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Kinetic study of the photo-induced copolymerization of *N*-substituted maleimides with electron donor monomers

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Abstract

The photo-induced copolymerization of electron donor/electron acceptor monomers has been studied by real-time infrared spectroscopy. With maleimide/vinyl ether mixtures, the reaction was found to proceed rapidly upon u.v. exposure in the absence of oxygen to reach nearly 100% conversion within seconds. The two monomers disappeared at similar rates, with formation of an alternating copolymer. Similar results were obtained with maleimide/*N*-vinylpyrrolidone and maleimide/styryloxy combinations. Highly crosslinked polymer networks have been produced by photo-induced copolymerization of bis-maleimide and divinyl ether monomers. These photoinitiator-free formulations were found to be less sensitive to oxygen inhibition than typical u.v.-curable acrylate resins. *N*-substituted maleimides were also shown to act as monomeric photoinitiators by inducing the polymerization of acrylate monomers upon u.v. irradiation. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymerization; Maleimide; Vinyl ether

1. Introduction

Acrylate-based resins are currently used in most photocuring applications because of their superior reactivity [1]. Increasing interest in the u.v.-curing industry for alternatives to acrylates and a general improvement of the technology has recently focused on the photo-induced copolymerization of donor/acceptor type monomers. For instance, the recently developed maleate/fumarate and vinyl ether combinations have been found to exhibit remarkable curing performance characteristics [2]. However, these combinations normally polymerize at somewhat lower rates than the corresponding acrylates. In this respect, the maleimide/vinyl ether combination appears to be a promising alternative to the acrylic resins, as it has been shown to undergo a fast copolymerization upon exposure to intense u.v.-radiation [3], [4], [5]. A distinct feature of such photo-induced reaction is that it does not require the addition of a photoinitiator, the u.v.-light being absorbed by the maleimide monomer. It has been proposed that initiating radicals can be generated by hydrogen abstraction from either a ground state maleimide monomer or the co-monomer by the excited maleimide (MI*), although some minor contribution to an initiation via an exciplex [6], [7], according to the following reaction scheme, has not been ruled out completely. In some cases (styryloxy/maleimide or *N*-vinylpyrrolidone/maleimide), excitation of ground-state charge transfer complex with red-shifted absorption spectra may contribute to the initiation process, in addition to hydrogen abstraction by locally excited maleimide.

The kinetics of the polymerization process has been thoroughly investigated in recent years by Jönsson, Hoyle and coworkers, by means of photocalorimetry [3], [4], [5], [6], [7]. This widely used technique, which measures the overall heat flux evolved by the exothermic reaction, is, however, incapable of following the polymerization of each one of the two monomer components. In addition, the DSC performance in u.v-curing analysis is handicaped by its relatively long time resolution, which prevents one from monitoring polymerization reactions proceeding extensively to completion within seconds.

Real-time infrared (*R.T.*i.r.) spectroscopy does not suffer from these limitations, and has proved to be a method well

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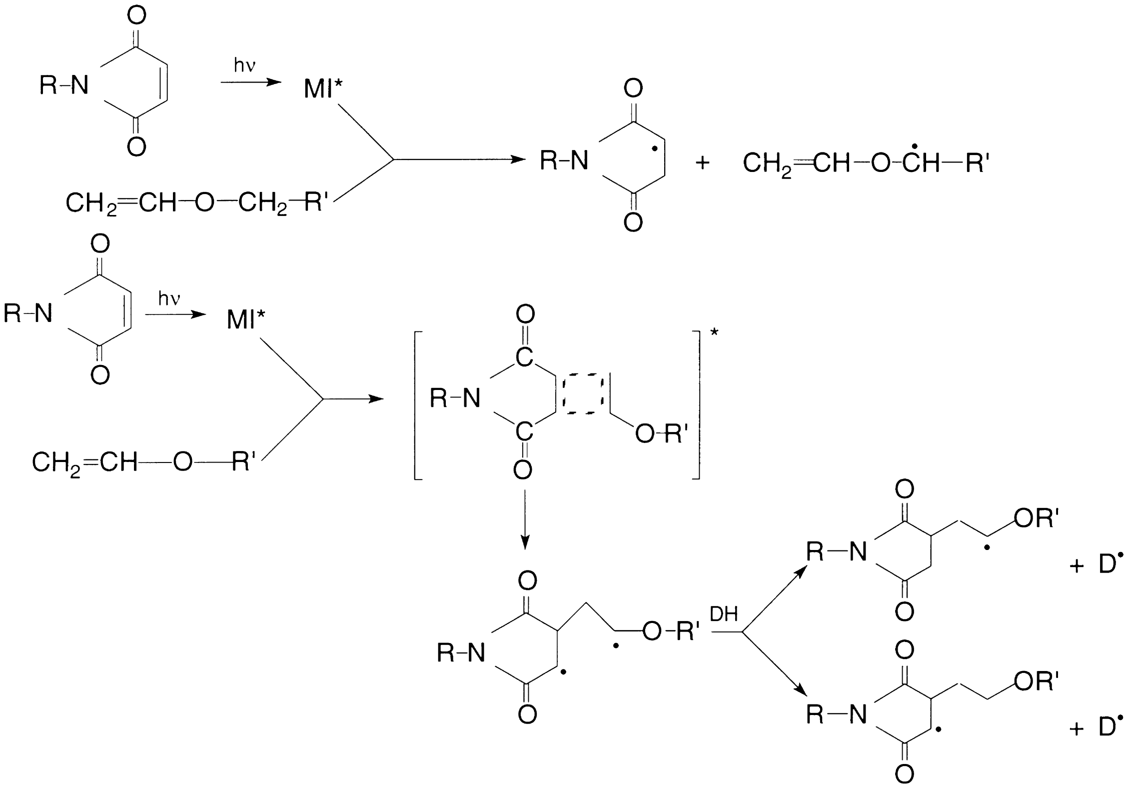


