Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Chemical Modification of A Vinyl Ester Resin by Acid Anhydrides and Characterization of the Products by ^{13}C NMR

B. S. Rao[a]; P. J. Madec[a]; E. Marechal[a]
[a] Laboratoire de Synthèse Macromoléculaire (UA 24-CNRS), Université Pierre et Marie Curie, Paris, France

To cite this Article Rao, B. S. , Madec, P. J. and Marechal, E.(1987) 'Chemical Modification of A Vinyl Ester Resin by Acid Anhydrides and Characterization of the Products by ^{13}C NMR', Journal of Macromolecular Science, Part A, 24: 7, 719 — 733

To link to this Article: DOI: 10.1080/00222338708082089

URL: http://dx.doi.org/10.1080/00222338708082089

J. MACROMOL. SCI.–CHEM., A24(7), pp. 719-733 (1987)

CHEMICAL MODIFICATION OF A VINYL ESTER RESIN BY ACID ANHYDRIDES AND CHARACTERIZATION OF THE PRODUCTS BY ^{13}C NMR

B. S. RAO, P. J. MADEC, and E. MARECHAL

Laboratoire de Synthèse Macromoléculaire (UA 24-CNRS)
Université Pierre et Marie Curie
12 Rue Cuvier
Paris 75005, France

ABSTRACT

A vinyl ester resin was modified into half ester-acids by reaction with phthalic, maleic, and succinic anhydrides, using pyridine as catalyst. GPC analysis indicated that the reaction proceeds without crosslinking or polymerization. ^{13}C-NMR analysis showed that the β-isomer of the vinyl ester resin containing a primary hydroxyl group reacts much more rapidly than the α-isomer with a secondary hydroxyl group.

INTRODUCTION

As unsaturated polyesters, mixtures of vinyl monomers and vinyl ester resins can be cured into network structures. However, their excessive flow during curing at elevated temperature and pressure, especially at high dilution of vinyl monomer, is an important problem as much of the material is wasted, leading to an ultimate composite starved of matrix resin. Therefore, it would be of great technical and economical interest to apply to these resins the thickening process that is used for unsaturated polyester sheet molding compounds (SMC). However, unsaturated polyester resins contain residual acid groups that are absolutely necessary for thickening but not present in vinyl ester resins, where they must be introduced by chemical modification of the side hydroxyl groups.

Although the thickening of vinyl ester resins modified by dicarboxylic acid anhydrides has been already mentioned [1-3], the details of the method and the characterization of the resulting materials are not available. We carefully characterized the influence of the experimental parameters of the synthesis and the structure of vinyl ester resin modified by dicarboxylic acid anhydrides. The results obtained with phthalic, maleic, and succinic anhydrides are reported in the present article. The initial and modified resins are characterized by GPC and ^{13}C-NMR spectroscopy.

EXPERIMENTAL

Materials

Vinyl ester resin was synthesized from the diglycidyl ether of Bisphenol A (LOPOX 200, CDF-Chimie; epoxy titration 5.714 equiv/kg; MW $\approx$ 350) and methacrylic acid (Aldrich-Chimie), using chromium di-isopropyl salicylate (CrDIPS), according to the procedure we reported earlier [4].

Phthalic anhydride-modified vinyl ester resin: Vinyl ester resin (0.03 mol; 15.6 g) and phthalic anhydride (0.06 mol; 8.85 g) are placed in a two-necked flask equipped with a mechanical stirrer. The mixture is heated to 110°C while stirring, pyridine (0.0036 mol; 0.25 g) is added and the reaction carried out for 2 h. The viscosity of the resin increases, resulting in a colorless solid at the end of the reaction.

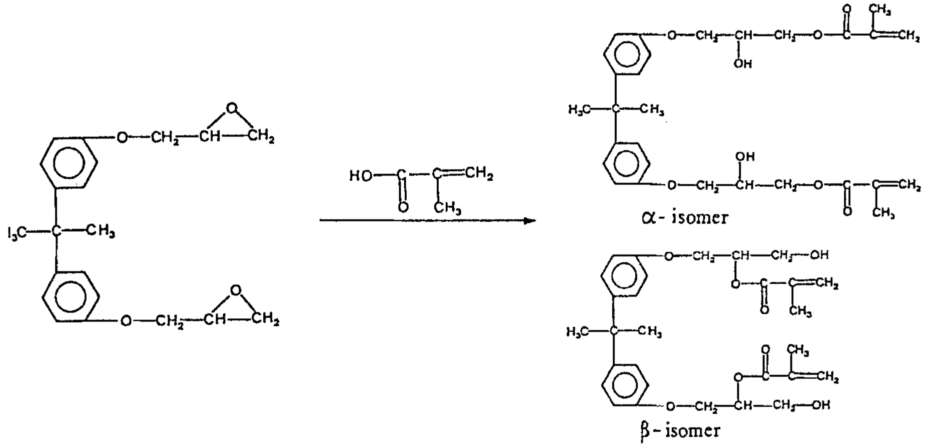
Resins modified by maleic and succinic anhydrides were obtained in the same way, using the same stoichiometric quantities of the reactants and keeping the reaction temperature slightly above the melting point of the anhydrides.

