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Photoinitiated radical polymerization of vinyl ether–maleate systems

C. Decker* and D. Decker
Laboratoire de Photochimie Générale (URA-CNRS N°431), Ecole Nationale Supérieure de Chimie, Université de Haute Alsace, 3 rue Alfred Werner, 68200 Mulhouse, France
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The photoinitiated radical polymerization of difunctional vinyl ether/maleate mixtures has been studied by real-time i.r. spectroscopy, a technique which records directly conversion vs time profiles for reactions occurring within seconds. Various factors were found to affect the polymerization kinetics, such as the photoinitiator concentration, the light intensity, the presence of oxygen and the composition of the monomer mixture. Whatever the monomer feed ratio, the two monomers were shown to polymerize at exactly the same rate, which reaches its maximum value for stoichiometric composition. The observed dependence of the polymerization rate on the monomer concentration argues in favour of a mechanism involving a donor–acceptor complex, with formation of an alternate copolymer. © 1997 Elsevier Science Ltd.

(Keywords: polymerization; vinyl ether; maleate; u.v.-curing; i.r. spectroscopy)

INTRODUCTION

Photoinduced polymerization of multifunctional monomers has become a well-accepted technology because of its distinct advantages, and it is presently used under the name u.v.-curing in a growing number of industrial applications[1]. Under intense illumination, the photosensitive liquid resin can be transformed within a fraction of a second into a solid insoluble material, at ambient temperature. Such solvent-free formulations are mainly based on acrylate monomers and telechelic oligomers, which are known to undergo a rapid free radical polymerization[2]. To reduce the formulation viscosity, vinyl ether monomers have recently appeared as an environment friendly alternative to the widely used acrylate monomers which show a strong odour and may cause skin and eye irritation[3].

In a previous paper[4], we have reported a recent study on the kinetics of the radical-induced copolymerization of divinyl ether with acrylate end-capped oligomers. The photocrosslinked copolymer formed was found to contain a large amount of unreacted VE double bonds because, in contrast to acrylates, vinyl ethers do not homopolymerize in the presence of free radicals, and also because acrylate radicals were shown to be twice more reactive toward the acrylate double bonds than toward the vinyl ether double bonds[5].

Vinyl ethers (VE) may also undergo a radical copolymerization with monomers having an electron-poor double bond, like maleimides or unsaturated esters, e.g. maleates (MA) or fumarates[6–10]. Because such monomers do not homopolymerize either, an alternating copolymer is formed upon u.v. irradiation in the presence of radical-type photoinitiators. The highest cure efficiency was reached for a stoichiometric mixture of the two types of monomers, on a double bond basis[9]. The mechanism of photoinduced charge transfer copolymerization of such vinyl monomers has been recently reviewed by Li *et al.*[7]. It can involve a cross-propagation of the two monomers and/or the homopolymerization of a donor–acceptor complex. Radiation curable hybrid resins, based on multifunctional vinyl ether and maleate monomers and oligomers, have been recently developed for various applications, and found to have nearly as good performances as acrylate-based resins[11,12]. As the viscosity of VE/MA monomer mixtures is too low for most applications, u.v. curable resins usually consist of a combination of either a telechelic vinyl ether oligomer with a dimaleate monomer or a telechelic unsaturated polyester with a divinyl ether monomer.

The objective of the present work was to study the kinetics of the copolymerization of divinyl ether and dimaleate monomers, and to elucidate its basic mechanism to know whether the reaction occurs by cross-propagation or through a donor–acceptor complex. Like in our previous kinetic studies of ultrafast photopolymerization processes, real-time infrared (*RT*i.r.) spectroscopy was used to record *in situ* conversion vs time curves[13]. This technique proved particularly well suited in the present study because, in contrast to the widely used differential scanning calorimetry (d.s.c.), it allows the polymerization profile of each one of the two monomers to be recorded during the whole liquid to solid transformation process.

EXPERIMENTAL

Materials

The photocurable formulation mainly used in this study contained three components: (i) the divinyl ether of triethyleneglycol (RapiCure DVE-3 from ISP), (ii) the dimaleate of diethyleneglycol (DMA-2 from DSM) and,

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* To whom correspondence should be addressed

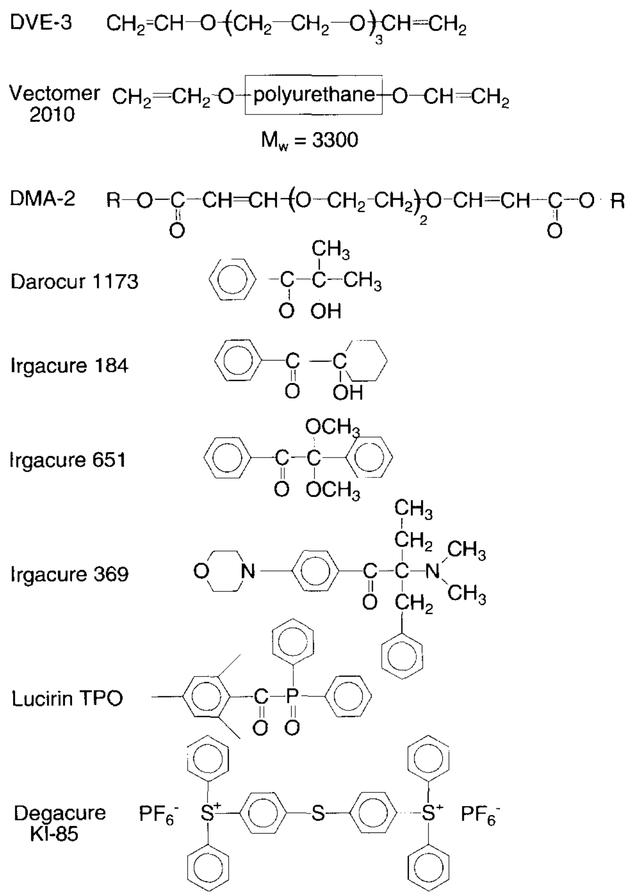


Figure 1 Chemical formulae of the compounds used in the study

(iii) a hydroxyphenylketone photoinitiator (Darocur 1173 from CIBA). A typical formulation contained 2% by weight of Darocur 1173 and a stoichiometric mixture of DVE-3 and DMA-2 (double bond ratio VE/MA = 1). The efficiency of some other radical photoinitiators was evaluated in the same type of formulation, namely Irgacure 184, Irgacure 651, Irgacure 369 (all from CIBA) and Lucirin TPO (from BASF). To achieve a more complete polymerization of the vinyl ether double bonds, a cationic photoinitiator was added to some formulations. A hexafluorophosphate triarylsulfonium salt (Degacure KI-85 from Degussa) was selected because it was previously shown to be very efficient to initiate the photopolymerization of vinyl ether based systems[5]. In some experiments, DVE-3 was partly replaced by a telechelic vinyl ether polyurethane, Vectomer 2010 from Allied Signal ($M_w = 3300$), to increase the formulation viscosity and to reduce the inhibitory effect of oxygen on such radical-induced polymerization. The chemical formulae of the various compounds used in this study are given in *Figure 1*.