suited to studying the disappearance of a given monomer undergoing ultrafast polymerization upon u.v. exposure [8]. This technique has been successfully used to monitor quantitatively the photoinitiated copolymerization of a dimaleate–divinyl ether resin, and to show that it proceeds through a charge transfer complex between the two monomers [9]. In this paper, we report a *R.T.*i.r. kinetic investigation of the high-speed copolymerization of vinyl ether- (VE) and maleimide- (MI) based formulations exposed to u.v. radiation in the absence of any added photoinitiator.

2. Experimental

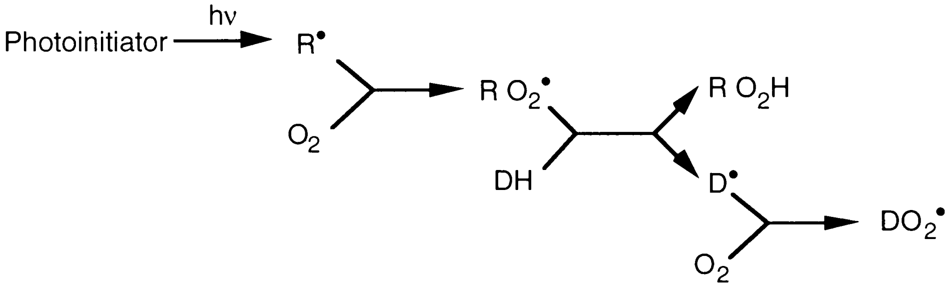
2.1. Materials

The following monomers were used in this study: 4-hydroxybutylvinylether (HBVE) from ISP, bis(4-vinyloxybutyl)isophtalate (iPDBVE) from Allied Signal, *N*-vinylpyrrolidone (NVP) from Aldrich, 5-hydroxypentylmaleimide (HPMI) from Ciba, 4,9-di oxo-*N*,*N*′-dodecane bismaleimide (DODBMI), and triethyleneglycolbiscarbonate bisethylmaleimide (TEGBCBMI), synthesized at the University of Southern Mississippi and *p*-glycidyloxystyrene, a gift from J. Ericsson at Perstop AB. For a comparison of the reactivity of photoinitiator-free monomer mixtures with typical u.v.-curable acrylates, hydroxypropylacrylate (HPA), hexanedioldiacrylate (HDDA) and tripropylene glycoldiacrylate (TPGDA), all from UCB, were used in combination with a radical photoinitiator (2% of Irgacure 651 from Ciba). The chemical formulae of the various monomers utilized in this study are given in Fig. 1.

2.2. Irradiation

The photopolymerizable formulation, made of a stoichiometric mixture of two monomers of each type (electron donor and electron acceptor) was coated onto a polypropylene film, at a typical thickness of 15 μm. The sample was placed in the compartment of an infrared spectrophotometer where it was exposed for a few seconds to the u.v. radiation of a medium pressure mercury lamp (HOYA-SCHOTT-UV-200 S). The light intensity at the sample position was typically 150 mW cm^{-2}, as measured by a radiometer (International Light IL-390).

In most experiments, a second polypropylene film was laminated on top of the liquid resin to prevent the diffusion of atmospheric oxygen into the sample. As the oxygen dissolved in the formulation was not removed prior to the u.v.-irradiation, the initiating radicals will be scavenged by O_2 to give peroxy radicals and ultimately hydroperoxides:



This process is considered to be responsible for the short induction period observed at the beginning of u.v.-exposure. Once all the dissolved oxygen has been removed by this photochemical reaction, polymerization will proceed in a O_2-free medium at essentially the same rate as in a nitrogen-purged sample [10].

