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1-Propenyl ethers of butanediol as effective modifiers of UV-cured epoxy coatings in cationic polymerization

RAPID COMMUNICATION

Summary — Models mono- and di-1-propenyl butane-1,4-diol ethers (MoPnE and DiPnE respectively) have been used as modifiers of coatings on the basis of epoxy resin Epidian 6, UV-cured at room temperature in the presence of air and cationic initiators (triarylsulfonium salts containing either SbF_6^- or PF_6^- anions). The effects of the type and amount of the ether used as a modifier as well as curing time on glass transition temperature, flexibility, hardness and drying time of coatings investigated have been determined. MoPnE appeared to be most reactive modifier because of the presence of two reactive points in the molecule: double bond and primary OH group. This ether can be included into a new class of the monomers active in cationic polymerization of so called monofers.

Key words: epoxy resins, cationically UV-cured coatings, propenyl ethers of butanediol, modification, flexibility, curing time.

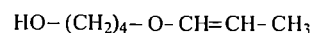
Photoinitiated polymerization (radiation curing) is a technologically important process which has found manifold industrial applications for paints, varnishes, inks, negative photoresists (stereolithography of formation of three-dimensional objects), adhesives (used in welding and sealing in electronic circuit boards) and fast-drying protective coatings (for paper, wood, board, tapes, CDs and holograms) [1—3].

The multifunctional liquid monomers undergo very rapid photopolymerization to cross-linked solid polymers, specifically by using photoinitiated cationic polymerization [4]. Cationic UV curable coatings have better adhesion for various substrates than the free radical cured coatings, and also are not subjected to oxygen inhibition [3, 5]. The heterocyclic compounds with oxygen atom, in particular epoxides (*e.g.* cycloaliphatic epoxides) and oxetanes, are the most important reactive monomers/oligomers used for cationic UV-cured coatings [3, 6—8]. The epoxy cured coatings have many useful properties (*i.e.* excellent adhesion, chemical resistance and mechanical properties) but, in general, their

toughness is not satisfactory [6, 9]. Recently, the cationic polymerization of epoxides is accelerated by the addition of different alcohols [6, 8, 10]. The epoxy resins containing alcohol groups in the same molecule were also used. This type of monomers containing both polymerizable groups as well as moieties that induce chain transfer were described by Goethals *et al.* [11], who named them — monofers.

Propenyl ethers of polyols containing double bonds as well as OH groups can play the role of such monofers. Such compounds are easily prepared, and economically attractive classes of rapidly and efficiently cationically photopolymerized monomers [12].

In the present work, we have described the use of the modelling 1-propenyl ethers (PnE) of 1,4-butanediol, *i.e.* 1,4-di(1-propenyl)oxybutane (DiPnE) and 4-(1-propenyl)oxybutane-1-ol (MoPnE) as cationically polymerizable modifying agents of epoxy coatings UV-cured in



MoPnE



DiPnE

the presence of cationic photoinitiators. Unrefined 1,4-di(1-propenyl)oxybutane including homogenized ruthenium(II) complex $[\text{RuClH}(\text{CO})(\text{PPh}_3)_3]$ (see Materials) was also applied as a modifier.

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EXPERIMENTAL

Materials

The epoxy Bisphenol A — based resin Epidian 6 was purchased from ZCh Nowa Sarzyna (Poland). The cationic initiators (CI), *i.e.* triarylsulfonium salts with anions either PF_6^- (CI_1) or SbF_6^- (CI_2) (as 50% solution in propylene carbonate) were supplied by Aldrich Chemical Co. (Germany). The synthesis of mono- and multi-1-propenyl ethers of diols and triols *via* isomerization of corresponding allyl ethers catalyzed by ruthenium complexes (particularly by $[RuClH(CO)(PPh_3)_3]$) was described in details previously [13, 14]. 1-Propenyl ethers were isolated from the post-reaction mixtures by distillation under reduced pressure. In our investigations both purified mono-1-propenyl (MoPnE) and di-1-propenyl ($DiPnE_{pure}$) ethers of butane-1,4-diol as well as unrefined di-1-propenyl monomer including very low amount (0.05 mol %) of homogenized ruthenium(II) complex ($DiPnE_{[Ru]}$) were applied.