Irradiation

The liquid resin was applied onto a KBr crystal or onto a polypropylene film by a calibrated wire-wound applicator. In most experiments a second polypropylene film was laminated onto the sample to prevent the diffusion of atmospheric oxygen into the sample during the u.v. exposure. The thickness of the monomer film, typically 20 μm, was determined accurately from its i.r. absorbance at 1628 cm^{-1}, by means of a calibration curve. The sample was placed in the compartment of an infrared spectrophotometer (Perkin–Elmer 780), where it was exposed for a few seconds to the u.v. radiation of a medium pressure mercury lamp (HOYA UVS-200). The light-intensity at the sample position was typically 50 mW cm^{-2}, as measured by radiometry (International Light IL-390 light bug).

A few experiments were performed on a u.v.-curing line equipped with a 80 W cm^{-1} medium pressure mercury lamp from IST. The light intensity was measured to be 500 mW cm^{-2}, at the sample position. The monomer film was polymerized, in the presence of air, by a single pass under the lamp at a speed of 30 m min^{-1}. This corresponds to an exposure time of 0.2 s and an incident fluence of 0.1 J cm^{-2}.

Analysis

The photoinitiated copolymerization of the vinyl ether and maleate mixture was studied by *RT*i.r. spectroscopy[14]. The sample was exposed simultaneously to the u.v. beam which induces the polymerization and to the analysing i.r. beam. The polymerization profile of each monomer was directly recorded by monitoring in real time the decrease of the distinct i.r. peak at 1415 cm^{-1} of the maleate double bond, and that at 1628 cm^{-1} of the vinyl ether double bond. It should be mentioned that the two types of double bonds absorb at 1645 cm^{-1} with similar extinction coefficients. Monitoring the decrease of this peak upon u.v. exposure gives therefore an undifferentiated view of the overall copolymerization process, very much like d.s.c. analysis does. It provides also an accurate evaluation of the total amount of unreacted double bonds which remain in the photocured polymer.

RESULTS AND DISCUSSION

Real-time i.r. spectroscopy is unique in that it allows one to record directly conversion vs time profiles for polymerizations occurring in less than 1 s. It proved particularly well suited to monitoring the photoinitiated copolymerization of DVE-3/DMA-2 mixtures and to studying the influence of various factors on the reaction kinetics. Of particular interest for u.v.-curing applications are the effects of the atmospheric oxygen, the light-intensity, the type of photoinitiator and the composition of the monomer mixture.

Kinetics of the polymerization

When the divinylether (DVE-3) or the dimaleate (DMA-2) monomer was exposed to u.v. radiation in the presence of a radical photoinitiator ([Darocur 1173] = 2 wt%), no significant homopolymerization could be detected after a 10 s irradiation at 50 mW cm^{-2} of the laminated film. In contrast, a fast copolymerization was found to proceed when a stoichiometric mixture of DVE-3 and DMA-2 (formulation A) was irradiated under the same conditions, with formation of a strictly insoluble polymer. *Figure 2* shows some typical conversion vs time profiles recorded by *RT*i.r. spectroscopy for two formulations having a double bond ratio VE/MA of 1 and 2. In the stoichiometric mixture, the same polymerization profile (curve a in *Figure 2*) was recorded at 1415 cm^{-1} (maleate) and at 1628 cm^{-1} (vinyl ether), as well as at 1645 cm^{-1} where both monomers absorb equally. The two monomers were found to disappear at exactly the same rate to give a

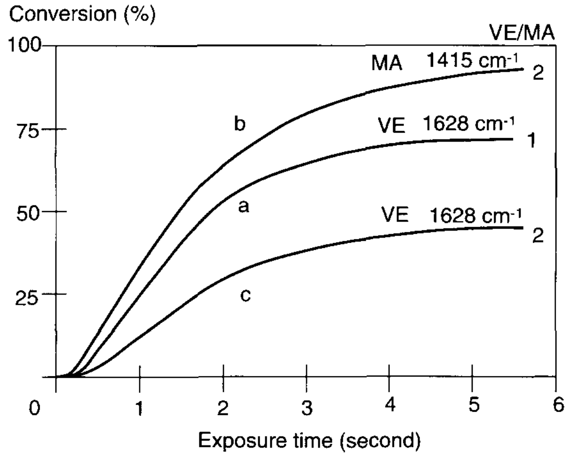


Figure 2 Polymerization profiles recorded by *RT*i.r. spectroscopy upon u.v. irradiation of a mixture of DVE-3 and DMA-2 in the presence of Darocur 1173 (2 wt%). Light-intensity: 50 mW cm^{-2}. Laminated films. Curve (a): stoichiometric mixture. Curves (b) and (c): molar ratio VE/MA = 2

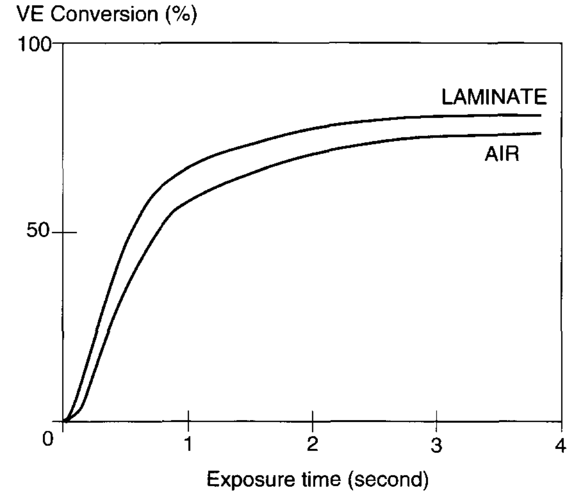


Figure 4 Photoinduced polymerization of a polyurethane-vinyl ether/dimaleate mixture (Formulation B; VE/MA = 1). I = 50 mW cm^{-2}. Film thickness: 24 μm