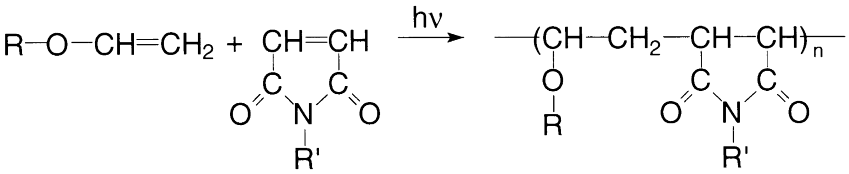
2.3. Analysis

The polymerization reaction was followed in situ by *R.T.*i.r. spectroscopy [8]. The disappearance of each one of the two monomers was monitored continuously by setting the wavelength of the i.r. detection at the value where the related double bond exhibits a characteristic peak: 1622 cm^{-1} for the vinyl ether, 829 cm^{-1} for the maleimide, and 812 cm^{-1} for the acrylate. By setting the spectrophotometer in the absorbance mode, conversion vs time curves are directly recorded. From the slope of these curves, the actual rate of polymerization (R_p) can be evaluated at any stage of the process. In most systems, R_p reached its maximum value in the 10–30% conversion range. This analytical method permits one to determine the final conversion, and thus the amount of residual unsaturation in the u.v.-cured polymer.

Maleimide monomers exhibit a strong u.v. absorbance in the 300 nm region. It is due to the C=C double bond conjugated with the carbonyl groups, and it disappears completely upon polymerization, as shown in Fig. 2. Real-time ultraviolet (*R.T.*u.v.) spectroscopy was used to follow the polymerization of MI monomers, upon u.v. irradiation in the presence of electron donor monomers. The sample was exposed simultaneously to the high intensity beam of the mercury lamp (150 mW cm^{-2}), which induces the reaction, and to the low intensity beam of the u.v. spectrometer (0.4 mW cm^{-2}) used to monitor the polymerization reaction.

3. Results and discussion

Vinyl ethers do not homopolymerize in the presence of a radical-type photoinitiator because of their electron-rich double bond. When mixed with a maleate or a maleimide monomer, they readily undergo copolymerization, with formation of an alternating type copolymer.



If the monomers contain at least two reactive groups, such as divinyl ethers (DVE) and bismaleimides (BMI), the polymerization develops in three dimensions to yield a highly crosslinked polymer network. A distinct feature of maleimide-based formulations is that they do not require the addition of a photoinitiator, the u.v. radiation being mainly absorbed by the maleimide chromophore. Generation of the initiating radicals is assumed to proceed by hydrogen abstraction by excited maleimide, as discussed in the Introduction. Photo-DSC studies of the reaction kinetics have shown that the polymerization of photoinitiator-free DVE–BMI formulations can develop as efficiently as in some acrylate-based resins, which are widely used in u.v.-curing applications [6].

3.1. Photopolymerization of vinyl ether and maleimide monomers

If the copolymerization is alternating, one would expect the two monomers to exhibit similar polymerization profiles upon u.v. exposure. This prediction has been fully confirmed by *R.T.*i.r. experiments carried out with different types of vinyl ether–maleimide formulations. Fig. 3 shows typical conversion vs time profiles recorded by this technique, when a stoichiometric mixture of two monofunctional monomers (HEMI and HBVE) was exposed to u.v. radiation at a light intensity of 150 mW cm^{-2}. Under O_2-free conditions (laminate), the two monomers were found to disappear at similar rates with the formation of an alternate

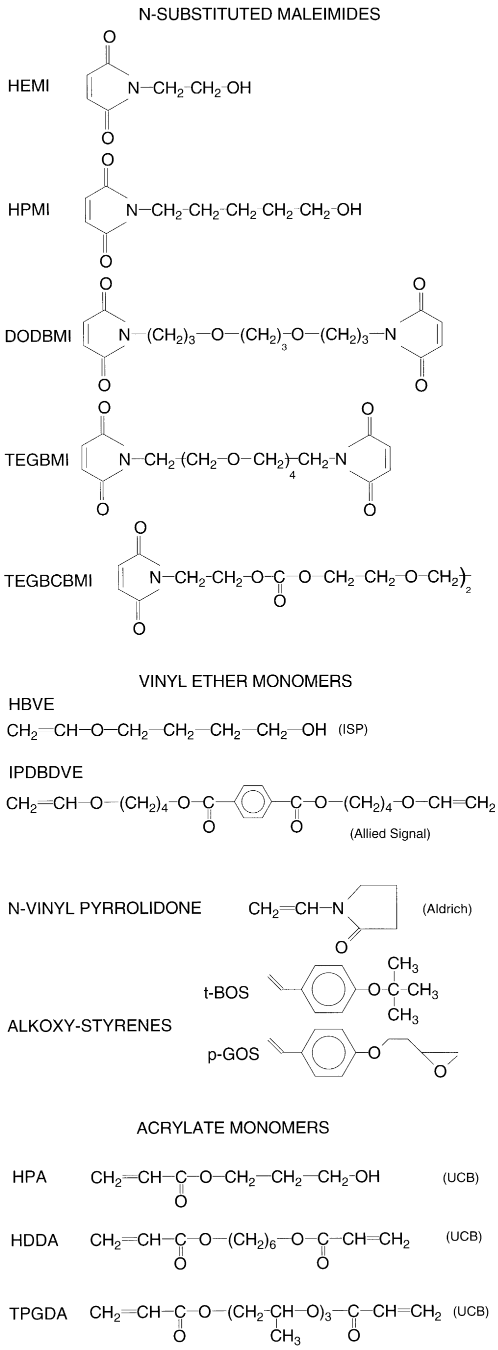


Fig. 1. Chemical formulae of the monomers used.

