

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Photoinitiated Polymerization of Vinyl Ether and Acrylate Monomer Mixtures

C. Decker<sup>a</sup>; D. Decker<sup>a</sup>

<sup>a</sup> Laboratoire de Photochimie générale (URA-CNRS N°431) Ecole Nationale Supérieure de Chimie Université de Haute Alsace 3, Mulhouse, France

**To cite this Article** Decker, C. and Decker, D.(1997) 'Photoinitiated Polymerization of Vinyl Ether and Acrylate Monomer Mixtures', *Journal of Macromolecular Science, Part A*, 34: 4, 605 – 625

**To link to this Article: DOI:** 10.1080/10601329708014988

**URL:** <http://dx.doi.org/10.1080/10601329708014988>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## PHOTOINITIATED POLYMERIZATION OF VINYL ETHER AND ACRYLATE MONOMER MIXTURES

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, 6820 Mulhouse, France

**Key Words:** Vinyl ether; Acrylate; Polymerization; UV radiation; Kinetics; Infrared spectroscopy

### ABSTRACT

The photoinitiated cationic polymerization of vinyl ether (VE) monomers has been studied by real-time infrared spectroscopy. For the divinyl ether of triethylene glycol, the chain reaction was shown to develop rapidly and extensively, with kinetic chain lengths on the order of 10,000. Interpenetrating polymer networks have been produced by UV curing of a vinyl ether/acrylate mixture in the presence of a cationic photoinitiator. The acrylate double bond polymerizes faster than the vinyl ether double bond and reaches 95% conversion in triacrylate monomers. Vinyl ether/acrylate hybrids were also found to polymerize readily upon UV exposure in the presence of a radical photoinitiator, according to a cross-propagation mechanism which generates a copolymer with isolated VE units. Acrylate radicals were shown to be twice as reactive toward the acrylate double bond than toward the vinyl ether double bond, thus leading to a UV-cured polymer which contains a relatively large amount of unreacted double bonds. The residual unsaturation content was markedly reduced by the addition of a cationic photoinitiator and by exposing the sample successively to filtered and unfiltered UV radiation.

## INTRODUCTION

Vinyl ethers (VE) are among the most reactive monomers known to polymerize by a cationic mechanism. Therefore, they are increasingly used in UV-curing applications, mainly as fast drying coatings, adhesives, and photoresists. These compounds appear as a valuable alternative to the widely utilized acrylate monomers, which present a strong odor and irritating properties. Since the early work of Crivello [1], who investigated the photoinitiated cationic polymerization of difunctional vinyl ethers, the performances of these monomers in UV-curable formulations have been thoroughly evaluated in both cationic- and radical-type systems [2–11]. The subject has been recently covered by Lapin in a comprehensive review [12].

Besides acting as effective viscosity reducers in UV-curable resins, VE monomers offer the great advantage of undergoing a fast and complete polymerization in the presence of photogenerated protonic acids to yield polymer materials showing excellent solvent resistance and physical properties which can be modulated by acting on the chemical structure of the vinyl ether monomer or oligomer. Although neat vinyl ethers do not polymerize in the presence of free radicals because of their electron-rich double bond, they are still able to undergo a radical-initiated copolymerization in the presence of either acrylate monomers [1, 3] or unsaturated polyesters like maleates [7, 9, 10].

The main objective of the present work was to monitor quantitatively both the cationic and the radical-induced polymerization of vinyl ether/acrylate hybrid systems exposed to UV radiation, in order to evaluate the important kinetic parameters. As in a previous study on UV-curable acrylate resins [13, 14], polymerization profiles were recorded directly by real-time infrared (RTIR) spectroscopy, a technique which permits one to follow ultrafast photochemical reactions and thus gives valuable information about the basic mechanism of such crosslinking polymerization. It proved particularly well suited to study the UV curing of hybrid systems because RTIR spectroscopy offers the unique advantage of allowing the polymerization of each monomer of the mixture to be monitored in-situ and quantitatively during the whole process.

## EXPERIMENTAL

### Materials

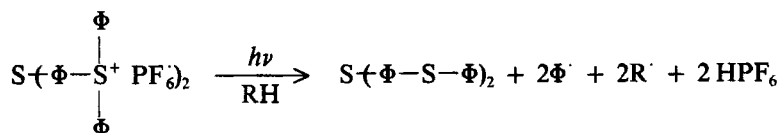
A typical UV-curable formulation contains three basic components: a difunctional vinyl ether monomer, an acrylate monomer or telechelic oligomer, and a cationic- or radical-type photoinitiator.

*Vinyl Ethers.* The following vinyl ethers from ISP were used in this study: the divinyl ether of diethylene glycol (RapiCure DVE-2), the divinyl ether of triethylene glycol (RapiCure DVE-3), and a divinyl ether derivative of bisphenol A (DVE-BA) obtained by reaction of hydroxybutylvinyl ether (HBVE) with the diglycidyl ether of bisphenol A (Aldrich).

*Acrylates.* The following acrylate monomer and telechelic oligomers from UCB Chemicals were used, in combination with a vinyl ether monomer: trimethylol-

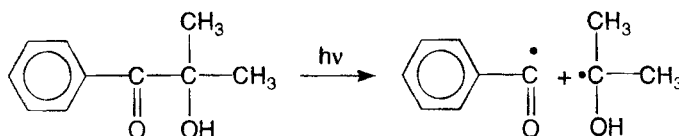
propane triacrylate (TMPTA), a diacrylate derivative of bisphenol A (Ebecryl 600), and a polyether tetracrylate (Ebecryl 80).

**Photoinitiator.** A hexafluorophosphate triarylsulfonium salt, TAS (Degacure KI-85 from Degussa), was used as a cationic photoinitiator at a typical concentration of 5% by weight. As the commercial product is a 40 wt% solution in propylene carbonate, the actual concentration of onium salt was 2 wt%. This compound is known to generate a strong protonic acid upon photolysis in the presence of a hydrogen donor molecule, which is an efficient initiator of cationic polymerization [15]:



Because the sulfonium salt also produces free radicals upon UV irradiation, it can serve to initiate both the cationic and the radical polymerization of vinyl ether/acrylate mixtures [1].

In the UV-curing experiments where the polymerization of the vinyl ether/acrylate mixture was to occur by a purely radical process, a hydroxy-phenyl ketone, HPK (Darocur 1173 from CIBA), was used as the photoinitiator. This compound is known to generate very reactive benzoyl and alkyl radicals upon UV irradiation by a Norrish I cleavage reaction, with a high quantum yield [16].



The chemical formulas of the various compounds used in this study are given in Fig. 1.

### Irradiation

The liquid resin was applied onto a 15- $\mu\text{m}$  thick transparent polypropylene film by a calibrated wire-wound applicator. In most experiments a second polypropylene film was laminated onto the sample to prevent oxygen diffusion and flowing when placed in a vertical position. The thickness of the monomer film, typically 25  $\mu\text{m}$ , was determined accurately from its IR absorbance at 810  $\text{cm}^{-1}$  by means of a calibration curve.

The sample was inserted into a slide frame and placed in the compartment of an IR spectrophotometer (Perkin-Elmer Model 781) where it was exposed for a few seconds to the UV radiation of a medium pressure mercury lamp. The light intensity at the sample position was measured by a radiometer (International Light IL-390). All irradiations were performed at a light intensity of 50  $\text{mW}\cdot\text{cm}^{-2}$ . A 340-nm cut-off filter was used in some experiments to select near-UV radiation.

