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# Preparation of Coatings via Cationic Photopolymerisation: Influence of Alcoholic Additives

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**Summary:** Coatings obtained through photopolymerisation of vinylethers, propenyl ethers and epoxy resins are described. The influence of alcohols and of comonomers bearing OH groups on the cationic mechanism of the curing process is discussed. The final properties of the coatings are evaluated and correlated to the structures of the additives.

**Keywords:** UV-curing, coatings, vinyl ethers, propenyl ethers, epoxides, alcohols

## Introduction

The UV curing process is getting an increasing importance in the field of coatings: it allows to obtain a fast transformation of a liquid monomer into a solid film with tailored physico-chemical and mechanical properties. In the process, radical or cationic species are generated by the interaction of the UV light with a suitable photoinitiator, which induces the curing reaction of suitable reactive monomers and oligomers [1]: in the case of the cationic polymerisation, onium salts are used to generate very strong Brönsted acids upon photodecomposition [2]. The cationic photoinduced process presents some advantages compared to the radical one [3], in particular lack of inhibition by oxygen, low shrinkage, good mechanical properties of the UV cured materials and good adhesion properties to various substrates. Moreover, the monomers employed are generally characterized by being less toxic and irritant.

Different types of monomers and oligomers have been proposed and reported in the literature [4,5]. Among them the epoxides are largely available and show good properties after curing, but their reactivity is relatively low, especially when compared to the widely used acrylic resins [6]. The vinyl ethers on the contrary are rather fast, but their availability is limited because the synthesis, which involves acetylene, is difficult. A good alternative is the use of propenyl ethers, as they are obtained by isomerisation of the allyl ethers and show good reactivity [7,8].

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In order to modify the curing process of epoxide systems, the use of alcohols was first indicated by Penczek and Kubisa [9], then confirmed by Crivello [10,11]. The occurrence of a chain transfer reaction involving the OH groups causes the change of the kinetics of the process and of the properties of the cured networks. A further refinement of this research line is the use of monomers that incorporate the groups taking part to the chain transfer reaction: these products are called monofers [12].

In the frame of a work on the preparation of coatings via cationic UV curing we have investigated the influence of alcoholic additives on different types of resins, namely vinyl ether, propenyl ether and epoxy systems. In this paper both the kinetics of photopolymerisation and the evaluation of the properties of the obtained coatings are discussed.

## Experimental

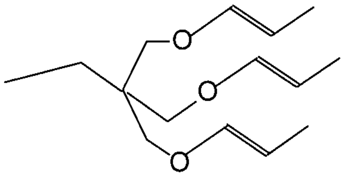
### Materials: Reference resins

The vinyl ether monomers are: triethyleneglycol divinyl ether (DVE3), supplied by ISP Europe and diethylene glycol divinylether (DVE2), purchased from Aldrich. Their structures are:

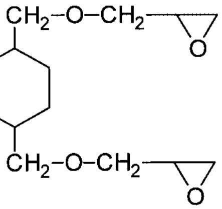
$$CH_2{=}CH{-}O{-}\left(CH_2CH_2{-}O\right)_3{-}CH{=}CH_2$$

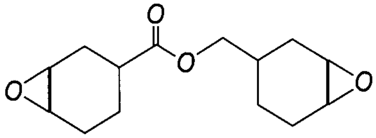
$$CH_2{=}CH{-}O{-}\left(CH_2CH_2{-}O\right)_2{-}CH{=}CH_2$$

The propenylether monomer is trimethylolpropane tripropenylether (TPE) synthesized in the laboratory of Perstorp according to the procedure described in [8]. The structure of TPE is:



The epoxy difunctional monomers are: 1,4-cyclohexanedimethanol diglycidyl ether (DGE) from Aldrich and 3,4-epoxycyclohexilmethyl-3',4'-epoxycyclohexanecarboxylate (CE), kindly supplied by Union Carbide. Their structures are drawn below:





## Materials: Alcoholic additives

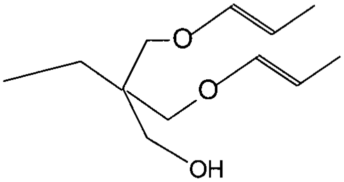
Alcohols employed are: 2-propanol, n-butanol, 2-phenyl-2-propanol, bisphenolA, diethylenglycol, trimethylolpropane, hydroxy functionalized polybutadiene (PBOH, Mn = 1200; 55% 1,4 trans; 20% 1,4 cis; 25% 1,2; hydroxyl number 1.7 meq/g) all purchased from Aldrich.