Methods

The processes of photopolymerization were conducted by placing prepared mixtures of resin/ether/initiator, used in definite ratios, onto glass plates at a typical thickness of 90 μm under 180 W medium — pressure arc lamp (λ_{max} — 366 nm, Famed-1, type VP 60) at a distance 10 cm and irradiating them at room temperature. We have determined hardness according to Persoz (PN-79/C-81530), dryness (PN-79/C-81519) and flexibility (PN-76/C-81528) of radiation cured coatings differing in compositions. The glass transition temperature (T_g) was determined using dynamic mechanical analysis (DMTA, MK II Polymer Laboratories, heating rate of 3°C/min) under nitrogen atmosphere [15].

The ethers were incorporated systematically into the lacquer formulations from 0 to 20 wt. %; CI_1 and CI_2 initiators were applied in a range 0.5—7 wt. %. The minimum irradiation time to produce a cross-linked solid polymer film, useful for further assessment, was determined as 2 min, independently on the type and amount of initiator used.

RESULTS AND DISCUSSION

All coatings obtained were colorless, transparent, insoluble in water and organic solvents (*i.e.* benzene, toluene, xylene, acetone, methanol, ethanol, diethyl ether), and had good quality and very good adhesion to glass, wood, metal and plastics (*e.g.* Estrofol film). The application of such systems seems to be very attractive and interesting from chemical and economical point of view, because in a very short irradiation time very good properties of the coatings can be achieved.

Table 1. Glass transition temperature (T_g) of the selected coatings^{*)}

Composition	T_g , °C	
Epidian 6/ CI_2 ^{**)}	58.0	137.9
Epidian 6/ $DiPnE_{pure}/CI_2$	57.6	107.6
Epidian 6/ $DiPnE_{[Ru]}/CI_2$	62.1	111.4
Epidian 6/ $MoPnE/CI_2$	58.1	99.9

^{*)} Weight content of component Epidian 6/ PnE/CI_2 = 100/5/3.

^{**)} CI_2 is a mixture in 1,2-propenediol cyclic carbonate.

The T_g values of the selected films prepared of epoxy resin Epidian 6 with MoPnE, $DiPnE_{pure}$ and $DiPnE_{[Ru]}$ are presented in Table 1. Unexpectedly, when unmodified resin Epidian 6 was cured in a presence of CI_2 , the two distinct T_g s were determined (perhaps it may be caused by presence of the photoinitiator solvent — propylene carbonate). The same appears also in case of modifier containing systems. From two T_g s which were measured, the higher one is taken for the discussion of results. The introduction of 1-propenyl ethers to the epoxy coating Epidian 6/ CI_2 causes appreciable drop in the second T_g (Table 1) and simultaneously substantially improves the flexibility of the cured coatings (Table 2). It was observed from the T_g and flexibility results that MoPnE shows the best plasticizing effect. It is also clear from Table 2 that CI_1 initiator makes evident the advantageous modifiers effect more effectively.

Table 2. Flexibility^{*)} of Epidian 6-based coatings modified by 1-propenyl ethers in the presence of cationic initiators CI_1 or CI_2 (Epidian 6/ CI = 100/3)

1-Propenyl modifiers	Flexibility	
	initiator CI_1	initiator CI_2
$DiPnE_{pure}$	5	20
$DiPnE_{[Ru]}$	3	10
MoPnE	1	5

^{*)} Flexibility is defined by the amount of 1-propenyl ethers sufficient to get not cracking coatings in the whole range of pins (2—20 mm).