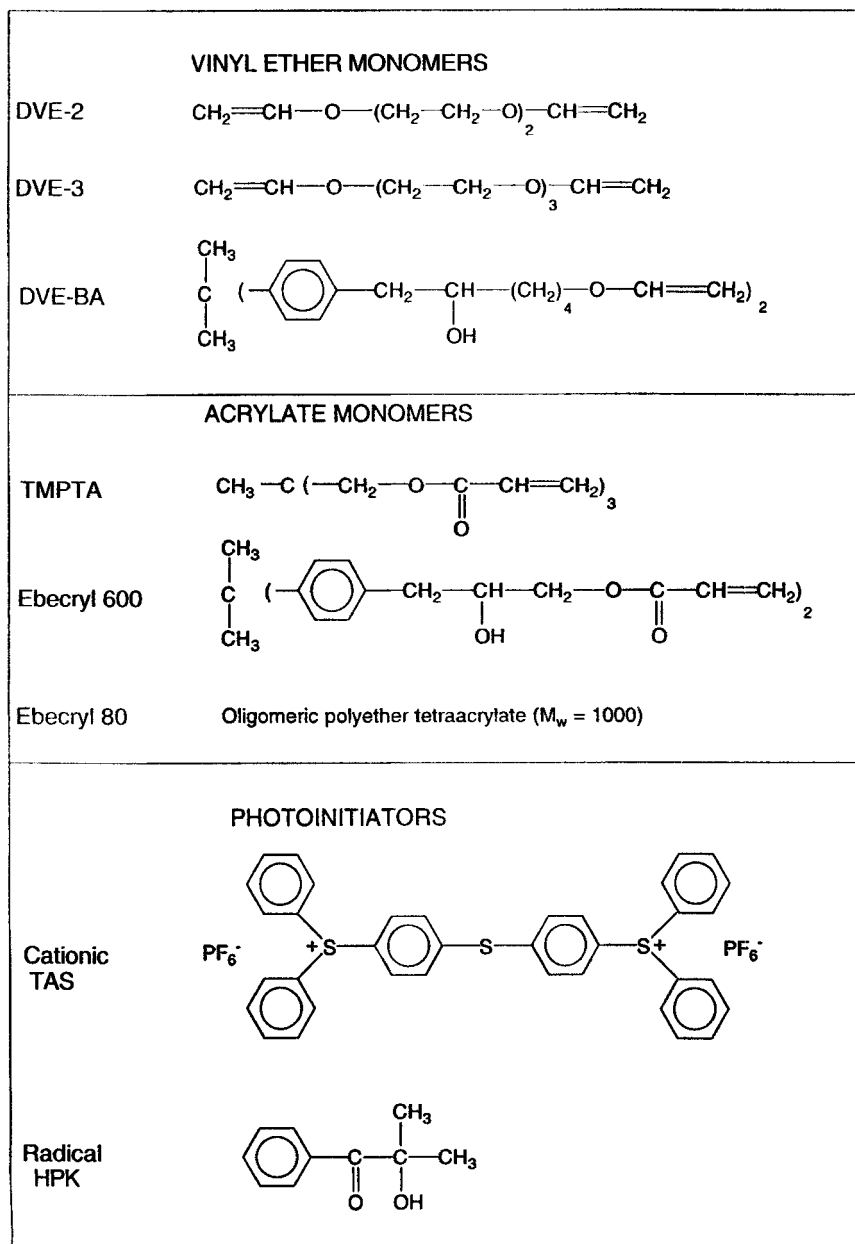


FIG. 1. Chemical formulas of the products used.

### Analysis

Real-time infrared (RTIR) spectroscopy was used to follow the polymerization of the two monomers continuously upon UV exposure. This technique has been described in detail in a previous paper [13]. The sample was exposed simultaneously to the UV beam which induces the polymerization reaction and to the IR beam

which detects the amount of monomer present. The wavenumber of the dispersive IR spectrophotometer (spectral resolution of  $2\text{ cm}^{-1}$ ) was set either at  $1415\text{ cm}^{-1}$  to monitor the decrease of the acrylate double bond or at  $1628\text{ cm}^{-1}$  to monitor that of the vinyl ether double bond. However, because the acrylate double bond also shows a weak absorbance at  $1628\text{ cm}^{-1}$ , it was necessary to subtract the acrylate contribution from the curve recorded at  $1628\text{ cm}^{-1}$  to obtain the actual polymerization profile of the vinyl ether monomer. The formulation reactivity ( $R$ ) was determined from the slope of the conversion versus time curve, which is directly recorded by RTIR spectroscopy:

$$R = \frac{1}{t_{100} - t_0} = \frac{R_p}{[\text{VE}]_0}$$

where  $t_0$  and  $t_{100}$  are extrapolated values of the exposure time for 0 and 100% conversion respectively,  $R_p$  is the maximum rate of polymerization, and  $[\text{VE}]_0$  is the initial concentration in vinyl ether double bonds. Because of its time resolution of only 50 ms, RTIR spectroscopy permits one to monitor quantitatively and in real time high-speed polymerization processes occurring within less than 1 second. This technique also provides an accurate evaluation of the amount of residual unsaturation (RU) of each type (acrylate or vinyl ether) which remains in the photocured polymer.

## PHOTOINITIATED CATIONIC POLYMERIZATION

As the first step we studied the polymerization of some vinyl ether monomers exposed to UV radiation in the presence of a cationic photoinitiator. The effect on the reaction kinetics of adding various multifunctional acrylate monomers to the formulation was then examined, in particular with respect to the actual rate of polymerization and the final conversion of each one of the two types of monomer.

### Vinyl Ether Monomers

The light-induced polymerization of three vinyl ether monomers (DVE-2, DVE-3, and DVE-BA) was monitored in real time by following the decrease of the strong IR absorbance at  $1628\text{ cm}^{-1}$  of the vinyl ether double bond. Figure 2 shows the polymerization profiles recorded by RTIR spectroscopy upon exposure of a  $25\text{-}\mu\text{m}$  thick film to UV radiation at a light intensity of  $50\text{ mW}\cdot\text{cm}^{-2}$ . The concentration of the triarylsulfonium salt used as the photoinitiator was set at 2% in order to achieve a uniform cure of the sample.

