

Cationic photopolymerisation of divinylethers systems containing hydroxyvinylethers

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Summary

Diethyleneglycoldivinylether (DVE2) and triethyleneglycoldivinylether (DVE3) were photopolymerised together with monovinylethers and hydroxyalkylvinylethers, in order to study the curing reaction and to evaluate the properties of the films obtained. In the presence of the monovinylethers, the flexibility of the cured films increased and the T_g values decreased. In the presence of a hydroxyalkylvinyl ether, a stronger plasticisation effect was obtained and attributed to a chain transfer reaction involving -OH groups.

Introduction

The cationic polymerisation of vinyl ethers is well known; a number of fundamentals papers were published by Japanese researchers focussed on the reactivity of the monomers and on the kinetics aspects of the process, on the living polymerisation conditions and on the structure of the polymers¹⁻³. The reaction can be initiated also by radiation, in the presence of the suitable photoinitiators: Crivello and co-workers were the first to photopolymerize vinyl ethers and epoxy compound^{4,5} using diaryliodonium or sulfonium salts. This route is more recent than the radical photopolymerisation, but is obtaining increasing importance for the combination of the great reactivity of the curable systems, the absence of oxygen inhibition and the good mechanical properties of the cured films, together with the low toxicity and the limited irritation effects of the reactive monomers.

Several reviews are reported on this technique⁶⁻⁸. In this field we investigated the photopolymerisation of vinyl ether systems in the presence of hydroxy compounds⁹ and studied the effect of the chain transfer reaction involving the -OH groups, previously described by Crivello¹⁰.

Pursuing this research, we have taken into account systems containing hydroxyvinylether monomers: in this paper we evaluate the reactivity of these compounds during the photopolymerisation and the properties of the obtained films. As a comparison some mono vinyl ethers were used as additives.

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Experimental

Materials

The following products were used:

- diethylene-glycol-divinyl-ether (DVE2)
- diethylene-glycol-monovinyl-ether (HDVE2)
- dodecyl-vinyl-ether (DDVE)
- triethylene-glycol-methyl-vinyl-ether (MDVE3)
- triethylene-glycol-divinyl-ether (DVE3)

DVE2, HDVE2, DDVE and MDVE3 were purchased from Aldrich, DVE3 was kindly supplied by ISP Europe (Guildford).

The photoinitiator, triarylsulfonium hexafluorophosphate (50% w/w solution in propylene-carbonate, Cyacure UVI-6990) was kindly given by Union Carbide. The concentration of the pure photoinitiator in the polymeric mixture was always 2% w/w.

Curing procedure

Films of the cured products were obtained following the procedure previously reported¹¹. The film thickness was about 100 μm .

The light intensity was about 10 mW/cm^2 ; the curing was performed over 50 seconds in the presence of air. After curing, the films were peeled off the polypropylene substrate.

Analyses

FT-IR analysis was performed on the product before and after the UV-curing, using a Spectrometer Genesis Series ATI Mattson: the reactive mixture was put between two polypropylene thin films. The FT-IR spectrophotometer operated in the absorbance mode and the residual unsaturations (R.U.) were calculated by the decrease of the 1620 cm^{-1} vinyl ether band upon UV exposure.

Dynamic-mechanical thermal analysis (DMTA) was performed by using a Polymer Laboratories Instrument MK II at the frequency of 1 Hz in the tensile configuration.

E' and $\tan \delta$ were measured as a function of temperature in the range $-80/+100^\circ\text{C}$. The size of the specimen strips was about 20x40x0.1mm.

DSC measurements were performed with a Mettler DSC 20 instrument, with a low temperature equipment.

The gel content of the cured films was determined by measuring the weight loss after a 16 h treatment with CHCl_3 . The sol fraction contains low M.W. vinyl ether oligomers, as revealed by FT-IR: the spectra exhibited a complex pattern, in which one can distinguish the intense ether band at 1130 cm^{-1} and small signals of the photoinitiator fragments in the range 1500-1600 cm^{-1} . The double bond band was absent.

Results and discussion

In Table 1 the properties of UV cured films containing HDVE2 as an additive are reported and compared with the films obtained from pure divinyl ethers, DVE2 or DVE3.