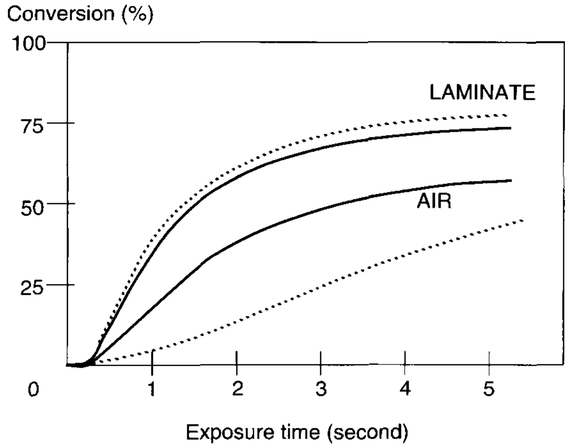


Figure 3 Influence of oxygen on the photopolymerization of a DVE-3/DMA-2 mixture (VE/MA = 1). – – – –: acrylate resin of same viscosity. Light intensity: 50 mW cm^{-2}. Film thickness: 24 μm

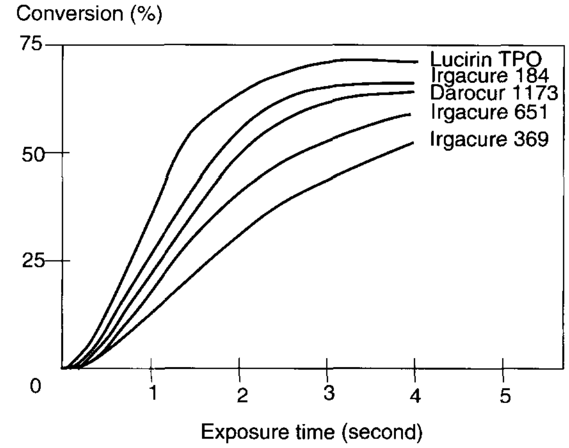


Figure 5 Influence of the photoinitiator (2 wt%) on the polymerization of a DVE-3/DMA-2 mixture exposed to u.v. radiation as a laminate film. VE/MA = 1; I = 50 mW cm^{-2}

highly crosslinked polymer which contains 25% of residual unsaturation.

The sigmoïd shape of the kinetic curve was attributed to two major factors: (i) the slight induction period observed initially is due to the well known inhibitory effect of the oxygen dissolved in the formulation on radical-induced polymerization[15]. Once O_2 has been consumed by the initiator radicals, the polymerization develops as rapidly in the laminated sample as in an inert atmosphere; (ii) the slowing down of the reaction for conversions above 30% results from both the progressive depletion of the reactive double bonds and the gel effect with its segmental mobility restrictions[16,17]. After a 5 s exposure, the conversion reaches its maximum value at 75%, the remaining VE and MA double bonds being trapped in the tridimensional polymer network formed and unable to react upon further exposure.

Figure 2 also shows the polymerization profiles recorded for a DVE-3/DMA-2 mixture having a VE/MA molar ratio of 2 (33.3% MA double bonds and 66.6% VE double bonds). The maleate conversion rises rapidly to reach a 95% value after 10 s (curve b). On the contrary, the vinyl ether conversion rises half as fast and is levelling out at 45% (curve c). From the slope of these curves, the rate of polymerization of each functional group was calculated by using the equation

$$R_p = \frac{\mathrm{d}\,(\text{conversion})}{\mathrm{d}t}[\mathrm{M}]$$

where [M] is the double bond molar concentration of the considered monomer. As expected for an alternate copolymerization process, the two monomers were found to disappear at exactly the same rate, like in the stoichiometric mixture. This is a general behaviour which was found in all the experiments, whatever the initial composition of the monomer mixture (see below).

Influence of oxygen

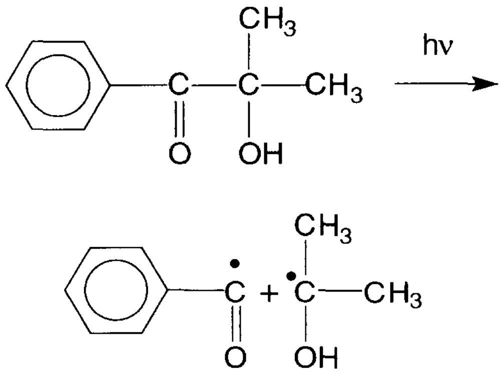
Although atmospheric oxygen inhibits this type of polymerization by scavenging both the initiating radicals and the propagating polymer radicals, its effect is substantially less pronounced than for acrylate resins irradiated in the presence of the same photoinitiator. The propagating species must therefore be less prone to O_2 scavenging, either because of a shorter lifetime, or because of a lesser affinity toward the oxygen molecule.

Figure 3 shows the polymerization profile recorded for a 25 μm thick DVE-3/DMA-2 film irradiated at a light intensity of 50 mW cm^{-2}, either in the presence of air, or as a laminate to prevent the diffusion of air into the sample. The reaction proceeds half as fast for the film in contact with air. For acrylate formulations of similar viscosity, a six-fold decrease in the polymerization rate was observed under the same experimental conditions (*Figure 3*).

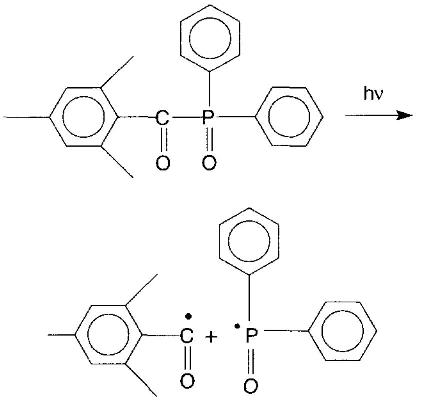
The inhibitory effect of O_2 in the VE/MA hybrid system was further reduced by increasing the formulation viscosity through a partial replacement of DVE-3 by a telechelic vinyl ether polyurethane (formulation B with VE/MA = 1). By slowing down the diffusion of atmospheric oxygen during the u.v. exposure, this will reduce the actual O_2 concentration in the irradiated sample. At a photoinitiator concentration of 4% by weight, the VE/MA copolymerization was found to develop nearly as fast and almost as extensively in the presence of air as in the laminated sample (*Figure 4*). An increase of the light intensity was shown to further close the gap between the two curves, as it shortens the reaction time during which air can diffuse into the liquid sample.