After a short induction period due to the presence of a nucleophilic stabilizer and traces of water in such commercial products, the polymerization of both DVE-2 and DVE-3 developed rapidly to reach nearly 100% conversion after a 5-second exposure, so that the crosslinked polymer contained no residual unsaturation. This is due to the elastomeric character of the polymer formed (low  $T_g$ ), which provides sufficient molecular mobility to the reactive species to complete the chain process. The divinyl ether bisphenol A derivative is much less reactive and polymerizes about 20 times slower than the other two monomers. This effect is a result of the lower concentration in vinyl ether double bonds in the telechelic monomer, and mainly of

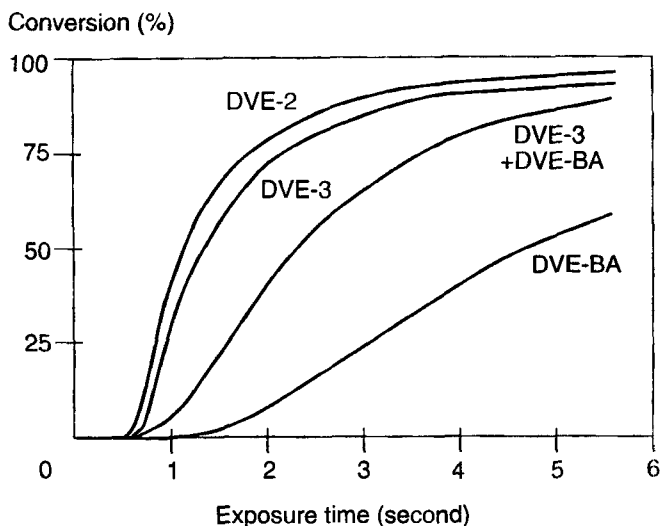


FIG. 2. Conversion versus time profiles recorded by RTIR spectroscopy in the photo-initiated cationic polymerization of various vinyl ether monomers. Photoinitiator:  $[TAS] = 2\%$ ; light intensity:  $I = 50 \text{ mW} \cdot \text{cm}^{-2}$ .

the much higher viscosity of DVE-BA (9,000 mPa·s, compared to 10 mPa·s for DVE-3). Indeed, the addition of DVE-2 to the DVE-BA formulation leads to a substantial increase of the reactivity, expressed as the ratio  $R_p/[VE]_0$  to take into account the variation of the initial concentration in vinyl ether double bonds. Figure 3 shows the marked influence of the initial viscosity on the reactivity of a UV-curable vinyl ether resin.

Such a pronounced effect was not observed in the radical-induced polymerization of acrylate monomers, where an increase of the viscosity first leads to an increase of the polymerization rate. This is due to the fact that a decrease in molecular mobility has a greater slowing down effect on the bimolecular termination reaction than on the propagation step, a phenomenon which was taken as responsible for the autoacceleration often observed in the early stage of bulk polymerization. In cationic polymerization the propagation rate constant is also expected to decrease with increasing viscosity, but the termination step should be less affected by mobility restrictions because it involves the reaction of cationic species with nucleophilic impurities, and not the encounter of two growing polymer chains.

Compared to the radical-induced polymerization of acrylate systems, the cationic polymerization of vinyl ethers presents two distinct advantages.

1. It is insensitive to oxygen inhibition because of the lack of reactivity of the propagating carbocation toward the  $O_2$  molecule. Indeed, we recorded similar polymerization profiles for samples irradiated either in the presence of air or in  $O_2$ -free conditions.
2. The carbocations do not react among themselves, so that the polymerization will continue to proceed in the dark in the absence of nucleophilic species after the light has been switched off and the initiating species are no longer generated.

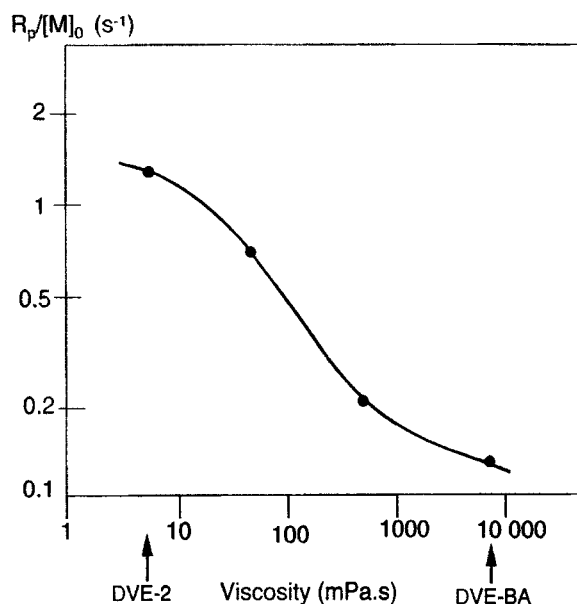


FIG. 3. Influence of viscosity on the photopolymerization of a DVE-2/DVE-BA mixture.

As a result of this postpolymerization, the photocured vinyl ether polymers contained no detectable VE unsaturation after a 24-hour storage in the dark. Figure 4 shows two typical polymerization profiles recorded by RTIR spectroscopy after a 0.8 and a 1.2 second exposure. Under those conditions, 85 and 60%, respectively, of the polymer have been produced after the UV irradiation. Because of such an important dark polymerization, the kinetic profile obtained by discrete measurements, which are usually carried out at least 10 seconds after the exposure, will greatly overestimate the cure speed, as shown on Fig. 4. It is only by a real-time technique, like RTIR spectroscopy with its short response time (50 ms), that it is possible to have access to the actual polymerization profiles, as illustrated in Fig. 2.

By taking the ratio of the number of vinyl ether double bonds polymerized after a short exposure to the number of photons absorbed by the sample, one can evaluate the quantum yield of polymerization,  $\Phi_p$ . For the most reactive system, DVE-3,  $\Phi_p$  was measured to be on the order of  $5,000 \text{ mol} \cdot \text{einstein}^{-1}$ . This quantity was found to be independent of the light intensity, as expected for a photoinitiated chain reaction where only one propagating species is involved in the termination reaction. The kinetic chain length can then be calculated from the ratio of  $\Phi_p$  to the initiation quantum yield (typically 0.5 for such onium salts [15]). It appears that each photogenerated proton is capable of initiating the polymerization of up to 10,000 vinyl ether functions, a value which clearly shows the efficiency of the chain reaction in such ultrafast polymerizations.



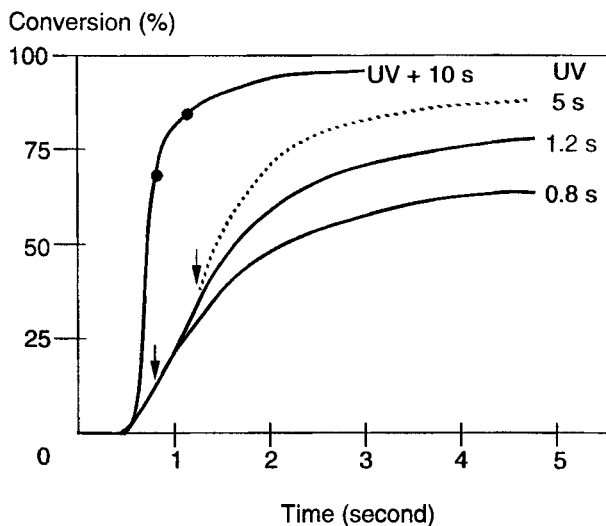


FIG. 4. Importance of the dark reaction in the UV curing of a DVE-3/DVE-BA mixture. (···) Continuous irradiation.  $I = 50 \text{ mW} \cdot \text{cm}^{-2}$ .

## Vinyl Ether–Acrylate Mixtures

### $\text{O}_2$ -Free Formulations

A distinct feature of sulfonium salts is to generate free radicals upon photolysis in the presence of a H donor molecule. Therefore, it is possible to use this type of photoinitiator to polymerize acrylate monomers like trimethylolpropane triacrylate (TMPTA), as shown in Fig. 5 (Curve a). However, the photopolymerization of bulk TMPTA carried out on a laminated film and monitored by the decrease of the acrylate peak at  $1415 \text{ cm}^{-1}$  appears to be much slower with the onium salt than with a conventional radical photoinitiator like Darocur 1173 (Fig. 5, Curve b). It also develops less extensively, leveling off at 40% conversion after a 30-second exposure compared to 60% for Darocur 1173. This is probably due to a faster consumption of the cationic photoinitiator [17] as well as to the poor H donor character of TMPTA.

