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Synthesis

Synthesis of vinyl ester resins
Evidence of secondary reactions by ^{13}C NMR

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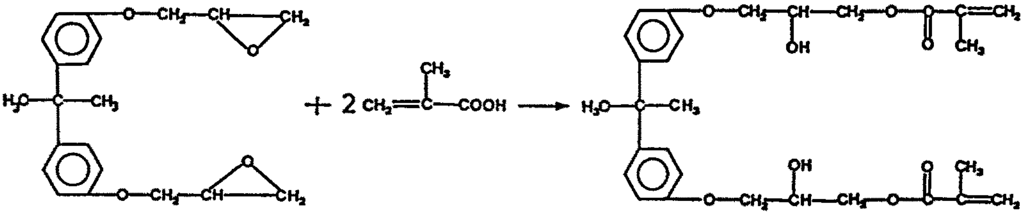
SUMMARY

The reaction of diglycidyl ether of bisphenol A with methacrylic acid was carried out in the presence of an amine catalyst (imidazole) or a chromium chelate (chromium diisopropylsalicylate). The resin products were analyzed by gel permeation chromatography and ^{13}C nuclear magnetic resonance spectroscopy. With both catalysts the reaction is characterized by an isomerization of the hydroxy-ester. The imidazole-catalyzed reaction product gave transesterification species in addition to isomerization product whereas these were absent with the chromium derivative catalyst.

INTRODUCTION

Vinyl ester resins form a family of thermosetting resins which combine the excellent thermal and mechanical properties of epoxy resins with the ease of processing and rapid curing of polyester resins. They are generally producted by addition of ethylenically unsaturated mono carboxylic acid to an epoxy backbone in the presence of basic catalysts(1,2).



Their resistance to acids, alkaline bases and chemicals is outstanding. Unfortunately the shelf life of the resin is very low when compared to that of epoxides and unsaturated polyesters(3). Mcreover, when using a basic catalyst like imidazole we often observed some styrene insoluble gel particles in the resin. This could be due to the fact that under such basic conditions it is difficult to prevent the polymerization of some methacrylic acid forming poly methacrylic acid, which might react with epoxy resin to give cross linked products. Another possibility could be the polymerization of epoxy resin under basic conditions; this was already been reported(4). The above facts prompted us to carry out further investigations in this field to obtain a wider knowledge of the side reactions.

In the present work we therefore, report the synthesis of vinyl ester resins from the diglycidyl ether of bisphenol A and methacrylic acid using imidazole or chromium(III) diisopropylsalicylate(CrDIPS). A compara-

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tive study of the two resin products is made by gel permeation chromatography and ^{13}C nuclear magnetic resonance spectroscopy.

EXPERIMENTAL

Materials:- Diglycidyl ether of bisphenol A (LOPOX 200,CDF-Chimie; epoxy titration:5.714eq.kg^{-1}; M=350), methacrylic acid(Aldrich-chemie), hydroquinone(PROLABO) and imidazole(Sigma) were used as such. Chromium(Ⅲ) diisopropylsalicylate(CrDIPS) is prepared from chromium(Ⅲ) triacetate (CARLO ERBA) and diisopropylsalicylic acid(Koch Light Laboratories Ltd) according to the proceedure given elsewhere(4).

Synthesis of the resin:- 200g of diglycidyl ether of bisphenol A, 99g of methacrylic acid, 0.3g of hydroquinone are placed in a one liter reaction kettle. The mixture is heated to 100°C and stirred continuously. At 100°C, CrDIPS(0.5g) is added and the reaction is continued for 3 hrs. The progress of the reaction is followed by epoxy titration at various intervals. The end product has a bluish green color due to the catalyst; its epoxy content is 0.016 eq.kg^{-1}(0.3%).

The same synthesis is repeated with imidazole(time 8 hrs). The resin product is amber colored.