Influence of the photoinitiator

The efficiency of various radical-type photoinitiators (PI) in promoting the copolymerization of DVE-3 and DMA-2 was determined in stoichiometric formulations containing 2 wt% of PI. The two hydroxyalkylphenones (Irgacure 184 and Darocur 1173) were found to be more efficient than the widely used dimethoxyphenylacetophenone (Irgacure 651) or the morpholino ketone (Irgacure 369), as shown in *Figure 5*. This result is in good agreement with previous observations on similar systems[11]. Just the opposite trend was observed in the photopolymerization of acrylate resins[18]. Since all four photoinitiators produce benzoyl radicals which should be of similar initiating efficiency, the better performance of the hydroxyalkylphenones can be attributed to a higher reactivity of the hydroxyalkyl radicals to initiate the copolymerization of VE and MA monomers. The fastest polymerization was observed by using as photoinitiator an acylphosphine oxide, Lucirin TPO from BASF, which generates benzoyl and phosphinoyl radicals upon photolysis[19]:



Darocur 1173



Photopolymerization studies on model compounds have indeed shown that phosphinoyl radicals are at least twice as effective as benzoyl radicals in the addition to vinyl double bonds[20].

The concentration of the photoinitiator plays a key role on the polymerization kinetics for it controls directly the rate of initiation. Photopolymerization experiments were carried out with the stoichiometric VE/MA formulation at various PI concentrations. The maximum rate of polymerization (R_p) was determined from the slope of the *RT*i.r. profiles recorded, and its value was plotted as a function of the square root of the PI concentration (*Figure 6*). A linear relationship was found to exist for $[PI] \leq 2$ wt%, i.e. as long as the light absorbance remains low, in good agreement with the rate equation for light-induced polymerization of low absorbing media[21]

$$R_p = \left[k_p/(2k_t)^{0.5}\right](\Phi_i I_0 \epsilon l[PI])^{0.5}[M] \quad (1)$$

where Φ_i is the initiation quantum yield, I_0 the light intensity, ϵ the PI extinction coefficient, l the thickness of the sample and [M] the monomer concentration.

A deviation of this law was observed at PI concentrations above 2% when the light absorbance (ϵl[PI]) increases and the inner filter effect limits the penetration of u.v. radiation into the sample. The rate equation then becomes[21]

$$R_p = \left[k_p/(2k_t)^{0.5}\right](\Phi_i I_0(1 - e^{-2.3\epsilon l[PI]}))^{0.5}[M] \quad (2)$$

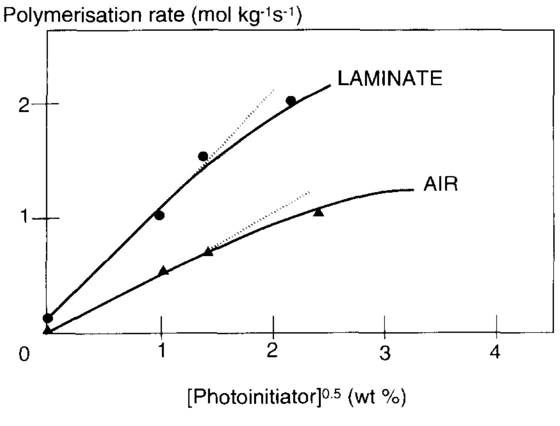


Figure 6 Influence of the photoinitiator concentration on the rate of polymerization of a DVE-3/DMA-2 mixture (VE/MA = 1). Photoinitiator Darocur 1173; I = 50 mW cm^{-2}

This leads to a surface to bottom polymerization gradient which will become more pronounced as the PI concentration is increased[22]. A similar effect was observed by raising the thickness of the sample. To achieve a fast and uniform through cure by photoinitiated polymerization, one should therefore use a PI concentration high enough to provide a large initiation rate, and low enough to avoid the inner filter effect. In the present case, this balance was achieved by working at a Darocur 1173 concentration of 2 wt%.

Influence of the light intensity

One of the distinct advantages of photoinduced polymerization is that the rate of initiation can be varied by several orders of magnitude by acting on the intensity of the light beam. It is even possible to change the initiation rate in the course of the reaction. For instance, sharper polymerization profiles as those represented in *Figure 2* have been recorded by increasing progressively the light intensity above 30% conversion to partly compensate the slowing down due to gelation.

In a systematic study, the stoichiometric VE/MA formulation was exposed to u.v. radiation of intensity ranging from 2 to 90 mW cm^{-2}, and the polymerization profiles were recorded by *RT*i.r. spectroscopy. A logarithmic plot of R_p vs the light intensity was found to yield a straight line with a slope of 0.6 (*Figure 7*). This value is slightly higher than the 0.5 exponent expected for a polymerization proceeding by a mechanism involving bimolecular termination [equation (2)]. It can be accounted for by considering that, in media undergoing cross-linking polymerization, a fraction of the polymer radicals will stop growing because they are becoming trapped in the polymer network. Kinetically, this will correspond to a monomolecular termination and will introduce a first order contribution in the rate equation, thus increasing the measured value of the light intensity exponent.

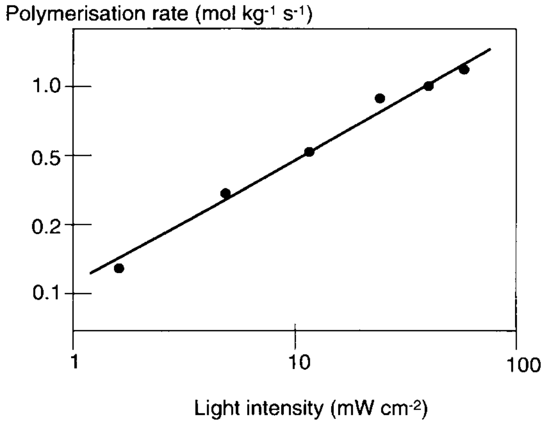


Figure 7 Influence of the light intensity on the polymerization rate of a DVE-3/DMA-2 mixture (VE/MA = 1). Laminated film [Darocur 1173] = 2 wt%

Some experiments have been performed with formulation B on a u.v.-curing line similar to those used in industrial applications. The 25 μm thick film was exposed to a light intensity of 500 mW cm^{-2} by passing under a high power mercury lamp at a speed of 30 m min^{-1}. The polymerization was shown to proceed extensively within the 0.2 s exposure, to yield a cross-linked polymer containing less residual unsaturation (20%) than when it was exposed to the same dose of radiation at a lower light intensity (30%), e.g. 2 s at 50 mW cm^{-2}. This behaviour was explained by a temperature effect. Indeed, we have recently shown that the heat evolved during the ultrafast photopolymerization of vinyl ether or acrylate monomers leads to a sharp increase of the sample temperature, which can rise up to 100°C in less than 1 s, even in thin films[23]. As a result, the molecular mobility will increase, particularly in the gelation stage, thus lifting some of the migration restrictions of the reactive species, which are known to be primarily responsible for the premature ending of the polymerization[16].