Monofers under investigation are:

- diethylene glycol monovinyl ether (HDVE2 from Aldrich)

$$CH_2{=}CH{-}O{-}\left(CH_2CH_2{-}O\right)_2{-}H$$

- di propenylether trimethylolpropane (DPE) which was synthesised on purpose as reported elsewhere [8]. The structure is below. As a reference the acetic ester of it was used.



- epoxidized hydroxypolybutadiene (PBE), having the same structure of PBOH and containing about 20% of epoxidized double bonds (epoxide equivalent = 260), where the epoxy units are mainly of 1,4-trans type.

## Materials: Initiator

In all the formulations triphenylsulfonium hexafluoroantimonate, from Union Carbide, was used as the cationic photoinitiator in a concentration equal to 2 wt%.

## Methods

### Film preparation

The photocurable mixtures were spread on a glass slide with a calibrated wire-wound applicator to obtain a thickness of about 100 μm.

The curing reaction was performed by UV irradiation with a medium pressure Hg lamp (Italquartz, Milano, Italy); the light intensity at the film surface was 120 W/m2. The irradiation was stopped when a constant reactive groups conversion was achieved, as determined by FTIR measurements (see below). The samples, after irradiation, were stored for one night and then put for 15 minutes in a closed system saturated with a 5% v/v water/ammonia solution vapors, in order to neutralize the acidic species.

### Film characterization

The degree of the reactive groups conversion was calculated coating the mixture on a KBr disk, and measuring the ratio of the corresponding IR absorbance before and after UV exposure. The kinetic curves were obtained by measuring the decrease of the reactive group absorption band, after different irradiation time. A Genesis Series ATI Mattson (USA) spectrometer was used.

The Gel Content of the films was determined by measuring the weight loss after 20 hours treatment at room temperature with chloroform. DSC measurements were performed with a Mettler DSC30 (Switzerland) instrument, equipped with a low temperature probe.Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at the frequency of 1 Hz in the tensile configuration.

## Results and discussion

### Curing of vinyl ethers

The kinetics curve of vinylethers such as DVE2 and DVE3 (in Figure 1 an example is reported) show that the rate of propagation of the photopolymerisation changes significantly in the presence of alcohols. The final conversion of double bonds increases, reaching even completeness in some cases, as reported in Table 1.

The alcoholic additive affects the polymerisation mechanism through a chain trasfer reaction as described previously [13,14]: FTIR analyses confirm this mechanism showing a decrease of the OH band at 3600 $cm^{-1}$ and an increase of the ether band at 1100 $cm^{-1}$.

Considering the DVE3 system containing the HDVE2 monofer, we can assume that the same chain transfer reaction takes place together with the copolymerisation of the vinyl ether group present in the monofer. From the kinetic curve of Figure 1, it is evident that 5% of HDVE2 allows to increase the polymerisation rate and to obtain the complete conversion of the double bonds.

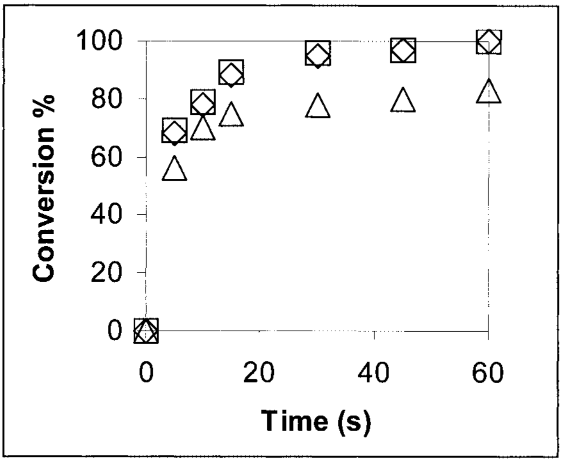


Figure .1 FT-IR kinetic curve of the pure DVE3 monomer (Δ) and in the presence of 5 wt% of HDVE2 (□) and 2-phenyl-2-propanol (◊).

The chain transfer makes the polyvinylether chain length decrease, so that free-dangling ends are introduced in the network. As a consequence, the network structure is more flexible and the mobility of the reactive species increases so that the polymerisation can be completed.