The addition of DVE-3 to TMPTA (in a 1-to-1 weight ratio) was found to markedly accelerate the polymerization of the acrylate function, as shown by Fig. 5 (Curve c). The 8-fold increase of the acrylate polymerization rate was attributed to the stronger hydrogen donor character of the vinyl ether. A greater number of radicals is generated by H abstraction upon photolysis of the sulfonium salt, thus increasing the initiation rate of the acrylate polymerization. An interesting two-step profile was recorded by monitoring the IR absorbance at  $1628 \text{ cm}^{-1}$ , where both TMPTA and DVE-3 absorb in a 1-to-4 ratio (Fig. 6a). It can be seen that, due to the longer induction period of the vinyl ether monomer (0.6 seconds), most of the acrylate functions have already reacted when DVE-3 starts to polymerize cationically. By subtracting the cure profile of TMPTA recorded at  $1415 \text{ cm}^{-1}$ , one can obtain the polymerization profile of DVE-3 (Fig. 6b). By taking the first derivative of Curve a, one can determine the polymerization rate of each monomer and its

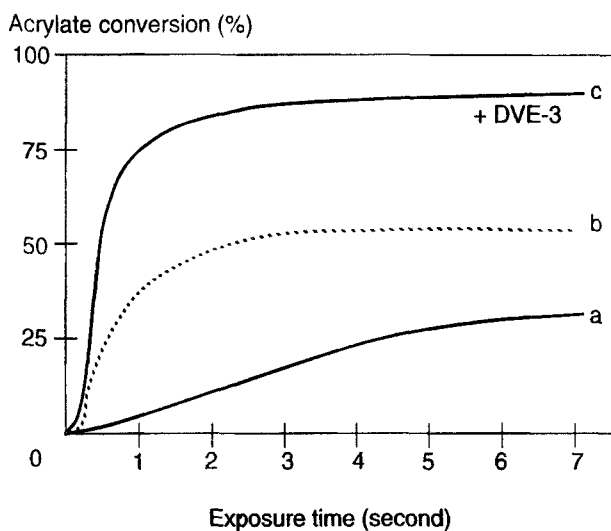


FIG. 5. Photopolymerization of TMPTA in the presence of 2% TAS (a), 3% HPK (b), and of a 1/1 mixture by weight of TMPTA and DVE-3 in the presence of 2% TAS (c).  $I = 50 \text{ mW} \cdot \text{cm}^{-2}$ . Laminate ( $\text{O}_2$ -free conditions).

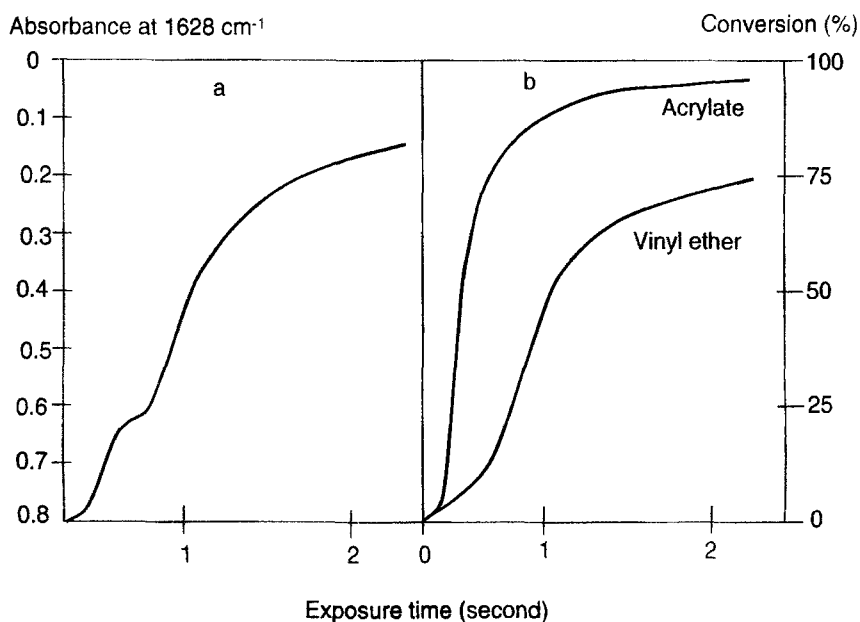


FIG. 6. Photopolymerization of a TMPTA/DVE-3 mixture in the presence of a cationic photoinitiator ( $[\text{TAS}] = 2\%$ ). (a) Variation of the absorbance at  $1628 \text{ cm}^{-1}$ . (b) Conversion versus time profiles of the acrylate and vinyl ether functions.

dependence on the exposure time. The bimodal rate obtained (Fig. 7) clearly shows that the radical-induced polymerization of the acrylate takes place before the cationic polymerization of the vinyl ether.

It should be noticed that in addition to the cationic polymerization of DVE-3, a radical-induced copolymerization of the vinyl ether and acrylate functions also takes place in the early stage of irradiation as long as acrylate double bonds are available. This process, which will be studied in the next section, is characterized by the slow polymerization of the vinyl ether which occurs during the first 0.6 second of exposure, i.e., the induction period of the cationic polymerization. In one experiment the sample was exposed to a 0.8-second flash of light. The profile recorded was essentially the same as that obtained upon continuous exposure (Fig. 6), the vinyl ether monomer then polymerizing cationically only in the dark to give the same UV-cured polymer. The presence of TMPTA was found to reduce significantly the DVE polymerization rate as well as its maximum conversion, as shown by Figs. 2 and 6(b), most probably because of chain mobility restrictions brought upon by the stiff acrylate network performed.

In such a hybrid system containing a cationic photoinitiator, the vinyl ether and acrylate monomers are expected to polymerize by cationic and radical mechanisms, respectively, with the formation of two interpenetrating polymer networks having well contrasting characteristics: on one hand a stiff and glassy acrylate polymer and on the other hand a highly flexible and elastomeric vinyl ether polymer. The latter will make chain migration and diffusional processes more easy, and will therefore favor the polymerization of the acrylate function, as shown by the marked increase in the extent of the final acrylate cure which rises from 60% for TMPTA to 93% conversion in the hybrid system (Fig. 5).

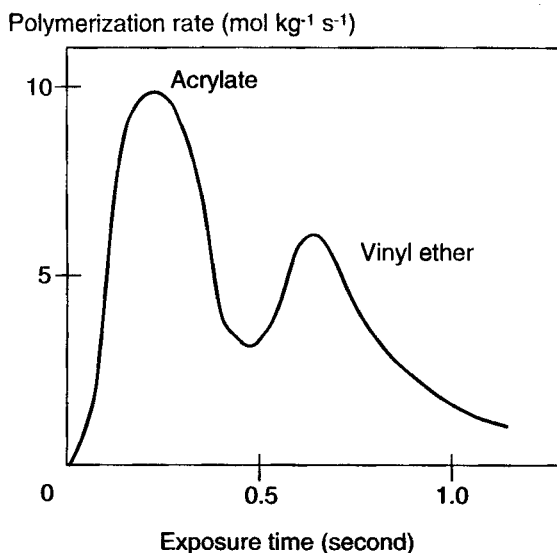


FIG. 7. Polymerization rate profile in the photoinitiated cationic polymerization of a TMPTA/DVE-3 mixture. [TAS] = 2%. TMPTA/DVE-3 = 1. Laminate.