Another approach that we used to decrease the amount of residual unsaturation in the photocured polymer was to add a cationic photoinitiator (1 wt% of a triarylsulfonium salt). The polymerization developed as efficiently upon u.v. irradiation as in the formulation containing only a radical photoinitiator, but it continued to proceed in the dark, at least that of the vinyl ether.

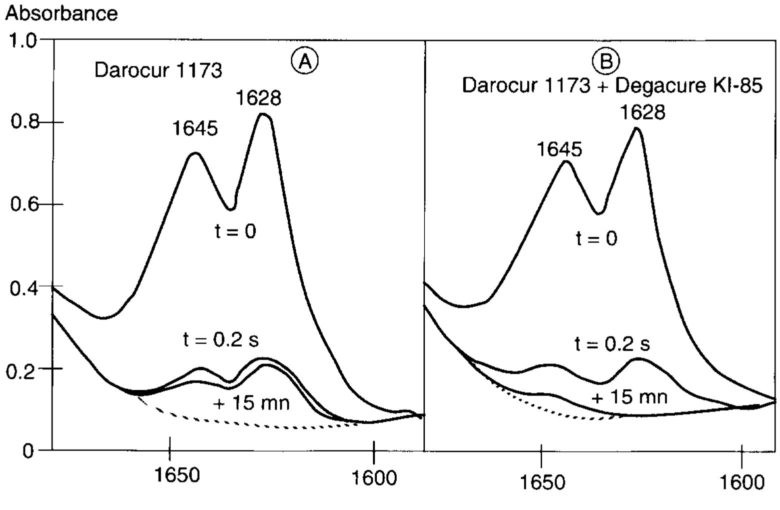


Figure 8 I.r. spectra of a polyurethane vinyl ether/dimaleate mixture before and after a 0.2 s u.v. exposure, and after a 15 min storage at ambient in the dark. Light-intensity: 500 mW cm^{-2}. Photoinitiator: A [Darocur 1173] = 4 wt%. B [Darocur 1173] = 4 wt%; [Degacure KI-85] = 5%

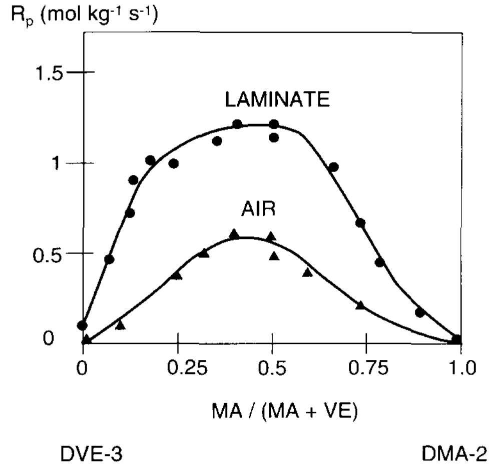


Figure 9 Influence of the composition of the monomer mixture on the polymerization of a DVE-3/DMA-2 formulation exposed to u.v. radiation. $I = 50\,\mathrm{mW\,cm^{-2}}$. [Darocur 1173] = 2 wt%

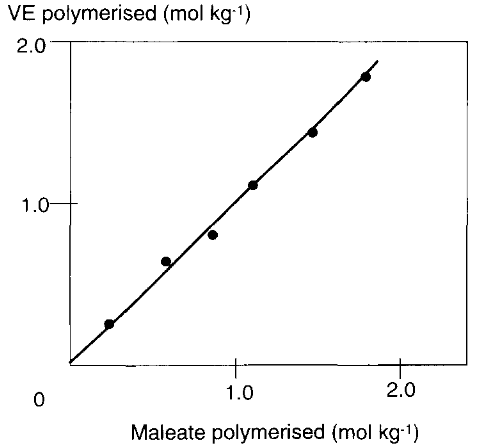


Figure 10 Amount of vinyl ether polymerized vs amount of maleate polymerized in photoinduced polymerization of DVE-3/DMA-2 mixtures of various compositions. $I = 50\,\mathrm{mW\,cm^{-2}}$. Laminated film

Figure 8 shows the i.r. spectra recorded for the two types of formulations before and after u.v. exposure for 0.2 s. It can be seen that, after a 15 min storage in the dark, the polymer crosslinked with the two photoinitiators contained no detectable vinyl ether double bonds (peak at 1628 cm^{-1}) and less than 15% of the initial amount of maleate double bonds (peak at 1645 cm^{-1}).

Influence of the monomer feed ratio

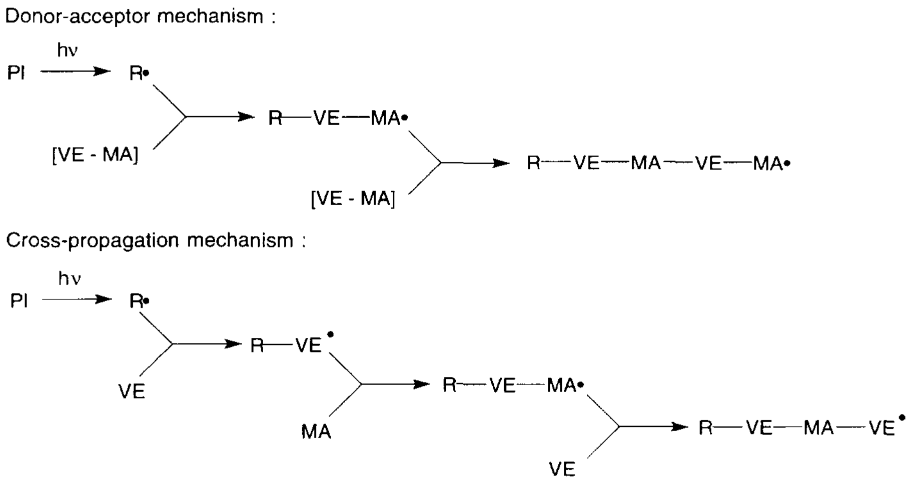
Curing experiments carried out with formulations having different monomer feed ratios have shown that the polymerization rate reaches its maximum value for a VE/MA ratio of 1. This is illustrated in *Figure 9*, where the R_p value has been plotted as a function of the molar ratio MA/(MA + VE) for a DVE-3/DMA-2 mixture exposed to u.v. radiation either in the presence of air or as laminated film (O_2-free). Whatever the initial composition, the amount of maleate polymerized was always found to be the same as that of vinyl ether polymerized (*Figure 10*), a result which implies the production of an alternate copolymer. It can be formed either by homopolymerization of a donor–acceptor complex, or by a cross-propagation mechanism where VE radicals would react only with MA double bonds and MA radicals only with VE double bonds.