Analysis

The chromatograms are recorded on a Waters 6000 A apparatus equipped with PL-GEL columns (60 cm, 50 + 100 Å), using THF as eluent (1 mL/min). ^{13}C-NMR spectra are recorded at 20.13 MHz on a Bruker spectrometer (WP 80); depending on the solubility of the resin, either $CDCl_3$ or $(CD_3)_2CO$ is used as solvent.

RESULTS AND DISCUSSION

In an earlier paper [4] we reported that the reaction of the diglycidyl ether of Bisphenol A with methacrylic acid, invariably proceeds with the formation of two isomers characterized by either secondary or primary hydroxyl groups, irrespective of the catalyst.



In the present work acid esters are prepared using phthalic, maleic and succinic anhydrides in the presence of pyridine as catalyst. The reaction does not proceed in absence of catalyst. Reaction conditions are given in Table 1.

The modified resins are nonsticky and easily soluble in commonly used solvents. To check whether any polymerization or crosslinking occurred during the esterification, chromatograms of the modified resins were recorded and compared with that of the initial vinyl ester resin (Fig. 1).

The initial resin chromatogram shows two peaks at elution volumes of 21.8 and 23.2 mL; they correspond to $n = 1$ and $n = 0$ (predominantly). Surprisingly, the chromatograms of the vinyl ester resins appear in a very narrow range of elution volume which means that the esterification of the hydroxyl side groups does not shift peaks toward lower elution volumes. We can assume that esterification involves a strong intramolecular hydrogen interaction between carboxylic functions, reducing the expected hydrodynamical volume. However, the GPC chromatograms show clearly that, in all cases, the molecular weight distribution has not changed, i.e., that no crosslinking (diesterification) or polymerization has taken place.

The major changes in the ^{13}C-NMR spectra of the anhydride-modified vinyl ester resins (Fig. 2) are observed in two regions: 160-180 and 60-80 ppm. The carbon atoms are numbered according to the following notation.

TABLE 1. Modification of Vinyl Ester Resin by Different Anhydrides: Experimental Conditions

No.	Sample	Anhydride type	Anhydride, g	Quantity of vinyl ester resin, g	Pyridine, g	Reaction temperature, °C
1	PR_1 [a]	Phthalic	4.42	15.6	0.12	110
2	PR_2 [a]	"	8.85	"	0.25	"
3	MR_1 [b]	Maleic	2.93	"	0.12	60
4	MR_2 [c]	"	5.86	"	0.25	"
5	SR_2 [d]	Succinic	5.97	"	0.25	85

[a] Colorless solid.
[b] Straw-yellow-colored highly viscous resin.
[c] Amber-colored semisolid.
[d] Colorless semisolid.