## Air-Saturated Formulations

In the presence of air, TMPTA was found to hardly polymerize under the experimental conditions used (thin films exposed to relatively low intensity radiation) because of the well-known inhibition effect of oxygen on radical-induced polymerization (Fig. 8). As cationic polymerization of vinyl ethers is not affected by the presence of oxygen, the polymerization profile of DVE-3 is essentially the same as that recorded in neat DVE-3 (Fig. 2). After a short induction period due to the stabilizer, the polymerization develops faster and more extensively in the presence of air than in the  $O_2$ -free laminated sample, as shown in Fig. 8. This behavior can be accounted for by the fact that the acrylate polymer network, which hinders VE polymerization in such a hybrid system, is hardly formed in the presence of air. Under those conditions the radical-induced copolymerization is not expected to take place either.

When the light intensity was increased tenfold to reach values comparable to those of industrial UV-curing lines, the exposure time was reduced in the same ratio and oxygen diffusion became much less important. The polymerization of both vinyl ether and the acrylate monomers developed extensively in the presence of air, as previously observed with the laminated samples. By acting on the  $O_2$  concentration or on the light intensity, one can drastically change the polymerization kinetics of the two types of reactive functions and consequently modify the structure of the crosslinked polymer.

By using a 200-mW krypton ion laser tuned to its UV emission lines at 337 and 356 nm as the light source, the polymerization of vinyl ether/acrylate hybrids was found to occur quasi-instantly in the presence of air to give tack-free and hard coatings, very much like those for acrylate resins [18]. Reducing the photoinitiator

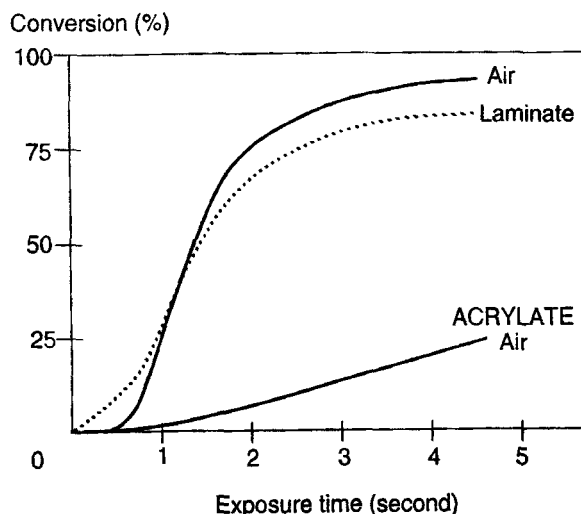


FIG. 8. Influence of oxygen on the photoinitiated cationic polymerization of a 1/1 mixture by weight of TMPTA and DVE-3. [TAS] = 2%. Film thickness: 24  $\mu\text{m}$ . (···) Vinyl ether conversion in  $O_2$ -free conditions.

concentration leads to the expected decrease of the polymerization rate, but also to a greater penetration of the laser beam, so that a deep cure of 3 mm thick samples was achieved within a few seconds.

### PHOTOINITIATED RADICAL POLYMERIZATION

Vinyl ether (VE) monomers have been shown to undergo fast radical-induced copolymerization when they are exposed to UV radiation together with an acrylate (A) monomer [1, 3, 8, 19, 20]. While inactive toward the electron-rich vinyl ether double bond, VE radicals are capable of reacting with the electron-poor acrylate double bond. These monomers can thus be used as reactive diluents to reduce the viscosity of acrylate functionalized oligomers and to give UV-curable resins having less odor and a lower irritation index.

#### Radical Photoinitiators

Figure 9 shows the polymerization profiles recorded by RTIR spectroscopy upon UV exposure of a mixture of DVE-3 and a polyether acrylate oligomer (Ebecryl 80) in the presence of a radical photoinitiator (2% HPK). The composition of the mixture was adjusted to have an acrylate to vinyl ether double bond ratio of 2. The acrylate function, monitored at  $1415\text{ cm}^{-1}$ , polymerizes faster and more extensively in the VE/A mixture than in the polyether acrylate alone, i.e., the same trend as that observed previously with TMPTA. Up to 95% conversion was reached after a 5-second exposure because of the greater chain mobility of the crosslinked copolymer formed.

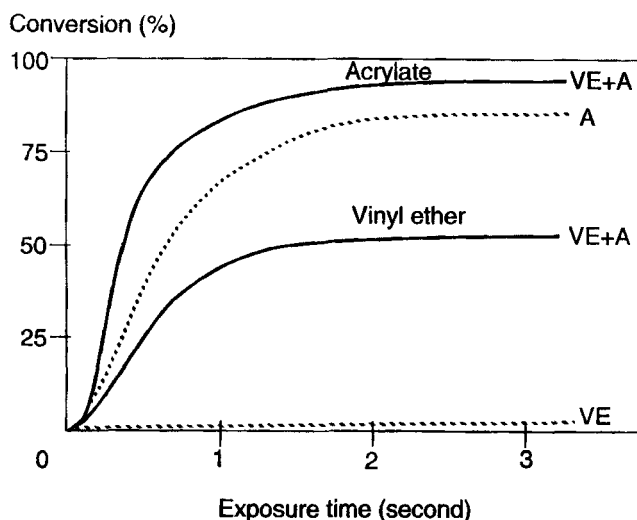


FIG. 9. Photoinitiated radical polymerization of a vinyl ether (DVE-3) and acrylate (Ebecryl 80) mixture. A/VE = 2; [HPK] = 2%. Laminate. (···) Neat Ebecryl 80 (A) or DVE-3 (VE).

The disappearance of the vinyl ether double bond was here again evaluated from the drop of the IR absorbance at  $1628\text{ cm}^{-1}$  after subtracting the acrylate absorbance at that wavelength. It clearly appears that the vinyl ether monomer participates to the polymerization from the very beginning of the irradiation, and that it stops polymerizing once the concentration of the acrylate double bond becomes too low. This result is in marked contrast with the conclusion of a recent study by DSC of the radical UV curing of a similar VE/A hybrid system [20] which stated that vinyl ether monomers participate in the polymerization toward the end of the reaction when the concentration of acrylate is low. Actually, the fact that similar heat flow profiles were observed with the pure acrylate and with the hybrid formulation [20] is a clear indication that the two types of monomers do polymerize simultaneously. A further confirmation is that the RTIR curve recorded at  $1628\text{ cm}^{-1}$  presents a typical S-shape profile, quite different from the two-step profile observed with the acrylate/vinyl ether formulation containing a cationic photoinitiator where the two monomers polymerized one after the other. In the presence of a radical photoinitiator, similar polymerization rate profiles were obtained for the acrylate and vinyl ether double bonds, as shown in Fig. 10. The vinyl ether polymerizes at half the rate of the acrylate, but the two monomers reach their maximum rate at the same time, after a 0.2-second exposure.

The cure limitation of the vinyl ether monomer at 50% conversion after 1 second irradiation was attributed to the fact that most of the acrylate double bonds have already polymerized at that time, or are trapped in the polymer network and are no longer accessible to the VE radicals, which are inactive toward the vinyl ether double bonds. Higher VE conversions can be reached by increasing the A/VE ratio. Figure 11 shows how the amount of vinyl ether and acrylate double bonds remaining in the UV-cured samples varies with the monomer feed composition. The amount of residual VE unsaturation was further reduced, down to 30%, by increasing the light intensity up to  $500\text{ mW}\cdot\text{cm}^{-2}$ .