copolymer, together with some maleimide homopolymer, because the quantity of $MI_{polymerized}$ is always slightly greater than that of $VE_{polymerized}$. The reactivity of the VE/MI system can be increased by introducing additional C_2 groups, and thus abstractable hydrogen atoms, in the *N*-substituted chain. In hydroxypentyl maleimide (HPMI) mixtures with HBVE, a 50% rise in the polymerization rate was observed, together with an increase in the final conversion which reached 90% after a 5-s exposure (Fig. 3). By contrast, when HBVE was mixed with *t*-butyl maleimide (*t*-BuMI), which does not contain any abstractable hydrogen, the light-induced copolymerization proceeded at a much slower rate than with HPMI, as shown in Fig. 4. With *n*-butyl maleimide as co-monomer, the reaction rate was double that with *t*-BuMI, as expected from the presence of the labile hydrogens on the *N*-alkyl chain, but only one-sixth as fast as with HPMI. This result suggests that the hydrogens

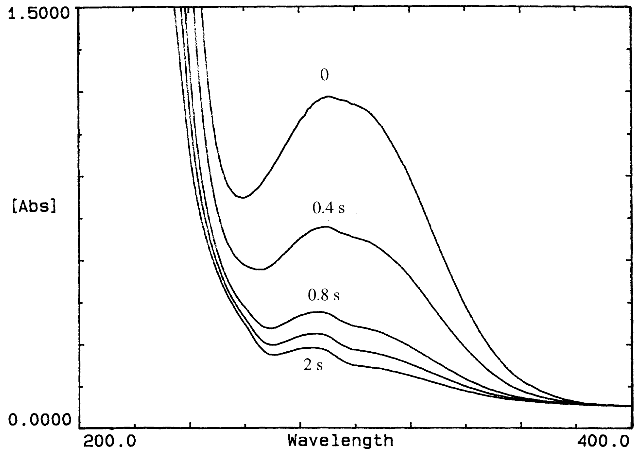


Fig. 2. u.v. Absorption spectra of the HBVE/HPMI combination, before and after u.v. exposure for various durations (0.4, 0.8, 1.2, 2 s).

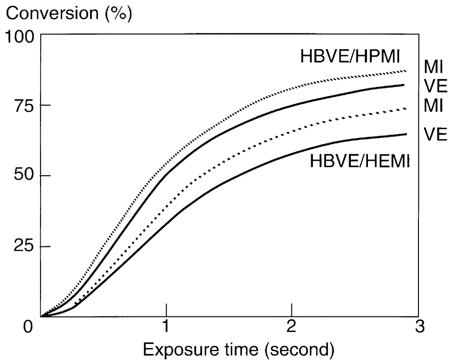


Fig. 3. Polymerization profiles recorded by *R.T.*i.r. spectroscopy upon u.v. exposure of a maleimide (MI) vinyl ether (VE) combination in the absence of added photoinitiator. (MI/VE = 1). Light intensity: 150 mW cm^{-2}.

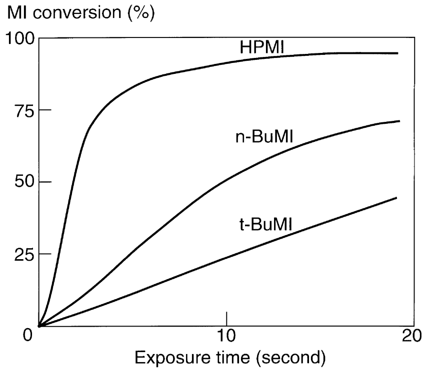


Fig. 4. Influence of the chemical structure of the maleimide co-monomer on the photo-induced polymerization of the HBVE/MI combination (VE/MI = 1). $I = 50$ mW cm^{-2}.laminate.

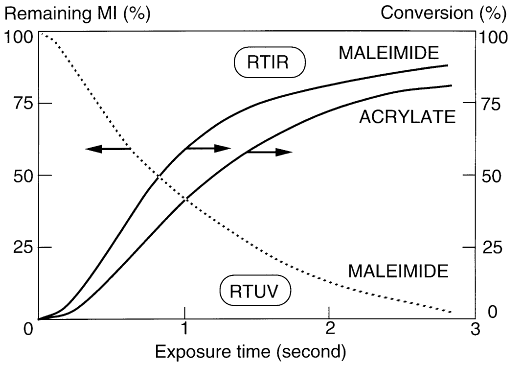


Fig. 5. Comparison of the polymerization kinetics of a monoacrylate (HPA + Irgacure 651—2 wt%) and a monovinyl ether–monomaleimide combination (HBVE/HPMI) upon u.v. exposure in O_2-free conditions.