Analysis:- The chromatograms are recorded on a WATERS 6000 A apparatus equiped with PL-GEL columns(60cm; 50+100 A°).THF is used as eluent at a flow of 1ml.mn^{-1}. ^{13}C NMR spectra are recorded on BRÜKER spectrometers (WP80 and WM250) using $CDCl_3$ as solvent(Ref.$CDCl_3$:77.0ppm).

RESULTS AND DISCUSSION

The catalyst plays an importent part in the reaction of diglycidyl ether of bisphenol A with methacrylic acid. For experiments carried out at the same temperature the completion of the reaction is obtained after 96hrs in the presence of triphenyl antimony(5) and 8hrs with imidazole(VER1).Using CrDIPS as catalyst we observed that the reaction progresses much more rapidly and is complete within 3hrs(VER2).

The chromatograms of the initial epoxy resin and of the vinyl ester resins (VER1 & VER2) are given in Fig.1. With epoxy resin three peaks are observed at the following elution volumes 23.9ml(a), 25.5ml(b) and 26.8ml(c) respectively.(a) corresponds to n=1,(b) is probably due to n=1 with one phenolic end group and the major peak (c) represents n=0. The chromatograms of the vinyl ester resins obtained either by using imidazole or CrDIPS as catalysts showed a shift towards a lower elution volume corresponding to n=1 and n=0(resp.22.5ml and 23.9ml). This lower shift agrees with the esterification of epoxy groups. However in the case of the amine-catalyzed reaction a new peak is observed after the major peak n=0(V_e=24.8ml); this corresponds to the tetra-alcohol(see reaction scheme B) of transesterification,as it is absent in the case of the CrDIPS catalyzed reaction(4). The other peaks appeared at almost the same elution volumes. It can be observed that,in these conditions the methacrylate polymerization of the resin does not take place. To confirm these facts and to obtain further information,^{13}C NMR studies were carried out.

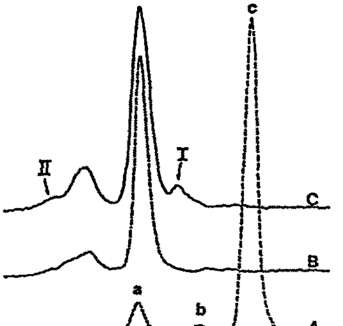


Fig.1:- GPC chromatograms of epoxy resin(A) and vinyl ester resins(VER1:imidazole catalyzed(B); VER2:CrDIPS catalyzed(C))

^{13}C NMR spectra of the two vinyl ester resins(VER1and VER2) are given in figure 2 and the assignment of the peaks of methacrylic acid,DGEBA,VER1 and VER2 in table 1.

Ester peaks are observed in the 167.3- 166.3ppm region. There is a complete disappearance of epoxy carbons in the case of the vinyl ester resin obtained by CrDIPS catalysis. On the other hand small peaks at 50.1 and 44.5ppm indicate the presence of slight amounts of epoxy function in the vinyl ester resin obtained by using imidazole as catalyst. In the region around 60-75ppm the two vinyl ester resins showed three carbons in addition to the main structure of the vinyl ester resin. They corresponds to α and β isomers of secondary and primary alcohols which results from the addition of methacrylic acid either on carbon 1 (α isomer) or on carbon 2(β isomer). The assignment of α and β isomers is given in table 1.