A formal representation of the alternate copolymer network formed upon u.v.-curing of a DVE-3/DMA-2 mixture is given in *Figure 11*.

A direct consequence of the data shown in *Figure 9* is that the amount of residual unsaturation in the photocured polymer will depend on the VE/MA feed ratio and be the lowest for a stoichiometric composition. If the monomer ratio is different, part of the monomer in excess will remain unpolymerized in the cured polymer. This behaviour is clearly apparent in *Figure 12* which shows how the amount of residual unsaturation in extensively irradiated sample varies as a function of the VE/MA feed ratio, for each monomer. The sum of the two curves gives the variation of the total unsaturation content, which passes through a minimum for VE/MA = 1. It should be noticed that this quantity can also be determined experimentally by monitoring the i.r. peak at 1645 cm^{-1} where both monomers absorb.

Mechanism of copolymerization

By studying the influence of the monomer concentration on the polymerization rate, one can obtain valuable information about the mechanism of the copolymerization and determine whether the chain reaction proceeds by cross-propagation or through a donor–acceptor complex.



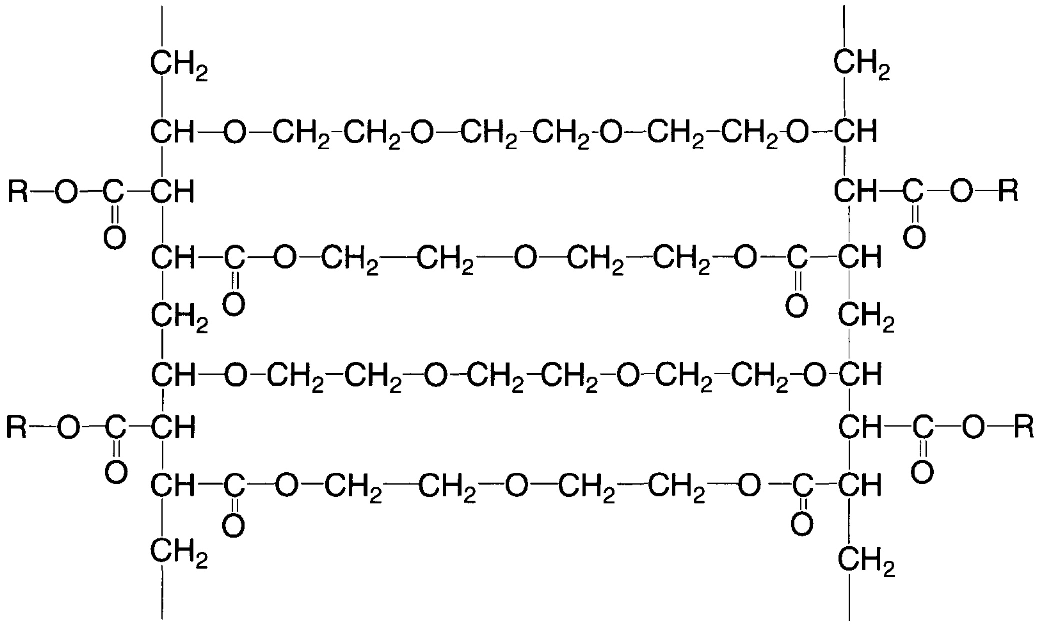


Figure 11 Structure of the vinyl ether/maleate alternate copolymer network (DVE-3/DMA-2)

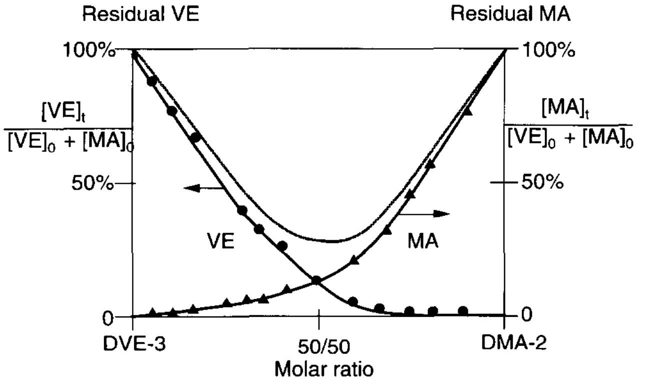


Figure 12 Influence of the composition of the monomer mixture on the amount of residual unsaturation in a photocured DVE-3/DMA-2 copolymer. $I = 50\,\mathrm{mW\,cm^{-2}}$; exposure time: 15 s. ······: VE + MA

As there is no homopolymerization of VE and MA monomers ($k_{11} = 0$, $k_{22} = 0$), only two reactions have to be considered in the cross-propagation scheme

Propagation

$$M_1^\bullet + M_2 \xrightarrow{k_{12}} M_2^\bullet \qquad R_{p_2} = k_{12}[M_1^\bullet][M_2]$$

$$M_2^\bullet + M_1 \xrightarrow{k_{21}} M_1^\bullet \qquad R_{p_1} = k_{21}[M_2^\bullet][M_1]$$

Termination

$$M_1^\bullet + M_2^\bullet \xrightarrow{k_{t_{12}}} M_1M_2 \qquad r_t = k_{t_{12}}[M_1^\bullet][M_2^\bullet]$$

The variation of the polymer radical concentration can be written as

$$\frac{d[M_1^\bullet]}{dt} = k_{21}[M_2^\bullet][M_1] - k_{12}[M_1^\bullet][M_2] = -\frac{d[M_2^\bullet]}{dt}$$