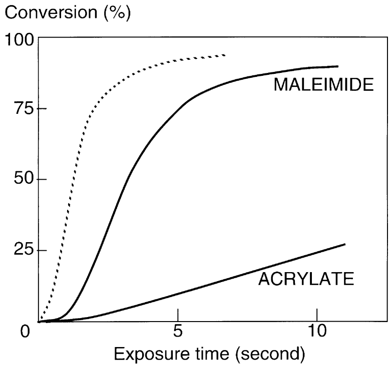


Fig. 6. Comparison of the polymerization kinetics of a monoacrylate (HPA + Irgacure 651—2 wt%) and a monovinyl ether–monomaleimide combination (HBVE/HPMI) upon u.v. exposure in the presence of air (----: O_2-free).

of the CH_2-OH group play a crucial role in the initiation step.

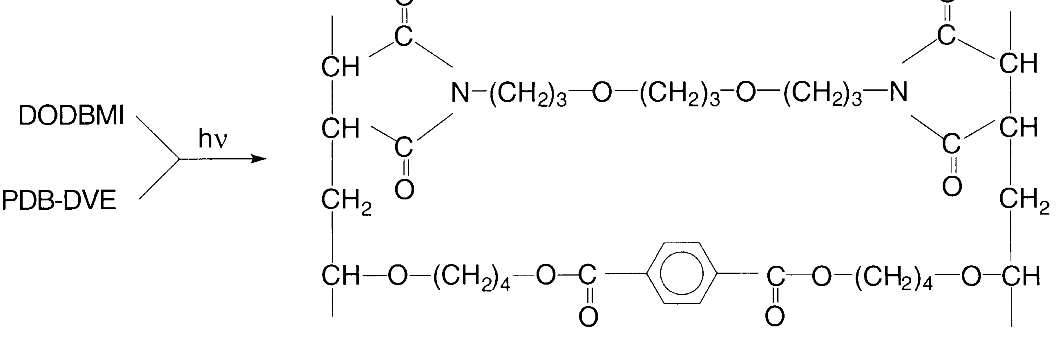
A good correlation was found when the maleimide polymerization was followed either by *R.T.*i.r. or by *R.T.*u.v. spectroscopy, as shown in Fig. 5. From these kinetic profiles, the formulation reactivity, i.e. the ratio of the maximum rate of polymerization (R_p) to the initial monomer concentration ($[M]_0$), was calculated to be in the order of 1 s^{-1}, at the light intensity used. This value is in the same order of magnitude as that determined previously for similar acrylate-based formulations [11]. It can be seen in Fig. 5 that the photoinitiator-free HBVE/HPMI formulation polymerizes twice as fast as hydroxy-propyl acrylate irradiated in the presence of 2 wt% dimethoxy phenylacetophenone, one of the most widely used photoinitiators in u.v.-curable resins [1].

In the presence of air, the inhibitory effect of O_2 on this radical-initiated copolymerization, carried out in thin films ($\sim$20 μm), leads to both an increase of the induction period (from 0.2 to 1 s) and a 4-fold decrease of the reaction rate (Fig. 6). However, the effect is much more pronounced on the acrylate monomer which barely reaches 50% conversion after a 20-s exposure (Fig. 6). The fact that molecular oxygen is a less efficient scavenger in the HBVE/HPMI system than in an acrylate monomer having a similar structure was unexpected. It could be due to either a lower reactivity towards O_2 of VE and MI radicals, or to a polymerization mechanism involving a donor–acceptor complex. Another explanation suggested by one of the referees would be to consider that the concentration of dissolved oxygen is lower in the VE/MI formulation than in the acrylate-based resin.

With difunctional monomers, such as DODBMI and iPDB-DVE, the polymerization of the laminated film occurred as rapidly as with the monofunctional monomers upon u.v. exposure (Fig. 7), but it levelled off at approx. 80% conversion for both monomers because of the severe mobility restrictions existing in the tridimensional polymer network formed. The amount of $MI_{polymerized}$ was found to be slightly higher than that of $VE_{polymerized}$, probably because small quantities of crosslinked MI homopolymer linkages were formed in addition to the alternating copolymer network.

The less pronounced inhibitory effect of atmospheric oxygen observed with such difunctional monomers than with the monofunctional monomers (Fig. 7) was attributed to their higher viscosity which slows down the diffusion of O_2 into the sample. All the maleimide/donor combinations evaluated so far show a significantly reduced sensitivity towards oxygen inhibition, in comparison with the photoinitiator containing acrylate system having the same average functionality and the same viscosity.

Similar results have been obtained by u.v.-irradiation of an equimolar mixture of divinyl ether of triethylene-12]. The fast photobleaching at 300 nm caused by the polymerization of the maleimide moiety allows the incident u.v.