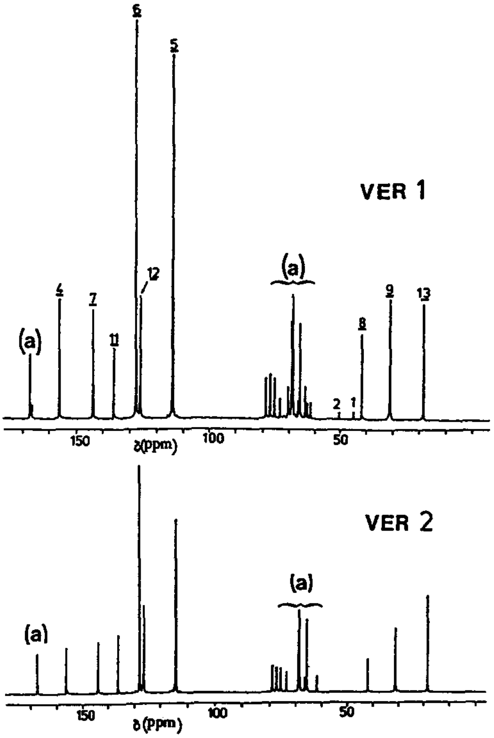


Fig.1:- ^{13}C NMR spectra(20.13 MHz) of the vinyl ester resins(VER1 and VER2); Ref. $CDCl_3$:77.0 ppm. For(a) see Fig.3

The mechanism is illustrated by the following reaction scheme:

Scheme A

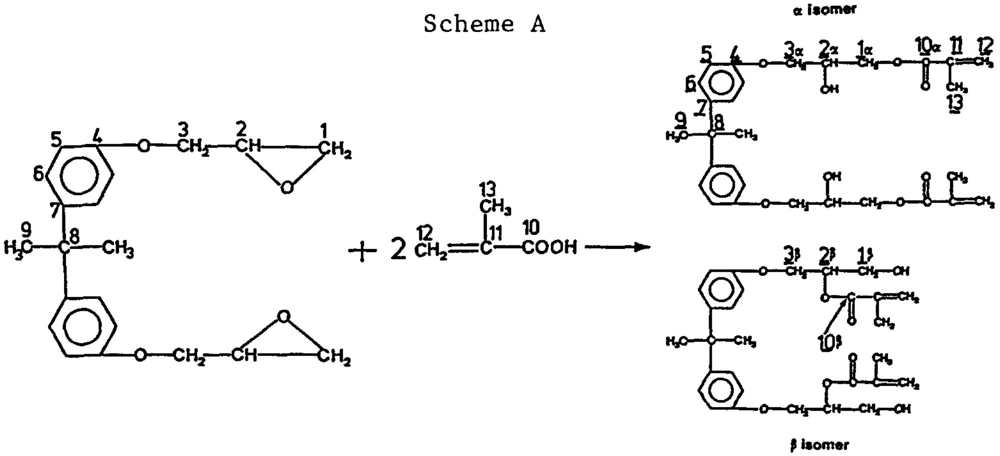


Table 1: ^{13}C NMR assignments of methacrylic acid, epoxy resin and vinyl ester resin.

C n°	Methacrylic acid δ(ppm)	Epoxy resin δ(ppm)	C n°	Vinyl ester resin α isomer δ(ppm)	Vinyl ester resin β isomer δ(ppm)
1		44.3	1	65.5	61.5
2		49.9	2	68.3	73.2
3		68.6	3	68.7	66.2
4		156.1	4	156.0	156.0
5		113.8	5	113.8	113.8
6		127.5	6	127.5	127.5
7		143.4	7	143.5	143.5
8		41.5	8	41.5	41.5
9		30.8	9	30.8	30.8
10	173.3		10	167.3	166.9
11	135.8		11	135.7	135.7
12	127.6		12	126.4	126.4
13	17.6		13	18.0	18.0

However, the imidazole catalysed vinyl ester resins show some additional peaks around the same region. The enlarged region of both the vinyl ester resins is given in fig 3. From the shape and position of these peaks and considering the absence of such peaks in CrDIPS catalysed vinyl ester resin it is obvious that, a transesterification takes place during the esterification of epoxy resin.

On a careful observation of the region around 170ppm(fig 3) the resin shows four different ester peaks in the case of the imidazole catalysed vinyl ester resin, whereas CrDIPS catalysed vinyl ester resin show only two peaks. This is further evidence of transesterification, which produces different esters and could be explained by the following reaction scheme.