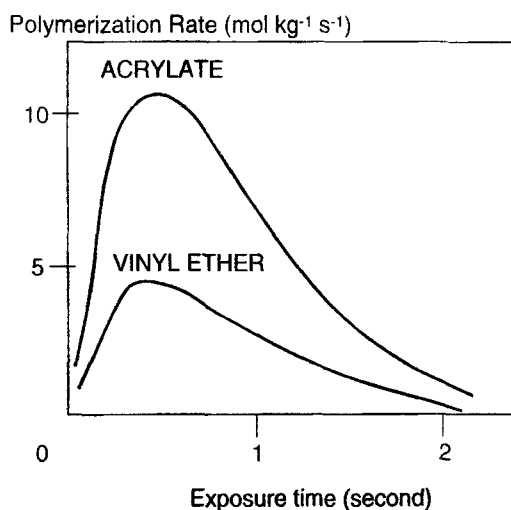


FIG. 10. Polymerization rate profiles in the photoinitiated radical polymerization of a DVE-3/Ebecryl 80 mixture. A/VE = 2; [HPK] = 2%. Laminate.  $I = 50\text{ mW}\cdot\text{cm}^{-2}$ .

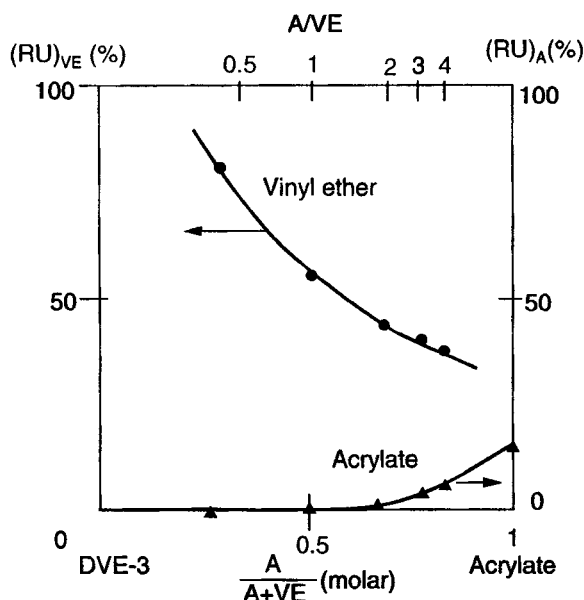


FIG. 11. Influence of the monomer feed ratio on the amount of residual vinyl ether and acrylate double bonds in a radical UV-cured DVE-3/Ebecryl 80 mixture, after 10 seconds exposure. [HPK] = 2%. Laminate.

### Radical and Cationic Photoinitiators

A more effective way to reduce the content of unreacted vinyl ether double bonds in the photocured copolymer is by the addition of a cationic photoinitiator. Figure 12 shows the polymerization profiles recorded upon UV exposure of a 70/30 mixture by weight of a bisphenol A diacrylate oligomer (Ebecryl 600) and DVE-3, which corresponds to a A/VE ratio of 1. The formulation contained both a radical (HPK) and a cationic (TAS) photoinitiator at a weight concentration of 2% each. After a rapid radical copolymerization of the vinyl ether and acrylate double bonds within the first 1 second exposure, the cationic polymerization of the unreacted vinyl ether functions continued to proceed at a sustained pace (Fig. 12, Curve b). However, because the triarylsulfonium salt is undergoing a fast photolysis [17] and has been mostly destroyed after a 2-second exposure, the cationic polymerization of the vinyl ether does not proceed to total completion. A simple method to overcome this difficulty is to perform the polymerization by a two-step irradiation (see below).

The accelerating effect of the vinyl ether monomer on the polymerization of acrylate oligomer is clearly apparent in Fig. 12 where the conversion versus time profile of Ebecryl 600 (Curve a) is compared to that of the Ebecryl 600/DVE-3 mixture (Curve c). In the presence of DVE-3, essentially all the acrylate double bonds polymerized within 2 seconds whereas the conversion hardly reached 50% upon prolonged exposure of the neat phenoxy-acrylate oligomer. The vinyl ether is acting here both as a reactive diluent to lower the formulation viscosity and as a plasticizer of the acrylate polymer network formed to increase its molecular mobil-

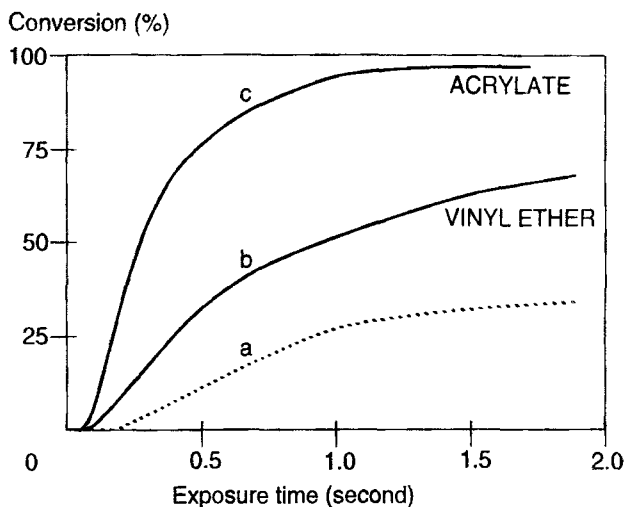


FIG. 12. Photoinitiated polymerization of a DVE-3/Ebecryl 600 mixture (30/70 by weight) in the presence of both a radical and a cationic photoinitiator. [TAS] = 2%; [HPK] = 2%. Laminate. (···) Neat DA-BA (Ebecryl 600) + HPK (2%).

ity. The product obtained upon UV curing of the hybrid formulation consists of two interpenetrating polymer networks: on the one hand a vinyl ether-acrylate copolymer with isolated VE units, and on the other hand a vinyl ether crosslinked homopolymer. Actually, the two networks are likely to be connected through the difunctional vinyl ether monomer which can polymerize by a radical mechanism at one terminal double bond and by a cationic mechanism at the other one.

A distinct feature of photoinduced polymerization of such hybrid systems is to allow each type of polymerization process to be temporally differentiated by selection of the proper photoinitiators and irradiation wavelengths. A first exposure at  $\lambda > 340$  nm will destroy only the radical photoinitiator and generate the benzoyl and alkyl radicals which will initiate the copolymerization of the acrylate and vinyl ether functions. A second exposure at  $\lambda > 250$  nm will destroy the sulfonium salt and generate the Brönsted acid which will initiate the cationic polymerization of the remaining vinyl ether functions.

This two-step generation of interpenetrating polymer networks (IPN) is clearly illustrated in Fig. 13 which shows the polymerization profiles of the vinyl ether and acrylate double bonds upon the two successive UV exposures. As the cationic photoinitiator is not consumed in the first exposure, a higher VE conversion can be reached by this two-step irradiation. A highly crosslinked polymer containing less than 1% residual unsaturation has thus been produced by a 10-second exposure at  $50 \text{ mW} \cdot \text{cm}^{-2}$ . This two-step procedure is easy to implement on an industrial UV-curing line by passing the sample successively under two lamps emitting in the near-UV for the first one and in the deep UV for the second one. With the DVE-3/Ebecryl 600 formulation, unsaturation-free IPNs were generated within less than 1 second by operating the line at a belt speed of 10 m/min.