The flexibilisation is reflected by the lowering of the glass transition temperature of the cured films: as reported in Table 1, in the case of DVE3, the original Tg (58°C) is reduced down to 15°C by the addition of about 15 %mol of 1-butanol or 8 % mol of 2-phenyl-2-propanol. 2-phenyl-propanol is the most effective alcohol, probably due to its higher nucleophilicity [14]. At the same OH groups concentration, the Tg values are higher in the presence of HDVE2 with respect to the systems containing alcohols. These results can be attributed to the photopolymerisation of the HDVE2 double bonds, which increases the crosslinking density of the network.

**Table 1: Effect of alcohols and hydroxylic monofers on the conversion and properties of vinylether systems (DVE3)**

| *Type of additive* | *% mol#* | *$\eta$ (%)* | *Gel content (%)* | *Tg (°C)* |
|---|---|---|---|---|
| - | - | 93 | 98 | 58 |
| 1-butanol | 15.2 | 98 | 93 | 14 |
| 2-phenyl-2-propanol | 8.3 | 100 | 92 | 15 |
| HDVE2 | 14.2 | 100 | 96 | 30 |
|  | 27.0 | 96 | 90 | 13 |
|  | 49.5 | 96 | 71 | -10 |

# Moles of additives per moles of double bonds

## Curing of propenyl ethers

The kinetics of the curing of TPE with and without alcohols or DPE are shown in Figure 2.

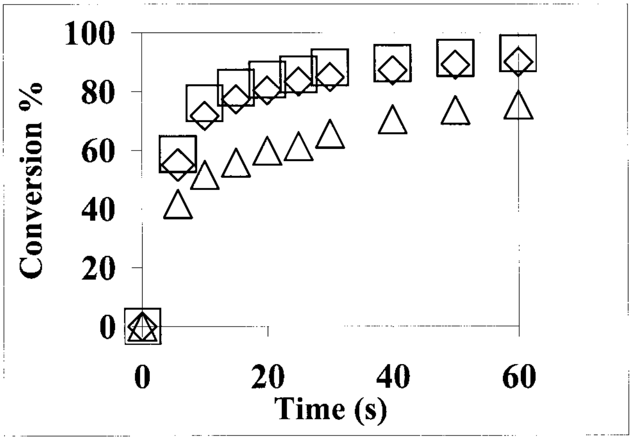


Figure 2. FT-IR kinetic curve of the pure TPE monomer (Δ) and in the presence of 5 wt% of DPE (□) and 2-phenyl-2-propanol (◊).

The kinetic rates are higher in the presence of 2-phenyl-2-propanol or DPE and the final conversions can reach 100%: for the TPE alone the yield never overcomes 80%. These results can be interpreted on the basis of a chain trasfer reaction involving the OH groups, as evidenced in the case of vinyl ethers systems. The FTIR spectra performed before and after the UV curing, confirm this mechanism.

A further evidence of this phenomenon comes from the investigation of the behaviour of the ester derivative of DPE. By adding the DPE acetate, there is no change in the polymerisation kinetics and the conversion is similar as in the case of the pure TPE [8].

In Table 2 some properties of the propenyl ether systems are reported.

**Table 2: Effect of alcohols and hydroxylic monomers on the conversion and properties of propenylether systems (TPE)**

| *Type of additive* | *% mol#* | *$\eta$ (%)* | *Gel content (%)* | *Tg (°C)* |
|---|---|---|---|---|
| Pure TPE | - | 80 | 85 | 140 |
| DPE | 4 | 100 | 85 | 120 |
| | 2 | 96 | 83 | 125 |
| 1-butanol | 6.5 | 93 | 83 | 108 |
| 2-phenyl-2-propanol | 5.2 | 99 | 81 | 107 |

# Moles of additives per moles of double bonds

The gel content decreases in the films containing additives, probably due to the formation of low M.W. branched products.

A further consequence of the presence of the additives is the clear decrease of the Tg: in the presence of DPE the decrease is less effective than in the presence of the alcohols, as obtained in the case of the vinyl ether systems.

Looking at the DMTA spectra of the TPE film without additive (Figure 3), one can see that the tanδ peak is quite broad and besides the maximum (from which the Tg value was estimated), a shoulder at lower temperature is present. There is therefore a hard domain, corresponding to a phase where the crosslinking is very high, together with a more flexible polymeric matrix. As the films are transparent, the heterogeneity of the networks are at submicron level. In the presence of additives, the DMTA thermograms are simpler (one signal in the tan δ curve), indicating that in this case homogeneous networks are formed (an example is reported in Figure 4).