The presence of the HDVE2 has a clear influence on the T_g of the systems: the higher the concentration of the additive the lower the T_g . On the contrary, notwithstanding the addition of the HDVE2, the double bond conversion is almost complete for all the

mixtures, as determined through FT-IR analyses: the spectra show the disappearance of the vinyl ether band at 1620 cm^{-1} upon UV exposure.

TABLE 1: Properties of the UV-cured films containing hydroxymonovinylether

Film	% w/w ^a	% mol ^b	R.U. % ^c	Tg (°C) ^d	Tg (°C) ^e	Gel Content %
DVE2	0	0	5.3	41.0	88.6	98.0
DVE2/HDVE2	10	11.8	0.0	23.2	54.7	92.5
DVE2/HDVE2	20	23.0	3.0	7.6	48.8	90.0
DVE2/HDVE2	40	44.5	3.8	-18.3	25.3	78.5
DVE3	0	0	6.7	31.0	58.2	98.0
DVE3/HDVE2	10	14.2	0.0	-5.7	30.2	95.8
DVE3/HDVE2	20	27.0	4.3	-33.2	13.0	90.0
DVE3/HDVE2	40	49.5	4.1	-52.7	-10.0	71.3

a: weight of hydroxyvinylether / total weight, b: moles of hydroxyvinylether / total moles, c: Residual Unsaturation obtained by FT-IR, d: by DSC, e: by DMTA

Examining the spectra before and after photopolymerisation, other interesting features are revealed. As typical examples, the spectra of the UV cured films obtained from the mixture DVE3/HDVE2 90:10 and 80:20 w/w are reported in Fig. 1: at 3500 cm^{-1} it is evident the decrease of the hydroxy group band, indicating that the OH groups are consumed during the process. These results can be explained on the basis of the chain transfer mechanism, which can take place in the presence of the hydroxy containing monomers⁹⁻¹⁰.

The mechanism is outlined in Scheme 1, where the formation of the polyvinyl chain as a consequence of the polyaddition process is sketched. The hydroxy group, present in the HDVE2, interacts with the carbocationic species, giving rise to the formation of an ether bond. HDVE2 behaves like a chain transfer agent and reduces the polyvinyl chain length, introducing flexible ether groups. At the same time the polar -OH groups disappear.

It is well known that in the cationic polymerisation also a chain transfer to the monomer is present, which reduces the polyvinyl chain length. Whenever this reaction takes place, we can assume that the two monomers have a similar reactivity. Therefore the higher flexibility of the copolymer can be explained on the basis of the chain transfer of Scheme 1. This is the only reaction able to modify the structure of the network of the copolymer with respect to the homopolymer. The structure was investigated by NMR and will be reported in a forthcoming work¹².