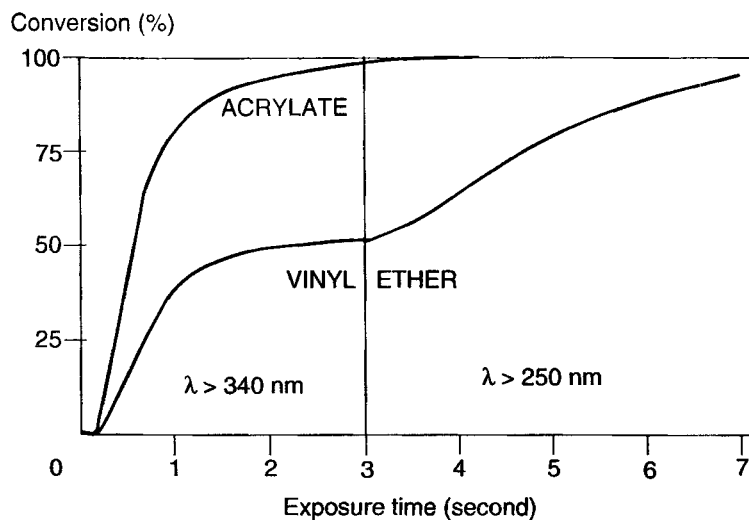


FIG. 13. Two-step polymerization of a DVE-3/Ebecryl 600 mixture (30/70 by weight) by successive exposure to filtered and unfiltered UV radiation. [TAS] = 2%; [HPK] = 2%. Laminate. (···) Neat DA-BA (Ebecryl 600) + HPK (2%).

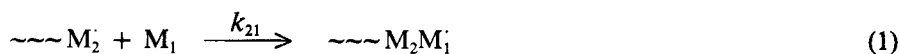
### Polymer Composition—Reactivity Ratio

A direct consequence of the faster polymerization of the acrylate function is that the UV-cured copolymer contains a larger amount of polymerized acrylate units than of polymerized vinyl ether units, as shown by Fig. 14. The composition of the monomer formulation appears to have a strong influence on the polymer composition for UV-curable vinyl ether/acrylate hybrids. For a monomer feed A/VE ratio of 1, the A/VE value of the copolymer was found to be 3. The copolymer composition was found to be related to the monomer feed composition by the following equation:

$$(A/VE)_{\text{polymer}} = 1 + 2(A/VE)_{\text{monomer}}$$

High values of  $(A/VE)_{\text{monomer}}$  will lead to an acrylate homopolymer containing a few VE units. Low values of this ratio will give an alternate copolymer with a large excess of unreacted vinyl ether monomer, which can then be homopolymerized by photoinitiated cationic polymerization. All these results point toward a copolymerization mechanism involving cross-propagation by the vinyl ether and acrylate radicals together with a homopolymerization of the acrylate moiety, as represented schematically in Fig. 15.

In the copolymerization of vinyl ether/acrylate hybrids, three propagation reactions have to be considered:



the rate of polymerization of the vinyl ether double bond will be

$$R_{p1} = k_{21}[M_2][M_1]$$



and the rate of polymerization of the acrylate double bond will be

$$R_{p2} = k_{12}[M_1][M_2] + k_{22}[M_2][M_2]$$

with  $M_1$  designating the vinyl ether and  $M_2$  the acrylate. Under steady-state conditions, the concentration of the radicals remains constant with time:

$$\frac{d[M_1]}{dt} = k_{21}[M_2][M_1] - k_{12}[M_1][M_2] = 0$$

The rate equation of the acrylate polymerization can thus be written as

$$R_{p2} = R_{p1} + k_{22}[M_2][M_2]$$

or after rearrangement:

$$\frac{R_{p2} - R_{p1}}{R_{p1}} = \frac{k_{22}[M_2]}{k_{21}[M_1]}$$

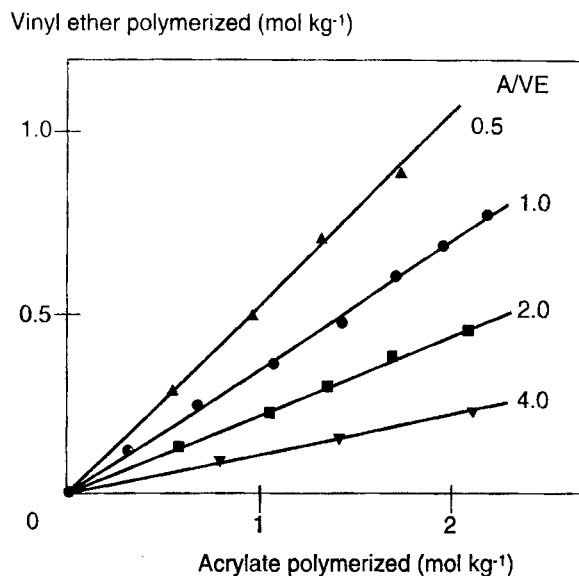


FIG. 14. Amount of vinyl ether polymerized versus amount of acrylate polymerized in radical-induced polymerization of DVE-3/Ebercryl 80 mixtures having different A/VE ratios. [HPK] = 2%. Laminate.

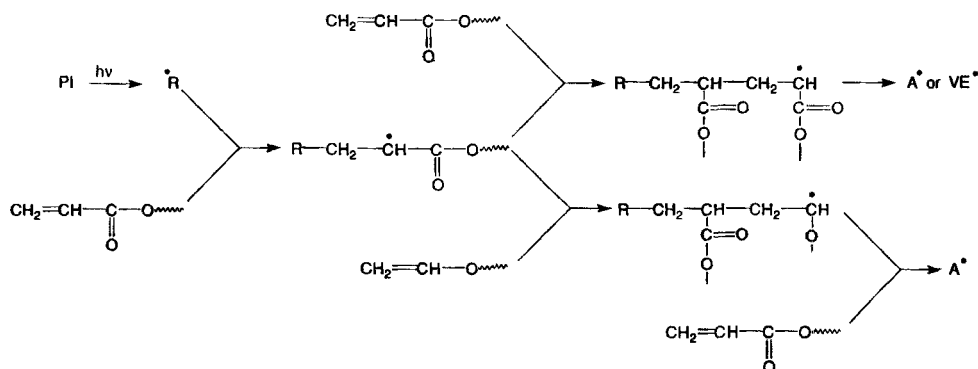


FIG. 15. Copolymerization mechanism of a vinyl ether/acrylate mixture exposed to UV radiation in the presence of a radical-type photoinitiator (PI).