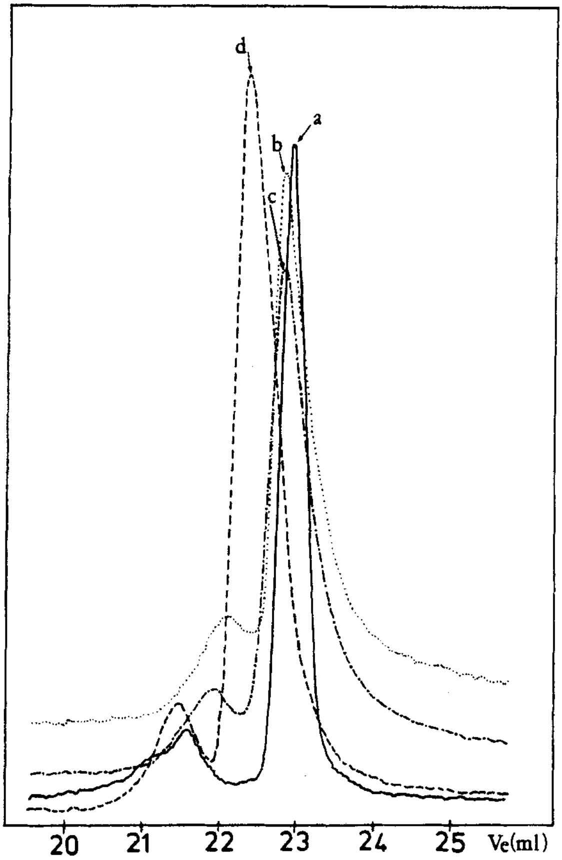


FIG. 1. GPC chromatograms of vinyl ester resin and anhydride-modified vinyl ester resins: (a) Vinyl ester resin, (b) phthalic anhydride-modified resin, (c) maleic anhydride-modified resin, (d) succinic anhydride-modified resin.

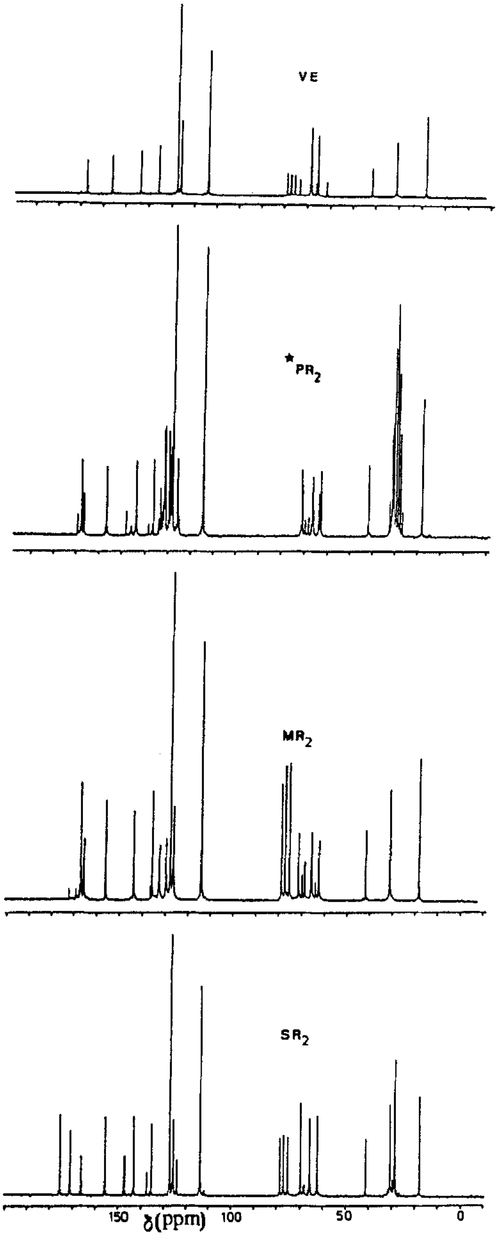
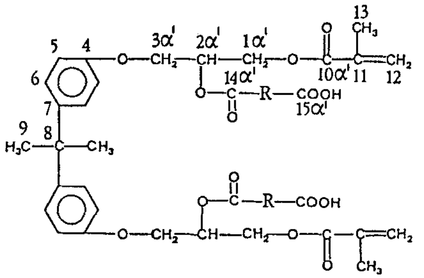
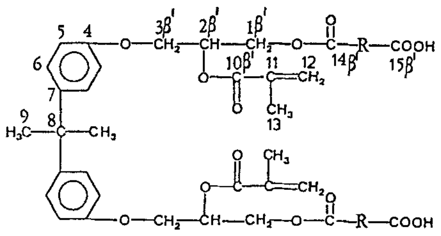


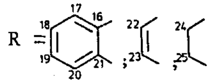
FIG. 2. ^{13}C-NMR spectra (20.13 MHz) of the vinyl ester resin and modified vinyl ester resins. References: $CDCl_3$ (77.0 ppm), $(CD_3)_2CO$ (207 ppm).



α - ester



β - ester



Carbonyl carbons of the acids and esters give peaks between 160 and 180 ppm, the attribution of which is rather difficult. The chemical shift of the carbonyl carbon depends on several parameters: nature of the isomer (*α* or *β*), of the function (acid or ester), and of R. Comparison of the expanded (160-180 ppm) region for the initial and the modified resins is given in Fig. 3 and Table 2.