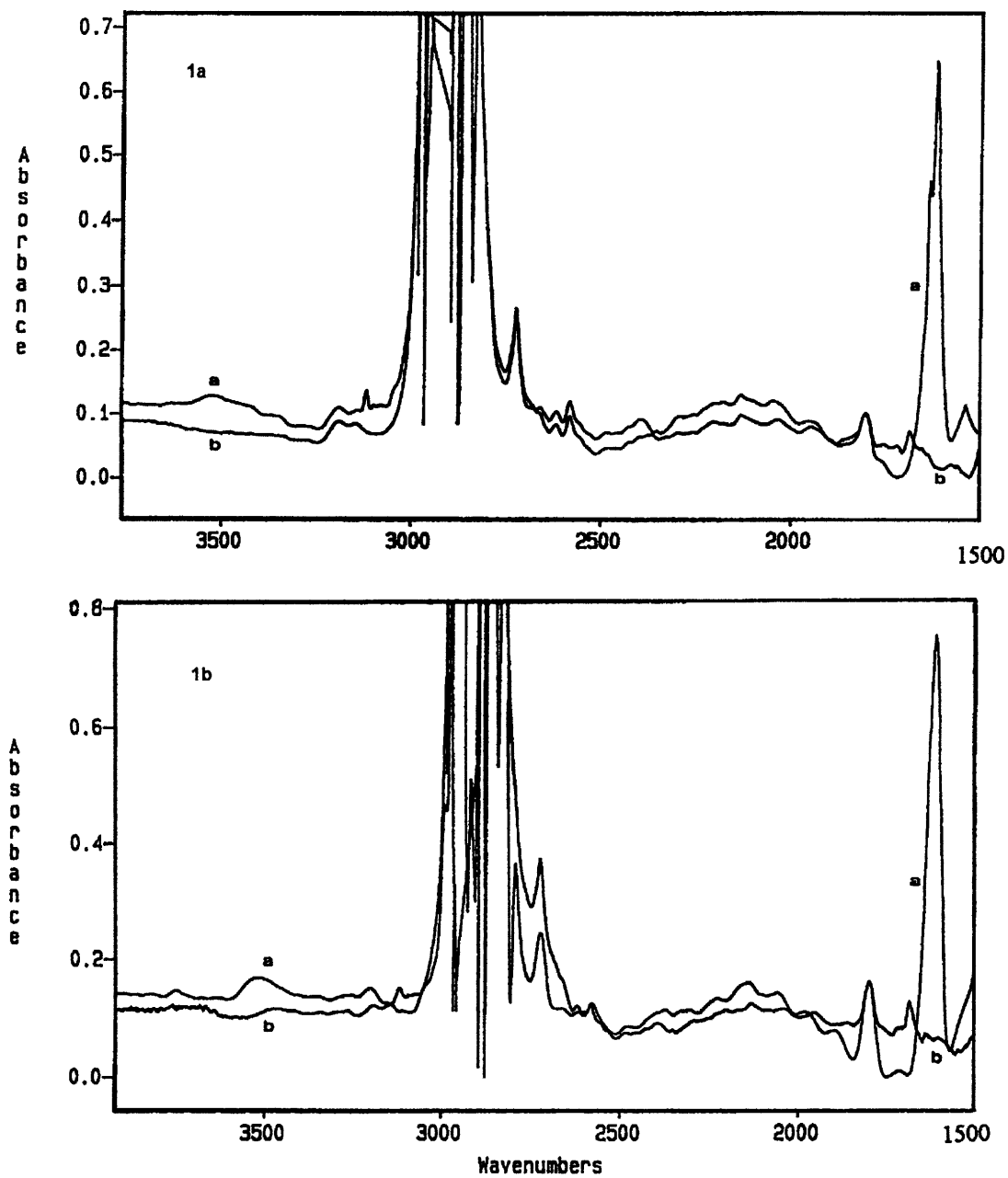
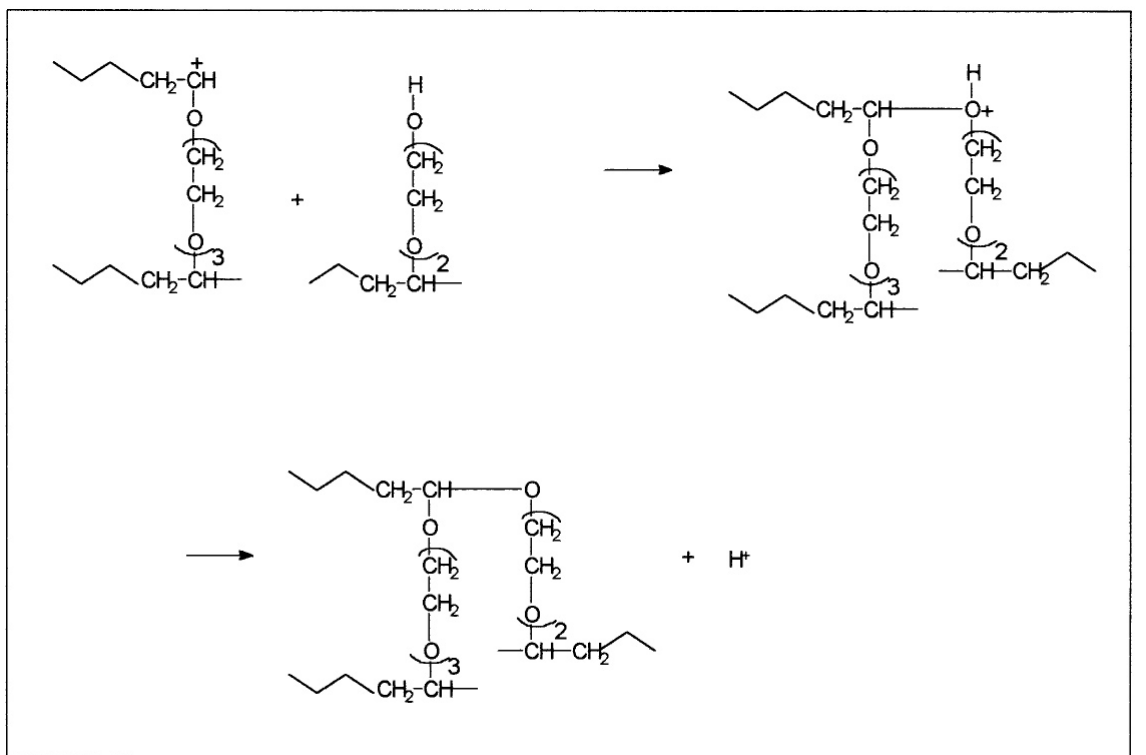