The polymerization rates of the vinyl ether ( $R_{p1}$ ) and of the acrylate ( $R_{p2}$ ) functions have been determined for hybrid formulations having different A/VE values. By plotting the quantity  $(R_{p2}/R_{p1}) - 1$  versus the ratio A/VE, a straight line was obtained (Fig. 16), in agreement with the rate equation of statistical copolymerization. The reactivity ratio of the acrylate radical ( $r_2 = k_{22}/k_{21}$ ) can be evaluated from the slope of the straight line. The calculated value,  $r_2 = 1.8$ , indicates that acrylate radicals are about twice as reactive toward the acrylate double bond as they are toward the vinyl ether double bond. Because VE double bonds do not homopolymerize by a radical mechanism, the crosslinked copolymer formed will contain isolated vinyl ether units, e.g.:

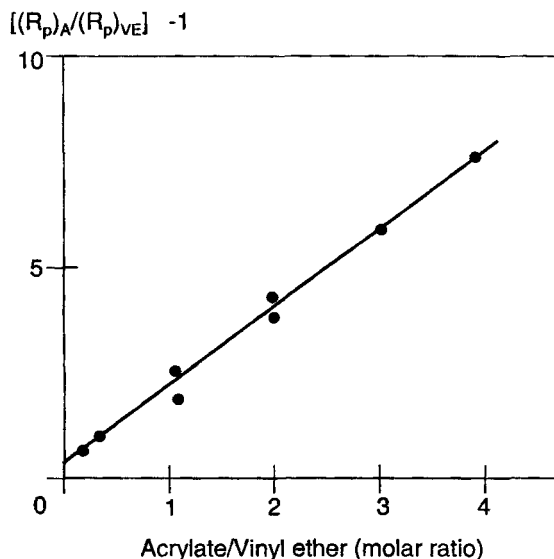


FIG. 16. Influence of the monomer feed ratio on the rate of polymerization of a vinyl ether/acrylate hybrid (DVE-3 + Ebecryl 80). [HPK] = 2%. Laminate.



The reactivity ratio can also be determined from the polymer composition which, for a statistical copolymerization, is given by the Mayo equation [21]:

$$\frac{d[m_1]}{d[m_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right)$$

where  $[m_1]$  and  $[m_2]$  represent the concentration of structural units  $M_1$  and  $M_2$  in the copolymer. For the VE/A hybrid, where the vinyl ether radical is inactive toward the VE double bond ( $r_1 = 0$ ), this equation becomes

$$\frac{d[VE]_{\text{polym}}}{d[A]_{\text{polym}}} = \frac{VE}{r_2[A] + [VE]}$$

or

$$r_2 = \frac{VE}{[A]} \left( \frac{d[A]_{\text{polym}}}{d[VE]_{\text{polym}}} - 1 \right)$$

It was previously found that 3 acrylate functions have polymerized per vinyl ether double bond polymerized for  $A/VE = 1$ , and 5 for  $A/VE = 2$  (Fig. 14). From these values the reactivity ratio was calculated to be 2, a value in good agreement with that determined from rate measurements.

It should be mentioned that radical-induced copolymerization of the VE/A hybrid might also occur via an acceptor-donor complex mechanism. This process would develop at the same time as the polymerization of the acrylate monomer and would lead to a tridimensional polymer network with crosslink chains made of both an acrylate homopolymer and an alternate A/VE copolymer. However, experiments carried out without added photoinitiator do not favor such a donor-acceptor mechanism. No polymer formation could be observed after a 50-second exposure of a DVE-3/TMPTA mixture, in contrast to the vinyl ether/maleate system where an alternate copolymer was shown to be formed by a donor-acceptor mechanism [22].

## CONCLUSION

Multifunctional vinyl ethers are extremely reactive monomers which undergo a fast and extensive photopolymerization by either a cationic process or a radical mechanism in the presence of a comonomer. One of the distinct characteristics of these compounds is their versatility; they can generate tridimensional polymer networks upon UV curing as well as statistical or alternate copolymers. Polymer materials having quite different properties can thus be obtained by adjusting the formulation composition and the selected monomers and photoinitiators.

Such ultrafast reactions can be easily monitored in real time by infrared spectroscopy, a technique which is unique in that it gives the conversion versus time profile directly for each of the monomers undergoing polymerization. The important kinetic parameters have been evaluated for both cationic and radical photoinitiated polymerization of vinyl ether-based systems, thus providing basic information about the mechanism of such processes. A most remarkable feature is that vinyl ether monomers tend to increase the polymerization rate as well as the overall cure

extent of multiacrylate monomers. Highly crosslinked polymers containing little residual unsaturation have thus been generated by a short UV exposure. The best results were obtained for such hybrid systems with a combination of a radical and a cationic photoinitiator.

Further progress on UV-curable vinyl ether systems can be expected to occur in the near future because of the recent development of new vinyl ether functionalized oligomers. This will enlarge the formulation range and help create UV-cured high performance polymer materials having well-designed properties for specific applications.

## REFERENCES

- [1] J. F. Crivello, J. L. Lee, and D. A. Conlon, *Proc. Radcure Conf. Chicago*, Society of Manufacturing Engineering, Dearborn, MI, 1982, pp. 4-28.
- [2] J. A. Dougherty, J. F. Vara, and L. R. Anderson, *Proc. RadTech Conf. Baltimore*, 1986, p. 15.
- [3] J. A. Dougherty and J. F. Vara, *Proc. RadTech Conf. Chicago*, Vol. 1, 1990, p. 402.
- [4] R. J. Brautigam, S. C. Lapin, and J. R. Snyder, *Ibid.*, Vol. 1, 1990, p. 99.
- [5] S. C. Lapin and J. R. Snyder, *Ibid.*, Vol. 1, 1990, p. 410.
- [6] S. Jonsson, P. E. Sundell, and A. Hult, *Ibid.*, Vol. 1, 1990, p. 417.
- [7] G. K. Noren, A. J. Tortorello, and J. T. Vanderberg, *Ibid.*, Vol. 2, 1990, p. 201.
- [8] S. R. Sauerbrunn, D. C. Armburster, and P. D. Schickel, *Ibid.*, Vol. 1, 1990, p. 303.
- [9] J. J. Schouten, G. K. Noren, and S. C. Lapin, *Proc. RadTech Conf. Boston*, Vol. 1, 1992, p. 167.
- [10] S. C. Lapin, J. J. Schouten, G. K. Noren, and E. J. Moschouis, *Proc. RadTech Europe Conf.*, 1993, p. 501.
- [11] J. F. Vara, E. A. Jurczak, J. A. Dougherty, and W. J. Balant, *Ibid.*, 1993, p. 513.
- [12] S. C. Lapin, in *Radiation Curing—Science and Technology* (S. P. Pappas, Ed.), Plenum Press, New York, NY, 1992, p. 241.
- [13] C. Decker and K. Moussa, *Makromol. Chem.*, **189**, 2381 (1988).
- [14] C. Decker, in *Radiation Curing—Science and Technology* (S. P. Pappas, Ed.), Plenum Press, New York, NY, 1992, p. 135.
- [15] J. V. Crivello and K. Dietliker, in *Chemistry and Technology of UV-EB Formulation for Coatings Inks and Paints* (P. K. T. Oldring, Ed.), SITA Technology, London, 1991, p. 327.
- [16] C. Decker and K. Moussa, *Macromolecules*, **22**, 246 (1989).
- [17] C. Decker, *J. Polym. Sci., Polym. Chem. Eds.*, **30**, 913 (1992).
- [18] C. Decker and K. Moussa, *J. Makromol. Chem.*, **191**, 963 (1990).
- [19] C. P. Chawla and J. M. Julian, *Proc. RadTech Conf. Orlando*, Vol. 1, 1994, p. 617.
- [20] J. R. Snyder and G. D. Green, *Proc. RadTech Conf. Boston*, Vol. 2, 1992, p. 703.

- [21] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, 66, 1594 (1944).
- [22] C. Decker and D. Decker, *Proc. RadTech Conf. Orlando*, Vol. 1, 1994, p. 602.

Received May 15, 1996

Revision received July 30, 1996