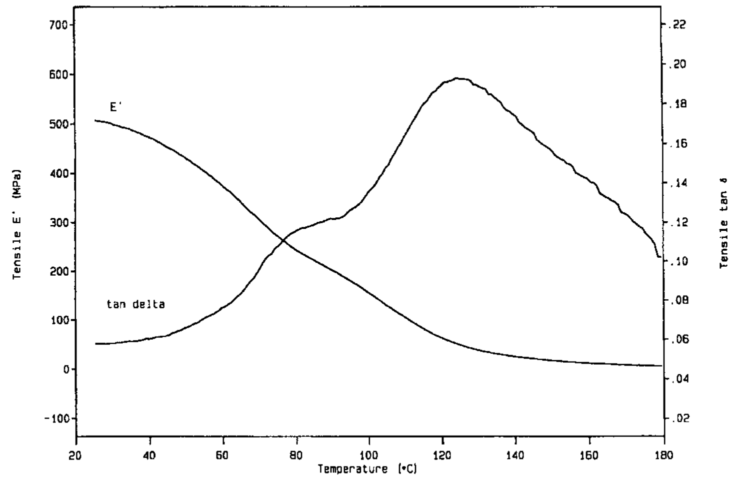


Figure 3. DMTA curves of TPE cured film.

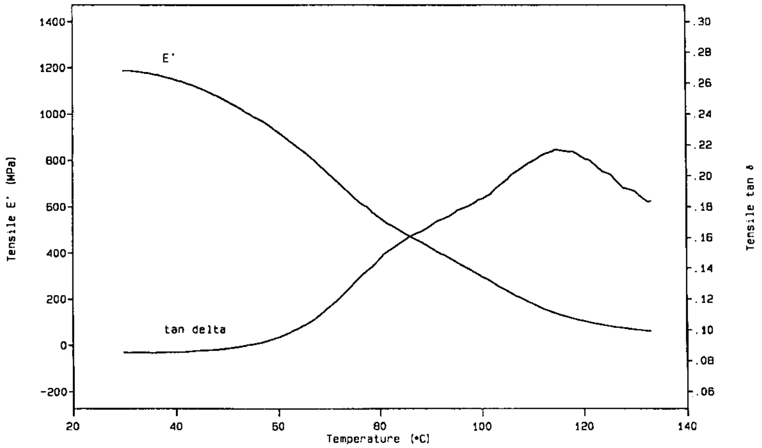


Figure 4. DMTA curves of TPE cured film containing 2-phenyl-2-propanol.

## Curing of epoxy systems

The kinetics of the curing of DGE monomer in the presence of PBOH and PBE was investigated. The kinetic curve (Figure 5) of the DGE alone shows an initial high rate of polymerization, then a plateau at about 55% epoxy groups conversion.

In fact the propagation rate constant of the system is strongly affected by the molecular mobility of the growing chain and at high conversion the highly crosslinked network formed hinders the chains and stops the reaction. The addition of PBE in different amounts (ranging between 10 to 50 wt%) induces a clear increase of the curing rate and of the epoxy groups final conversion (Figure 5, Table 3 ). In the presence of 50 wt% of PBE the conversion is almost complete.

At the same time the gel content is very high (97-98 %), indicating that PBE is linked into the polymer network. Moreover the PBE contains also hydroxyl groups: in order to investigate the the chain transfer reaction, PBE was substituted, in the photocurable mixture, by PBOH. The results of Table 3 show an increase of the gel content to 98% and of the epoxy group conversion. We can assume that the hydroxyl groups interact with the growing chains, giving chain transfer reactions that increase the flexibility of the films so that the enhanced mobility permits a higher conversion. However this is lower than the final conversion achieved in the presence of PBE: this means that PBE is involved in the copolymerization with DGE through its epoxy groups[15].

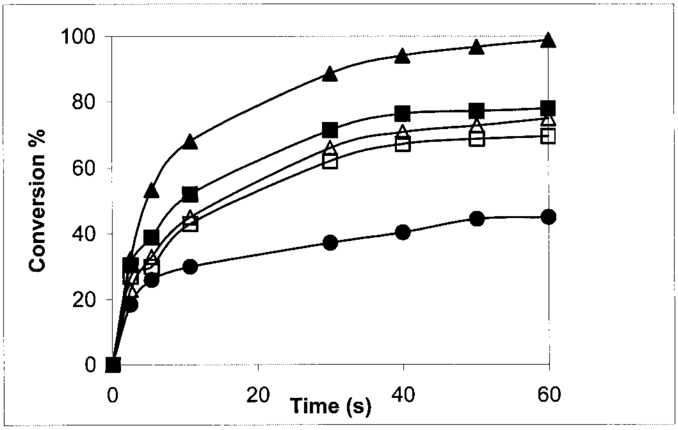


Figure 5 FT-IR kinetic curves of the pure DGE monomer (●) and in the presence of 20 (■) and 50 (▲) wt% of PBE or 20 (□) and 50 (Δ) wt% of PBOH.

