer, T.; Decker, U. *Vib Spectrosc* 1999, 19, 385–398.
26. von Sonntag, J. *J Photochem Photobiol A* 1999, 126, 1–5.
27. von Sonntag, J.; Knolle, W. *J Photochem Photobiol A* 2000, 132, 25–27.
28. Bensasson, R. V.; Gramain, J. C. *J Chem Soc Faraday Trans I* 1980, 76, 1801–1810.
29. Becke, A. D. *J Chem Phys* 1993, 98, 5648–5652.
30. Becke, A. D. *J Chem Phys* 1996, 104, 1040–1046.
31. Lee, C.; Yang, W.; Parr, R. G. *Phys Rev B* 1988, 37, 785–789.
32. Wadt, W. R.; Hay, P. J. *J Chem Phys* 1985, 82, 284–298.
33. Bauernschmitt, R.; Ahlrichs, R. *Chem Phys Lett* 1996, 256, 454–464.
34. Scaiano, J. C.; Barra, M.; Krzywinski, M.; Sinta, R.; Calabrese, G. *J Am Chem Soc* 1993, 115, 8340–8344.
35. Ikeda, N.; Nakashima, N.; Yoshihara, K. *J Am Chem Soc* 1985, 107, 3381–3382.
36. Bossy, J. M.; Buhler, R. E. *Int J Radiat Phys Chem* 1974, 6, 85–94.
37. Hall, M.; Chen, L.; Pandit, C. R.; McGimpsey, W. G. *J Photochem Photobiol A* 1997, 111, 27–33.
38. Shoute, L. C. T.; Neta, P. *J Phys Chem* 1990, 94, 2447–2453.
39. McGimpsey, W. G.; Scaiano, J. C. *Can J Chem* 1988, 66, 1474–1478.
40. Merenyi, G.; Lind, J. *J Am Chem Soc* 1994, 116, 7872–7876.