All the resins show two carbonyl signals due to the carboxylic acid group of the half ester acids. In the case of SR_2 these signals are observed at lower fields (at 176 ppm) compared to MR_2 and PR_2. Four new ester peaks are present in all the modified resins. However, two additional ester peaks were also observed for MR_2. These are possibly due to fumaric ester acids, formed by isomerization of maleic anhydride during the reaction which was carried out at temperatures above the melting point of maleic anhydride. In all the modified resins a small peak at 167 ppm is observed, which is due to the 10*α* carbon of the initial vinyl ester resin.

Very slight shifts in the absorptions of the aromatic carbons of the bisphenol ring and of the olefinic carbons are observed in the modified resins. The olefinic absorptions of MR_2 are clearly separated into maleic (129.2, 129.6) and fumaric parts (132.4, 132.9). The signals due to the phthalic group of PR_2 (128-134 ppm) are also separated into two isomers (Table 3). In addition to these peaks, all the modified resin spectra show three signals due to pyridine (catalyst) and the signals due to unreacted initial resin.

More significant information is obtained from the 60-80 ppm region. The ^{13}C-NMR spectra of the product of the reaction of phthalic anhydride with vinyl ester resin is shown in Fig. 4. The initial vinyl ester resin is represented

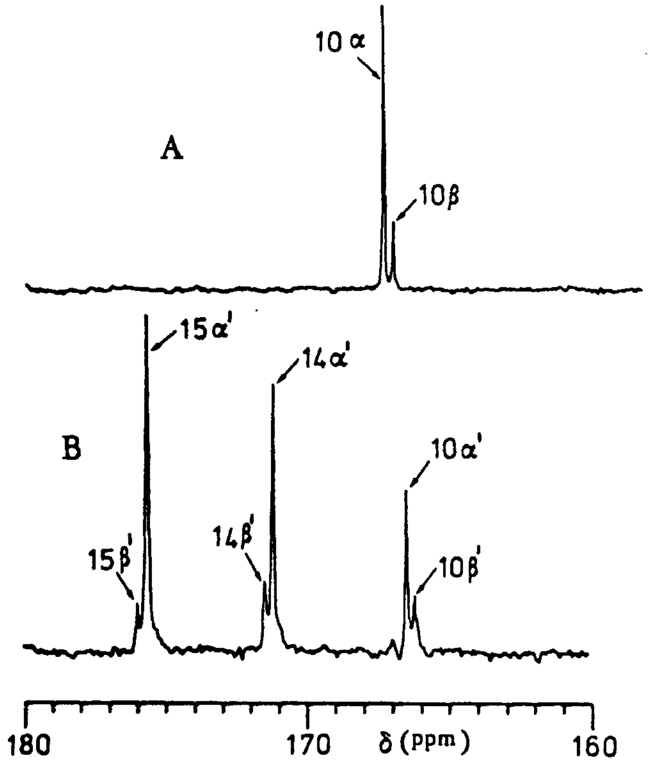


FIG. 3. ^{13}C-NMR spectra (20.13 MHz) of initial and succinic anhydride-modified vinyl ester resins. Expanded region, 160–180 ppm. (A) Vinyl ester resin. (B) Succinic anhydride-modified resin.

by A. In B, half of the hydroxyl groups of the vinyl ester resin were modified with phthalic anhydride. The content of β-isomer in the initial resin (β(/α + β)) decreases. Six new peaks appears due to the α,β-isomers of the modified resin. Spectrum C shows that there is no more β-isomer in the unmodified resin. Moreover, in the modified resin, the content of β-isomer is above its value in the initial compound: the β/(α + β) ratio of the phthalic anhydride-modified resin is 0.312, whereas this ratio is 0.187 for the starting resin. This suggests that there is an equilibrium between α- and β-isomers of the initial resin and that the conversion of α- to β-isomer involves a cyclic transition which can be shown in Scheme 1.

TABLE 2. ^{13}C-NMR Assignments for Isomeric Esters and Acids of Modified Resins[a]

	Ester						Acid	
Sample	10α	10α′	10β	10β′	14α′	14β′	15α′	15β′
VE	167.3		166.9					
PR_2		166.5		166.3	167.3	166.8	167.6	167.7
MR_2		166.5		166.3	165.7	165.2	167.4	167.7
					167.0[b]	166.8[b]		
SR_2		166.6		166.2	171.6	171.2	175.8	176.0

[a] δ, ppm; reference $CDCl_3$ (77.0).

[b] Fumaric ester acids.