**Table 3: Properties of the UV cured films obtained from DGE-PBE and DGE-PBOH mixtures.**

| *Sample* | *Gel Content %* | *$\eta$ %* | *Tg °C* |
|---|---|---|---|
| Pure DGE | 90 | 56 | 53 |
| DGE:PBOH 90:10 wt/wt | 98 | 61 | 40 |
| DGE:PBOH 80:20 wt/wt | 97 | 70 | 39 |
| DGE:PBOH 50:50 wt/wt | 98 | 71 | 33 |
| Pure PBE | 95 | 48 | 30 |
| DGE:PBE 90:10 wt/wt | 98 | 68 | 47 |
| DGE:PBE 80:20 wt/wt | 97 | 80 | 43 |
| DGE:PBE 70:30 wt/wt | 98 | 85 | 38 |
| DGE:PBE 50:50 wt/wt | 98 | 99 | 32 |

The film properties are different depending on the type of reactive additive employed, PBE or PBOH. As reported in Table 3, by increasing the amount of PBE and PBOH in the mixture, a decrease of Tg is obtained. In particular the Tg values of the mixtures containing PBE are always higher than those obtained with the mixtures containing PBOH. These results can be attributed to a higher degree of crosslinking of the films obtained in the presence of PBE, due to the occurrence of the copolymerization reaction.

Similar results were obtained using the same additives and the CE as a monomer. In this case the ring opening polymerization proceeds more rapidly upon UV irradiation, but only 45% degree of conversion is achieved due to the vitrification effect. It increases in the presence of PBE, reaching completion in the presence of 50 wt% of the additive.

The gel content and the Tg values of the UV cured films obtained in the presence of PBE or PBOH additives, show the same behavior as obtained for DGE monomer, confirming the proposed reaction mechanism.

**Table 4: Properties of the UV cured films obtained from CE/PBE and CE/PBOH mixtures.**

| *Sample* | *Gel Content %* | *η %* | *Tg °C* |
|---|---|---|---|
| Pure CE | 88 | 45 | 214 |
| CE:PBE 90:10 wt/wt | 99 | 66 | 200 |
| CE:PBE 80:20 wt/wt | 98 | 77 | 190 |
| CE:PBE 70:30 wt/wt | 95 | 80 | 182 |
| CE:PBE 50:50 wt/wt | 97 | 100 | 172 |
| CE:PBOH 90:10 wt/wt | 97 | 56 | 200 |
| CE:PBOH 80:20 wt/wt | 98 | 65 | 184 |
| CE:PBOH 50:50 wt/wt | 97 | 73 | 171 |

In the case of the DGE system, the effect of the high molecular weight polibutadiene additives was compared with small alcohols, such as diethylenglycol, trimethylolpropane and bisphenol-A. The data of gel percent, conversion and thermal transitions are collected in Table 5: they indicate that in the presence of small alcohols a higher increase of conversion can be obtained.

**Table 5: Effect of alcohols and hydroxylic monofers on the conversion and properties of epoxy systems (DGE)**

| *Type of additive* | *% eq* | *η (%)* | *Gel content (%)* | *Tg (°C)* |
|---|---|---|---|---|
| - | - | 56 | 90 | 45 |
| PBOH 50% | 7 | 71 | 98 | 33 |
| Bisphenol-A 5% | 4.3 | 90 | 99 | 39 |
| Trimethylolpropane 5% | 11.2 | 82 | 98 | 40 |
| Diethyleneglycol 5% | 9.4 | 78 | 98 | 19 |

## Conclusions

We investigated the behaviour of typical cationic UV-curable systems such as vinylethers, propenyl ethers and epoxy in the presence of alcoholic additives either in the form of alcohols or in the form of hydroxy comonomers. The presence of such additives changes the kinetics of photopolymerisation and the properties of the cured films. The results can be interpreted on the basis of a chain transfer reaction involving the OH groups which determines a flexibilisation of the network and increases the curing rate. In the presence of a monofer the flexibilisation is lower, but the curing rate remains clearly higher than the pure resin.

## Acknowledgements

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