Figure 1: FT-IR spectrum of the UV cured film obtained from the mixture DVE3/HDVE 90:10 w/w (1a) and DVE3/HDVE2 80:20 w/w (1b) before (a) and after (b) photopolymerisation



Scheme 1: Chain transfer mechanism

The DMTA analyses confirm the modification of the cured films when the HDVE2 monomer is added to the divinylether. As an example, we can compare in figure 2 the thermodynamomechanical response of the pure DVE3 film and of the DVE3/HDVE2 80:20 w/w mixture.

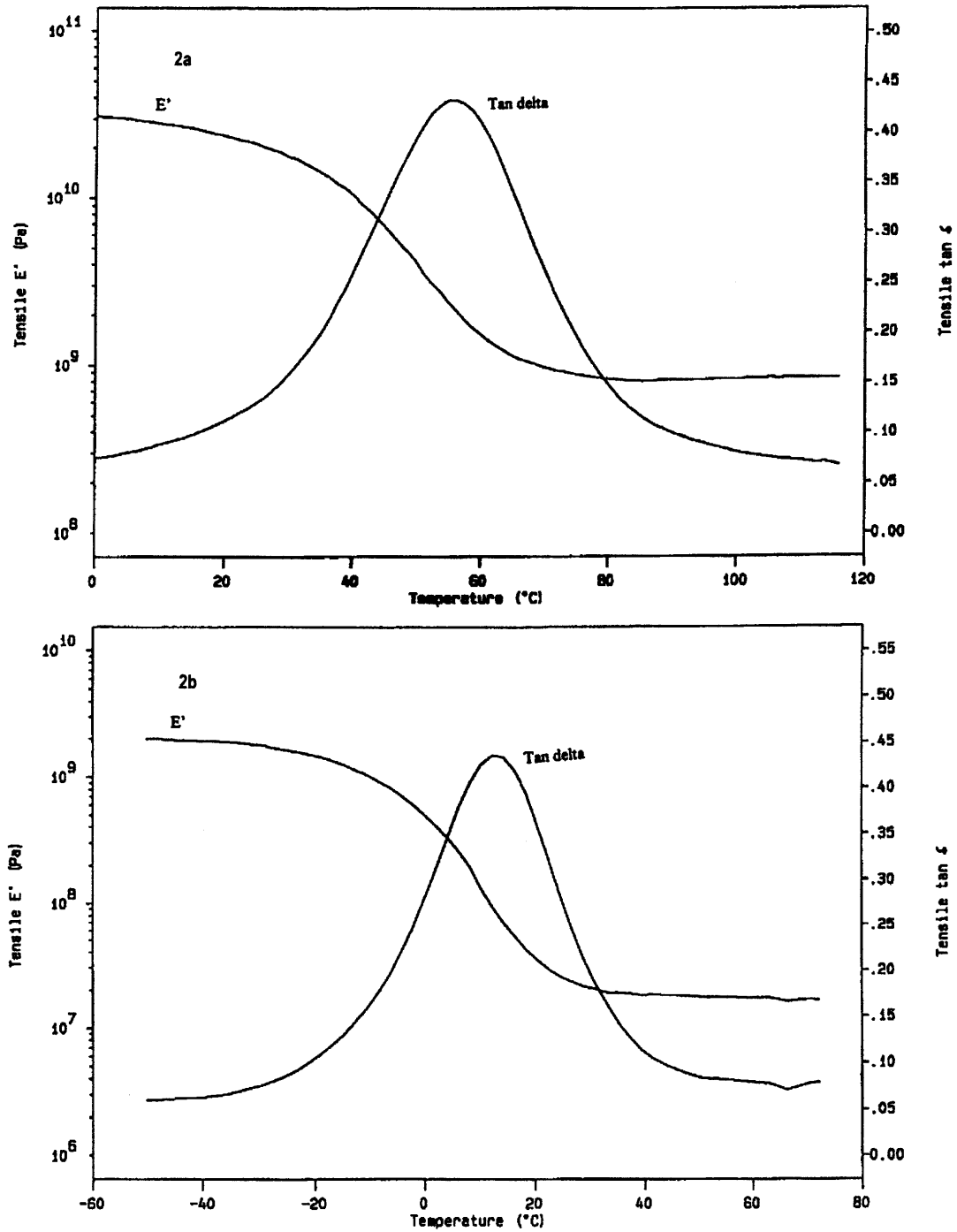


Figure 2: DMTA spectra of the cured films:
DVE3 (2a) and DVE3/HDVE2 80:20 w/w (2b)

The T_g value, expressed by the maximum of the tan δ curve, is clearly shifted to lower temperatures in the presence of HDVE2. Moreover the E' values of the homopolymer are at least one order of magnitude higher than the copolymer in all the range investigated.

In order to evaluate the influence of a monofunctional vinyl ether on the properties of the difunctional system and to confirm the role of the –OH group in the reaction mechanism, we investigated the photocopolymerisation with dodecyl-vinyl ether (DDVE3) and triethylen-glycol-methyl-vinyl-ether (MDVE3) at different concentration ratios. The main results obtained are collected in Table 2.

Changing the content of the monofunctional monomer in the mixture, from 0 to 40% w/w, the Tg value decreases and the flexibilisation of the networks is achieved. Similar results were obtained working on acrylic UV-curable systems¹³ and the effect can be attributed to the decrease of the crosslinking density of the networks¹⁴.

Comparing the results of Table 2 with those obtained with films containing HDVE2 (Table 1), we can see that the flexibilisation effect is stronger in the presence of the hydroxy vinyl ether monomer. This behaviour is surprising because the homopolymers containing –OH groups in the repeating unit have a higher