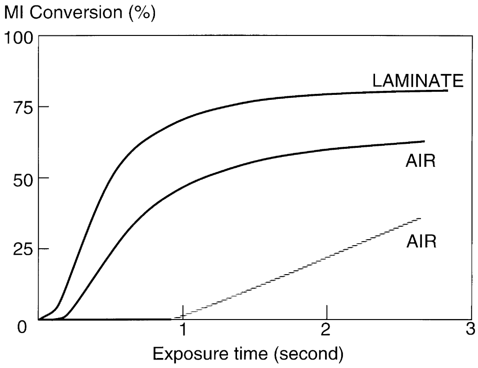


Fig. 7. Photo-induced copolymerization of difunctional maleimide/vinyl ether monomers (DODBMI/IPDB-DVE) (——: HBVE/HPMI in air).

radiation to penetrate deeper into the sample and thus to cure thick samples. A distinct feature of this system is that the material formed by such photo-induced frontal polymerization [13] is perfectly clear and non-coloured, in contrast to u.v-curable acrylate-based resins where coloured products are formed upon photolysis of the initiator. The cross-linked polymer is therefore likely to be more resistant to photodegradation when exposed to natural weathering.

3.2. Photopolymerization of maleimide and N-vinyl pyrrolidone

A substantial increase in polymerization efficiency was observed when the vinyl-ether monomer was replaced by *N*-vinyl pyrrolidone (NVP) in the HPMI–HBVE formulation [14]. The polymerization of NVP, monitored by *R.T.*i.r. spectroscopy at 1635 cm^{-1}, was found to proceed nearly as fast as that of the maleimide, but it levelled off at a final conversion of 80%, when essentially all of the maleimide had reacted (Fig. 8). The HPMI/NVP combination proved to be the most reactive of all the photoinitiator-free formulations studied so far, with a $R_p/[M]_0$ value of nearly 2 s^{-1} under the given irradiation conditions, a result in full agreement with previous observations by DSC analysis [7]. The disappearance of the maleimide was also followed by real-time u.v. spectroscopy, by monitoring the decrease of its absorbance at 300 nm. The MI polymerization profiles recorded by these two techniques are in good agreement, as shown in Fig. 8 (curves 1 and 3). The fast photobleaching of the formulation is one of the main advantages of these photoinitiator-free systems, as it allows one to achieve a deep through cure of thick samples by performing a frontal polymerization. In addition, this type of u.v-cured polymer could also (in addition to vinyl ether/maleimide combinations) be of interest for outdoor applications, as they are essentially transparent in the range of the terrestrial solar emission spectrum.

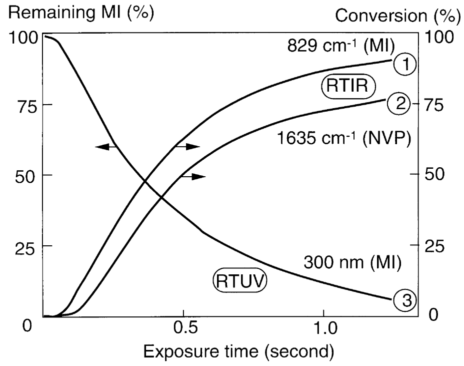


Fig. 8. Photo-induced copolymerization of a maleimide/*N*-vinylpyrrolidone combination (HPMI/NVP), monitored by *R.T.*i.r. and *R.T.*u.v. spectroscopy. $I = 150$ mW cm^{-2}.laminate.

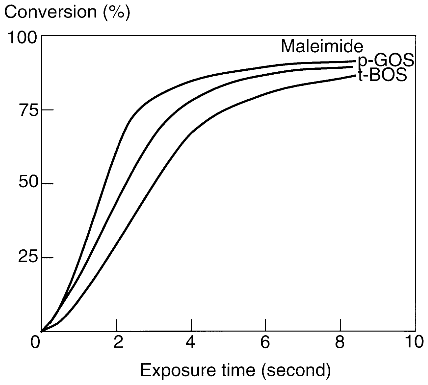


Fig. 9. Photo-induced copolymerization of maleimide (HPMI) and *p*-alkoxystyrene monomers. $I = 150$ mW cm^{-2}.laminate.

3.3. Photopolymerization of maleimide and alkoxy-styrene monomers

Styryloxy monomers

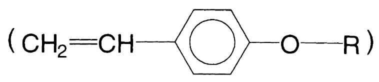


exhibit a strong electron donor character and they are therefore potential candidates to give, in combination with maleimides, photoinitiator-free u.v.-curable formulation proceeding by an alternating copolymerization process. It was recently shown by Jönsson et al. [6] that *p*-alkoxystyrenes like vinyl ethers undergo an effective copolymerization with *N*-substituted maleimides by simple u.v. exposure in the absence of any added photoinitiator. Fig. 9 shows the polymerization profiles recorded by *R.T.*i.r. spectroscopy upon u.v. exposure of a stoichiometric mixture of HPMI and *p*-glycidyloxystyrene (*p*-GOS). The styrene and maleimide double bonds were found to disappear according to similar kinetics, but less than half as fast as in the HBVE/HPMI combination, which suggests that the copolymerization propagation reaction is slower in the styryloxy than in the vinyl ether-based formulation. Replacing *p*-GOS by the *p*-tert.butoxystyrene(*t*-BOS), which does not contain any abstractable hydrogen in its monomeric form, causes only a minor drop in cure speed (Fig. 9), probably because there are still ample abstractable hydrogens on the HPMI moiety. The higher final conversion reached in the *p*-GOS/HPMI combination may be attributed in part to a greater molecular