Low molecular weight epoxy resins as Epidian 6 form very hard, tack-free but very brittle coatings. We have found that 3 wt. % of cationic initiators and 10 min of UV-cure (for Epidian 6/ CI compositions 100/3) appeared sufficient to obtain coatings with highest degree of drying (*i.e.* 7). The addition of 1-propenyl monomers up to 20 wt. % did not deteriorate this property. The exceptions are coatings modified $DiPnE_{[Ru]}$ and initiated by PF_6^- sulfonium salts. For them considerable decrease of dryness extent (from 7 to 3) was observed, especially when higher amounts (15 wt. % and 20 wt. %) of $DiPnE_{[Ru]}$ were added.

The Persoz hardness data of the selected UV coatings are shown as a function of the content of PnE (Fig. 1) and photocuring time (Fig. 2). Not surprisingly, the hardness

of films modified by MoPnE (Fig. 1, curve 1) was much higher than those in cases of DiPnE_{pure} (curve 2) and DiPnE_[Ru] (curve 3). Generally, when the concentration of the ethers in the lacquers increased, the coatings become softer and, consequently, hardness was reduced.

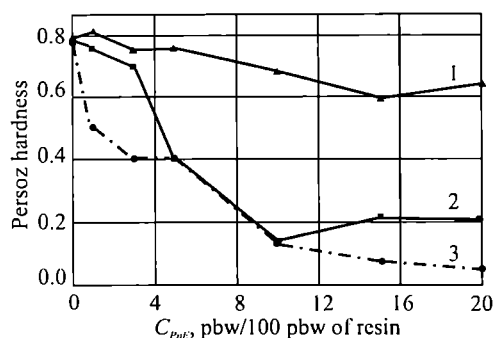


Fig. 1. Persoz hardness of the coatings as a function of modifier (PnE) amounts (C_{PnE}) in cationic photopolymerization catalyzed by Cl_1 (Epidian 6/ $Cl_1 = 100/3$); 1 — MoPnE, 2 — DiPnE_{pure}, 3 — DiPnE_[Ru]

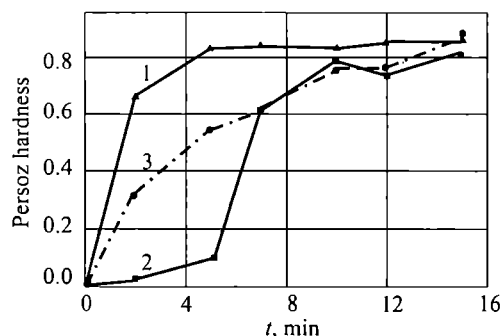


Fig. 2. Persoz hardness of the modified coatings as a function of the photocuring time (t) in cationic photopolymerization catalyzed by Cl_2 (Epidian 6/PnE/ $Cl_2 = 100/5/3$); for symbols see Fig. 1

The comparison of reactivity of used 1-propenyl monomers could be indirectly discussed using the hardness results, especially those from the dependence of the photocuring time (Fig. 2). It was found that, in case of using of DiPnE as a modifier, the photopolymerization process initiated by Cl_1 and Cl_2 runs faster in the presence of homogenized ruthenium complex (curves 2 and 3). For the DiPnE_{pure} modifier the induction period was observed (curve 2). Summarizing, the most reactive modifier is MoPnE (curves 1 on both Figures). This fact could be connected with the presence of 1-propenyl group and primary hydroxyl group. It is generally accepted that the presence of alcohols has a considerable effect on the cationic ring-opening polymerization of epoxides [6, 7, 10]. The mono-1-propenyl ether seems to

be the high reactive modifier in cationic photopolymerization because MoPnE, containing double bonds as well as OH groups, surely plays the role of mentioned monomer.

CONCLUSIONS

On the basis of our investigations it was demonstrated that 1-propenyl ethers are very attractive modifiers for epoxide UV-cured coatings. The results of measurements show that MoPnE, DiPnE_{pure} and DiPnE_[Ru] may improve flexibility of the UV-cured polymer. Moreover, the films can be readily cured by a short UV irradiation in the presence of air and at room temperature.

From the results of investigations it has been also concluded that mono-1-propenyl ethers containing both 1-propenyl and hydroxyl groups could be used as novel class of cationically activated polymerizable monomers with enhanced reactivity. These potentially inexpensive monomers may have many potential applications.

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