Tg value than their homologues without –OH groups. In the literature many examples are reported, e.g. the Tg of poly-n-propylmethacrylate and poly-2-hydroxypropylmethacrylate are 35°C and 76°C respectively¹⁴. The effect observed in our systems can be understood only by considering the structure formed after the chain transfer reaction of Scheme 1: the polyvinyl chain is shortened, the –OH groups are consumed and flexible ether bonds are introduced in the network.

TABLE 2: Properties of the UV-Cured films containing monovinylethers

Film	% w/w ^a	% mol ^b	R.U. % ^c	Tg (°C) ^d	Tg (°C) ^e	Gel Content %
DVE2	0	0	5.3	41.0	88.6	98.0
DVE2/DDVE	10	7.61	0.0	34.3	80.3	95.3
DVE2/DDVE	20	15.6	2.0	25.6	72.8	93.0
DVE2/DDVE	40	33.1	4.3	-12.4	43.2	90.5
DVE3	0	0	6.7	31.0	58.2	98.0
DVE3/MDVE3	10	10.3	0.0	26.2	47.6	97.0
DVE3/MDVE3	20	20.5	2.3	-8.3	34.0	92.8
DVE3/MDVE3	40	40.5	4.7	-41.6	0.5	90.3

a: weight of monovinylether / total weight, b: moles of monovinylether / total moles, c: Residual Unsaturation obtained by FT-IR, d: by DSC, e: by DMTA

Conclusions

The divinylether systems photopolymerised through a cationic mechanism are made more flexible when a monofunctional vinyl ether is added to the reactive mixture. Also the hydroxy terminated monovinylethers have this effect: surprisingly the obtained films show a Tg even lower than the homologous copolymers without –OH groups. The plasticisation due to the introduction of a monofunctional monomer is attributed to the decrease of the crosslinking density. The better performance of the –OH terminated additives can be explained on the basis of a chain transfer mechanism involving the –OH groups. As a consequence of the reaction, the –OH terminated

monomer decreases the vinyl chain length and at the same time introduces flexible ether bonds in the network.

Acknowledgements

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