Under steady state conditions

$$d[M_1^\bullet]/dt = 0 \quad \text{and} \quad R_{p_1} = R_{p_2}$$

As radicals do not accumulate, the rate of radical production, r_i, is always equal to the rate of termination

$$r_i = \Phi_i f I_0 = k_{t_{12}}[M_1^\bullet][M_2^\bullet]$$

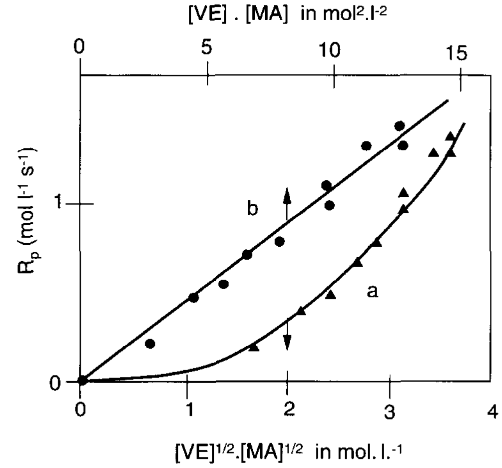


Figure 13 Dependence of the rate of polymerization on the monomer concentration in the photocuring of a DVE-3/DMA-2 mixture. $I = 50\,\mathrm{mW\,cm^{-2}}$. Laminated film. [Darocur 1173] = 2 wt%

where f is the fraction of incident light absorbed by the sample ($f = 1 - e^{-2.3\epsilon l[PI]}$). By making the product of the polymerization rate of VE and MA monomers,

$$R_{p_1}R_{p_2} = k_{21}k_{12}[M_1][M_2]r_i/k_{t_{12}}$$

and taking into account that $R_{p_1} = R_{p_2} = R_p$, one finally obtains the rate equation

$$R_p = \left(\frac{k_{21}k_{12}}{k_{t_{12}}}\right)(\Phi_i f I_0)^{1/2}[M_1]^{1/2}[M_2]^{1/2} \qquad (3)$$

The cross-propagation mechanism should therefore give a square root dependence of the polymerization rate on the product of the monomer concentration, i.e. $([VE][MA])^{1/2}$.

The second mechanism is based on the homopolymerization of a MA–VE acceptor–donor complex. This complex is in equilibrium with the non-complexed monomers, K being the equilibrium constant

$$A + D \overset{K}{\rightleftharpoons} (\overset{\delta^-}{A}\,\overset{\delta^+}{D}) \qquad K = \frac{[AD]}{[A][D]}$$

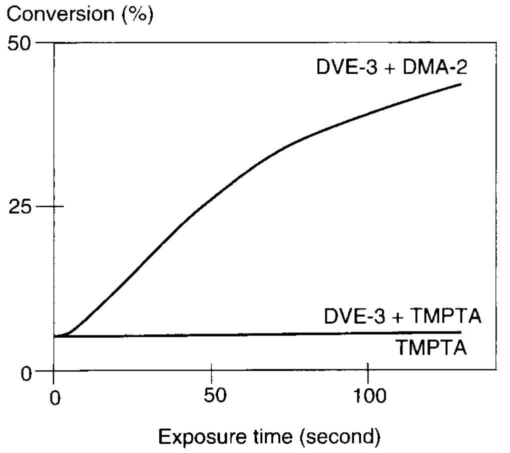


Figure 14 Polymerization profiles recorded by *RT*i.r. spectroscopy upon u.v. exposure of photoinitiator-free formulations. $I = 50\,\mathrm{mW\,cm^{-2}}$. Laminated film

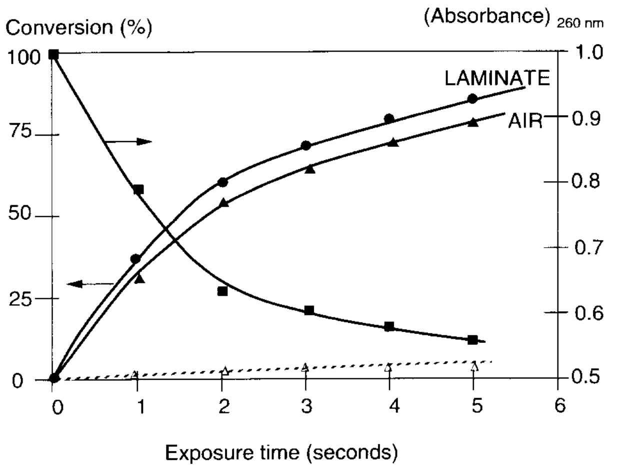


Figure 15 Polymerization of a photoinitiator-free mixture of polyurethane divinyl ether/dimaleate (VE/MA = 1) upon exposure to intense u.v.-radiation ($I = 500\,\mathrm{mW\,cm^{-2}}$) in the presence of air. Film thickness: 24 μm. – – –: polyurethane-diacrylate/hexanediol diacrylate in 1/1 weight ratio

For $K > 0.01$, the copolymerization can proceed via the (AD) complex, which is the propagating species, and its kinetics obeys the rate equation

$$R_p = \frac{k_p}{k_t^{1/2}} r_i^{1/2}[\mathrm{AD}]$$

or

$$R_p = \frac{k_p}{k_t^{1/2}} (\Phi_i f I_0)^{1/2} K[\mathrm{A}][\mathrm{D}] \qquad (4)$$

It can be seen that the homopolymerization of an acceptor–donor complex leads to a linear dependence of the polymerization rate on the product of the monomer concentrations, i.e. [VE] [MA].

The rate of polymerization of the vinyl ether or maleate monomer $[(R_p)_{\mathrm{VE}} = (R_p)_{\mathrm{MA}}]$ has been determined for various compositions and its value has been plotted as a function of either the product $[\mathrm{MA}]^{1/2}[\mathrm{VE}]^{1/2}$ (*Figure 13*, curve a), or the product [MA] [VE] (*Figure 13*, curve b). The straight line obtained in the latter case indicates that the photoinitiated copolymerization of DVE-3 with DMA-2 occurs by a mechanism where the propagating species is a donor–acceptor complex. This result is in good agreement with the work of Lee and Hall[24] on the photoinduced copolymerization of various acceptor and donor monomers which was shown to occur by direct photolysis of charge-transfer complexes.

Such a mechanism would also account for the fact that oxygen has a less pronounced inhibitory effect on the polymerization of the VE/MA system than on acrylate monomers. Indeed, if VE and MA radicals were formed by a cross-propagation mechanism, they should be rapidly scavenged by O_2, as acrylate radicals are. On the other hand, polymerization proceeding through donor–acceptor complex are generally considered to be less sensitive to oxygen[24], in full agreement with our results.