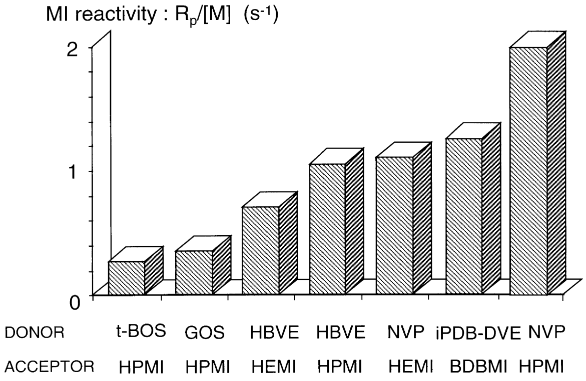


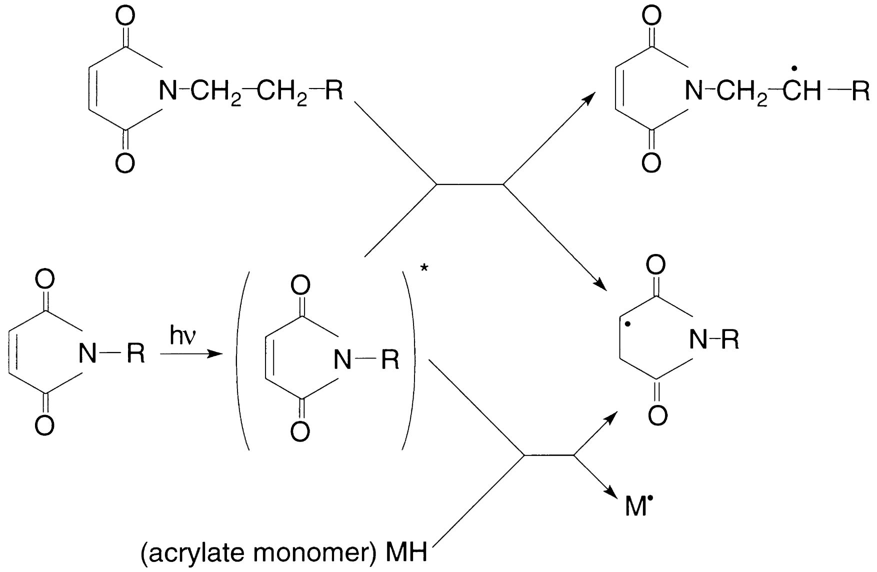
Fig. 10. Performance analysis of u.v.-curable maleimide-based formulations. Stoichiometric composition. $I = 150$ mW cm^{-2}.laminate.

mobility and lower T_g of the polymer formed, compared with the *t*-BOS/HPMI system.

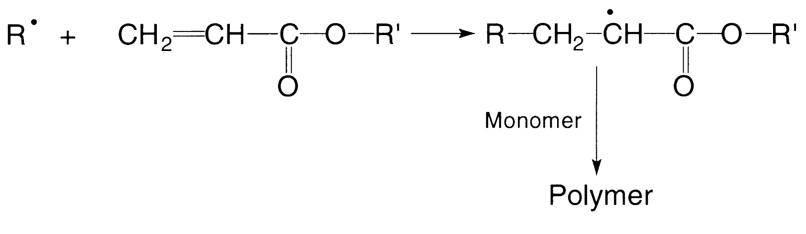
The performance of the various u.v.-curable maleimide-based formulations are summarized in Fig. 10. For a reliable comparison, the ratio of the maximum rate of polymerization to the initial monomer concentration was selected as a criterion, as the various stoichiometric formulations do not contain the same MI molar concentration. The NVP/HPMI combination appears to be the most reactive, with a $R_p/[M]_0$ value more than 8 times that of the least reactive combination *t*-BOS/HPMI. These results emphasize the crucial role, in the polymerization of MI-based photoinitiator-free systems, of the co-monomer.