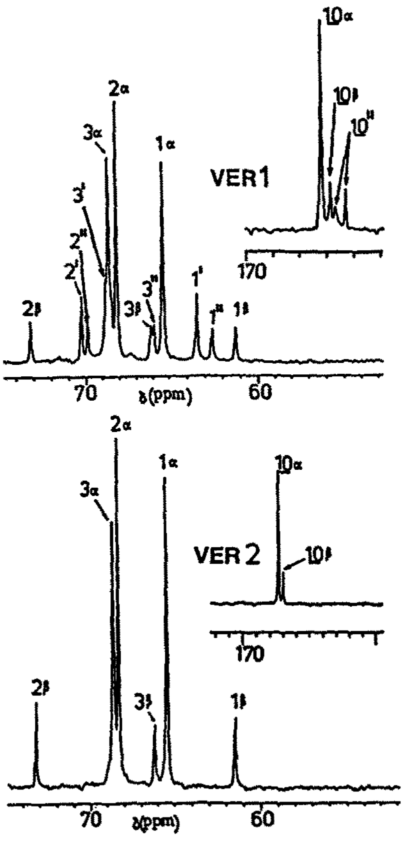
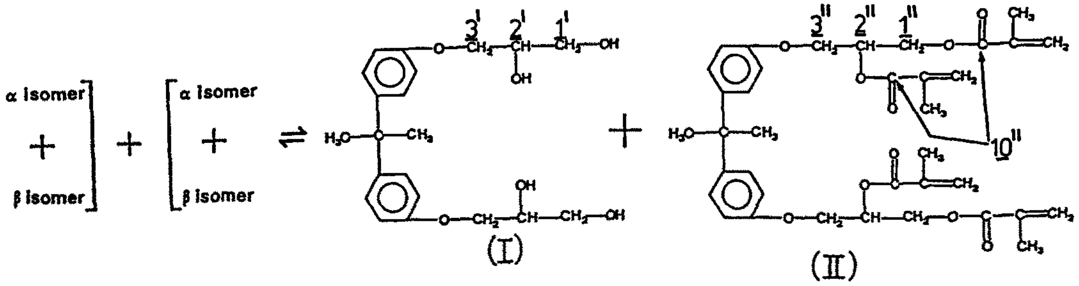


Fig.3:- ^{13}C NMR spectra(20.13MHz) of VER1(a) and VER2(b).Regions 60-80ppm and 160-170ppm.

Scheme B



Intermediary species corresponding to transesterification of only one group also exist, resulting in a triol and a triester, but they are not spectroscopically different from I and II.

The assignment of peaks corresponding to the above scheme are reported in table 2. Comparison of peak heights show that the contribution of transesterification is significant.

Table 2:-^{13}C NMR assignments relative to tetra- alcohol and tetra-ester of imidazole catalysed vinyl ester resin product.

C n°	I δ(ppm)	C n°	II δ(ppm)
1'	63.5	1''	62.6
2'	70.3	2''	70.0
3'	68.8	3''	65.9
		10''	166.7, 166.3

CONCLUSION

From the above results we can conclude that the reaction of diglycidyl ether of bisphenol A with methacrylic acid in presence of a CrDIPS catalyst proceeds with out transesterification and methacrylic polymerization and is much more rapid than the imidazole catalysed reaction.

Irrespective of the catalyst system the reaction yields very rapidly two isomers α and β corresponding to secondary and primary alcohols respectively.

REFERENCES

1. W.H.LINOW, C.R.BEARDEN, W.R.NEVENDORF, 21st SPI Reinforced Plastics/ Composites Conference , paper 1-D,(1966).
2. I.K.VARMA, B.S.RAO, M.S.CHOUDHARY, V.CHOUDHARY, D.S.VARMA, Angew. Makromol. Chem. 130, 191 (1985).
3. T.AWAJI, D.ATOBE, U.S.Patent 4,129,609 (1978)
4. F.LEBLAINVAUX, P.J.MADEC, E.MARECHAL, Polymer Bull. 13, 237 (1985)
5. AJIT K.BANTHIA, I.YILGOR, J.E.MCGRATH, G.WILKES, Polymer Preprints 22, 209 (1981)

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