Another argument in favour of the charge transfer mechanism is the fact that polymerization was also found to occur by simple irradiation of a DVE-3/DMA-2 mixture containing no added photoinitiator. *Figure 14* shows the polymerization profile recorded upon u.v. exposure of a stoichiometric VE/MA formulation, and that of neat trimethylpropanetriacrylate (TMPTA) and of a DVE-3/TMPTA mixture, which both remain unaffected under those conditions. In the DVE-3/DMA-2 mixture, direct excitation of the donor–acceptor complex leads to the production of a short living exciplex (VE–MA)* which generates the initiating species. The polymerization proceeds still much slower than in the presence of an added photoinitiator, because of the weak absorbance of the complex (indicating a small K value) and a lower initiation efficiency.

The more viscous formulation B consisting of a telechelic polyurethane vinyl ether and a dimaleate was also found to undergo an effective polymerization when it was exposed to intense u.v. radiation in the absence of any added photoinitiator, as shown in *Figure 15*, A 5 s exposure proved to be sufficient to reach 80% conversion of both VE and MA functions, even in the presence of air. At the same time, the absorbance at 260 nm of the charge transfer complex was shown to decrease according to a very similar kinetics as that of the vinyl ether double bond monitored by i.r. spectroscopy (*Figure 14*), in good agreement with the proposed mechanism. Similar results have been obtained recently with photoinitiator-free mixtures of vinyl ether and maleimide monomers[25,26], except that the copolymerization developed more efficiently than in the VE/MA system because of a larger K value in this type of complex.

CONCLUSION

The vinyl ether/maleate system appears to be an attractive alternative to the acrylate resins which are widely used in u.v.-curing applications. Under intense illumination, the photoinitiated radical copolymerization of such difunctional monomers proceeds within seconds, and transforms the liquid mixture into a solid and insoluble polymer. The reaction kinetics, which was studied by *RT*i.r. spectroscopy, can be finely controlled by acting on the light intensity, the type of photoinitiator and its concentration, and on the composition of the monomer mixture.

The physico-chemical characteristics of the alternate copolymer network formed are strongly dependent on the chemical structure of the crosslinking chains. They can be modulated in a large range, from low modulus to high modulus polymers, by a proper selection of the telechelic oligomer and the monomer acting as reactive diluent, in the same way as in u.v.-curable acrylate systems. One of the distinct characteristics of the photoinitiated copolymerization of vinyl ether and maleate monomers is that it proceeds through a donor–acceptor mechanism, which makes the process less sensitive to oxygen inhibition. Such photosensitive resins appear to be well suited for specific applications where high cure speed, together with well designed physico-chemical properties, are required, in particular as fast-drying coatings and adhesives, and as negative photoresists in microlithography.

REFERENCES

1 Oldring, P. K. T. (Ed.) 'Chemistry and Technology of UV-EB Formulation for Coatings, Inks and Paints', SITA Technology, London, 1991

2 Pappas, S.P. (Ed.) 'Radiation Curing', Plenum Press, New York, 1992

3 Lapin, S. C. in ref. 2, p. 241

4 Decker, C. and Decker, D. *J. Macromol. Sci.* 1997, **A34**, 4

5 Decker, C. and Decker, D. 'Proc. RadTech Conf.', Vol. 1, RadTech Intern, Northbrook, IL, 1994, p. 602

6 Korkubo, T., Iwatsuki, S. and Yamashita, Y. *Macromolecules* 1968, **1**, 482

7 Li, T., Cao, W. and Feng, X. *J. Macromol. Sci. Rev.* 1989, **C29**, 153

8 Li, T., Luo, B., Chu, G. and Hall, H. *J. Polym. Sci., Polym. Chem. Ed.* 1990, **28**, 1735

9 Noren, G. K., Tortello, A. J. and Vanderberg, J. T. 'Proc. RadTech. Conf.', Vol. 2, RadTech Intern, Northbrook, IL, 1990, p. 201

10 Friedlander, C. B. and Diehl, D. A. Europ. Pat. 322 808, 1989

11 Schouten, J. J., Noren, G. K. and Lapin, S. C. 'Proc. RadTech. Conf.', Vol. 1, RadTech Intern, Northbrook, IL, 1992, p. 167

12 Lapin, S. C., Schouten, J. J., Noren, C. K. and Mosehovis, E. J. 'Proc. RadTech. Europ. Conf.', RadTech Europe, Fribourg, Switzerland, 1993, p. 502

13 Decker, C. and Moussa, K. *Makromol. Chem.* 1989, **189**, 2381

14 Decker, C. and Moussa, K. *J. Coat. Technol.* 1990, **62**, 55

15 Decker, C. and Jenkins, A. *Macromolecules* 1985, **18**, 1241

16 Aronkine, M. T. and Gillham, J. K. *J. Coat. Technol.* 1984, **56**, 35

17 Decker, C. in ref. 2, p. 152

18 Decker, C. and Moussa, K. *Makromol. Chem.* 1990, **191**, 963

19 Jacobi, M. and Henne, A. *J. Radiat. Curing* 1983, **19**, 16

20 Baxter, J. B., Davidson, R. S., Hageman, H. J. and Overeem, T. *Makromol. Chem.* 1988, **189**, 2769

21 Vanderhoff, J. W. in 'Ultraviolet Light Induced Reactions in Polymers' (Ed. R. F. Gould) ACS Symp. Series 25, Amer. Chem. Soc. Washington DC, 1976, p. 162

22 Decker, C. in 'Process on Photoreactive Polymers' (Eds V. V. Krongauz and A. D. Trifunac), Chapman and Hall, New York, 1995, p. 34

23 Decker, C., Decker, D. and Morel, F. *Polym. Mater. Sci. Eng.* 1996, **74**, 350

24 Lee, C. and Hall, H. K. *Macromolecules* 1989, **22**, 21

25 Jönsson, S., Schaeffer, W., Sundell, P. C., Shimose, M., Owen, J. and Hoyle, C. 'Proc. RadTech. Conf.', Vol. 1, RadTech Intern, Northbrook, IL, 1994, p. 194

26 Decker, C., Morel, F., Jönsson, S., Clark, S. C. and Hoyle, C. *Polym. Mater. Sci. Eng.* 1996, **75**, 198