3.4. Monomeric copolymerizable photoinitiator

It was recently stated that maleimides can be considered as ‘monomeric copolymerizable photoinitiators’, as they are capable of generating free radicals by hydrogen abstraction from their excited states [6]. As pointed out in the Introduction, the photoinitiated homopolymerization of *N*-alkyl maleimides is considered to proceed through hydrogen abstraction by the ene portion of the maleimide [15]. In a recent study [16], it was shown that different types of *N*-substituted maleimides act as efficient initiators of the polymerization of hexanediol diacrylate upon u.v. exposure, when readily abstractable hydrogens are available. For such maleimide/acrylate formulations, the initiating process can be represented schematically as follows:



The free radicals (R•) generated by these various hydrogen abstraction reactions would then initiate the polymerization by reacting with the acrylate double bond of another monomer:


$$R^{\bullet} + CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}R' \longrightarrow R{-}CH_2{-}\dot{C}H{-}\underset{\underset{O}{\|}}{C}{-}O{-}R' \xrightarrow{\text{Monomer}} \text{Polymer}$$

The addition of small amounts (1 wt%) of triethyleneglycol bis-carbonate bis-ethylmaleimide (TEGBCBMI) was indeed found to accelerate substantially the polymerization of tripropyleneglycol diacrylate (TPGDA) upon u.v. exposure (Fig. 11). Although the reaction developed less efficiently than in the presence of the usual radical photoinitiators, half of the diacrylate monomer was polymerized within 15 s, compared with only 15% for neat TPGDA. A similar trend was observed with hexanediol

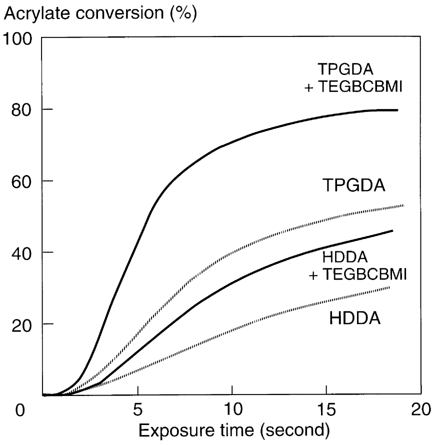


Fig. 11. Influence of a bis-maleimide ([TEGBCDMI] = 1 wt%) on the photo-induced polymerization of tripropyleneglycol diacrylate (TPGDA) and hexanediol diacrylate (HDDA). $I = 150$ mW cm^{-2}.laminate.

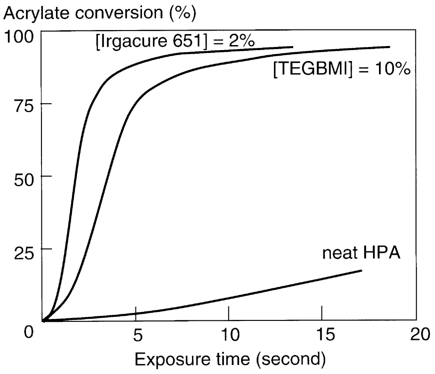


Fig. 12. Influence of tetraethyleneglycol bis-maleimide (10 wt%) on the photo-induced polymerization of hydroxypropylacrylate (HPA). $I =$ 150 mW cm^{-2}.laminate.

diacrylate (HDDA), except that the polymerization proceeded at a slower rate because of the weaker hydrogen donor character of this monomer. The reaction can be greatly accelerated by the addition of typical H-donor molecules, such as trithiols, polyalkyleneglycols and tertiary amines [6]. Increasing the maleimide concentration is another way to speed up the polymerization of the acrylate monomer, as shown in Fig. 12 for hydroxypropyl acrylate. While this monomer undergoes essentially no polymerization upon u.v. exposure under air-free conditions, it was found to reach 85% conversion within 5 s when irradiated in the presence of 10 wt% tetraethyleneglycol bis-maleimide. Table 1 summarizes the photoinitiating performance of these *N*-substituted bis- maleimides in the light-induced polymerization of acrylate monomers, in terms of reactivity (ratio $R_p/[M]_0$) and degree of conversion of the acrylate monomer after a 1-min exposure.

4. Conclusion

N-substituted alkyl maleimides undergo an easy copolymerization when they are exposed to u.v.-radiation in the presence of electron donor monomers, such as vinyl ethers, *N*-vinyl pyrrolidone or *p*-alkoxy styrenes. Photoinitiator-free vinyl ether/maleimide combinations proved to be as reactive as acrylate-based resins containing a radical-type photoinitiator. The presence of labile abstractable hydrogen atoms on either one of the two monomers enhances substantially the polymerization efficiency, thus showing that the initiation mechanism involves hydrogen abstraction by the excited maleimide groups. Oxygen inhibition appears to be less pronounced in these photoinitiator-free u.v.-curable systems than in acrylate-based resins. This property, together with the high reactivity and the fast photobleaching allowing thick items to be readily cured, are making such maleimide-based resins well suited for specific applications of the u.v.-curing technology, in particular to produce fast-drying coatings and adhesives.

Table 1
Photoinitiating performance of *N*-substituted bis-maleimides in the light-induced polymerization of acrylate monomers

Monomer	Reactivity $R_p/[M]$ (m s^{-1})	Acrylate Conversion after 1 min (%)
HDDA	30	48
HDDA + TEGBCBMI (1%)	60	70
TPGDA	70	65
TPGDA + TEGBCBMI (1%)	150	88
HPA	20	30
HPA + TEGBMI (10%)	210	95

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