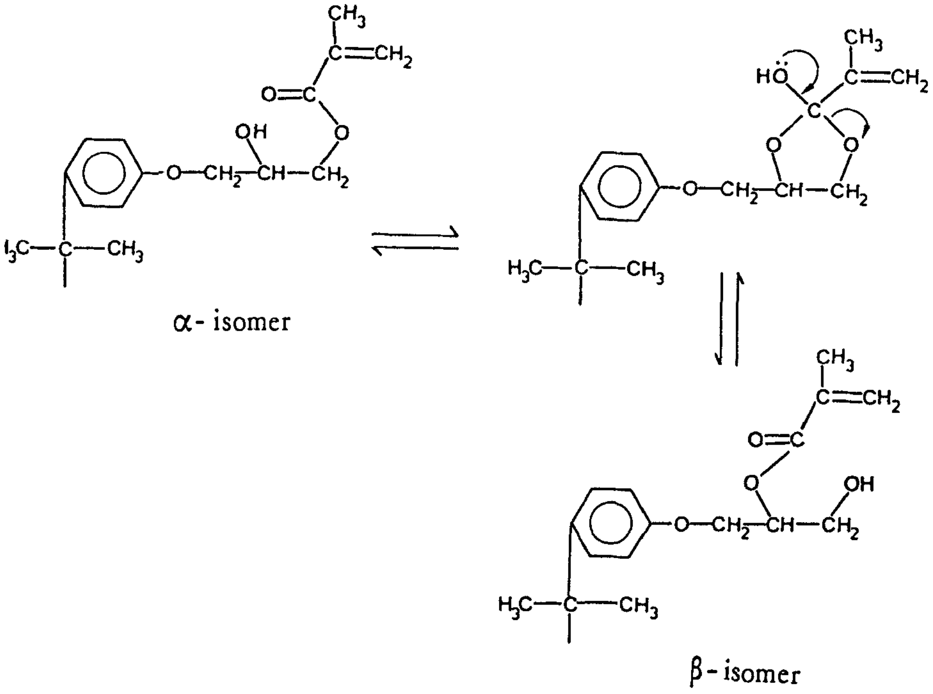
TABLE 3. ^{13}C-NMR Assignments of Half Ester Acid Moiety of Modified Vinyl Ester Resins[a]

	PR$_2$		MR$_2$		
Carbon no.	α-Isomer	β-Isomer	Maleic	Fumaric	SR$_2$
16	133.9	133.3			
17	128.5	128.7			
18	131.0	131.0			
19	131.8	131.6			
20	129.4	129.5			
21	132.9	132.1			
22			129.2	132.4	
23			129.6	132.9	
24					28.6
25					29.6

[a] δ, ppm; reference $CDCl_3$ (77.0).

To confirm this fact, the synthesis of vinyl ester resin was carried out at two different temperatures, 100 and 110°C. The ^{13}C-NMR spectra (Fig. 5) clearly show an increase in the ratio $\beta/(\alpha + \beta)$. Thus it may be assumed that, during the reaction of phthalic anhydride with vinyl ester resin, part of the α-isomer first is converted to β-isomer, which increases the ratio of $\beta/(\alpha + \beta)$.

Some α-isomer of the original vinyl ester resin is still present, indicating that the stoichiometry was not perfectly balanced. The reason for this is that some of the anhydride was sublimed during the course of the reaction, as it was carried out above the melting temperature of the anhydride. An almost similar pattern was observed with maleic anhydride (Fig. 6). However, only three new peaks were observed in the case of succinic anhydride-modified resin (Fig. 6). This indicates that the α- and β-isomers are not distinguishable and that their corresponding carbons overlap. The chemical shifts of α- and β-isomers of anhydride-modified vinyl ester resins were assigned by gated decoupling sequences of ^{13}C-NMR spectra (Table 4).



SCHEME 1.

CONCLUSIONS

Vinyl ester resins can be modified by phthalic, maleic, or succinic anhydrides with pyridine as catalyst. No reaction is observed in the absence of catalyst. Moreover, the β-isomer (primary hydroxyl group) reacts much faster than the α-isomer.

The higher proportion of the β-isomer in the modified resin compared to the original one suggests the existence of a cyclic transition state between the two isomers.

Owing to the sublimation of the anhydrides above their melting points, a slight excess of anhydride is necessary to ensure perfect stoichiometric balance. This may be necessary for the purpose of characterization but it is always better to have some hydroxyl groups left in the resin to obtain good adhesion with glass fibers.

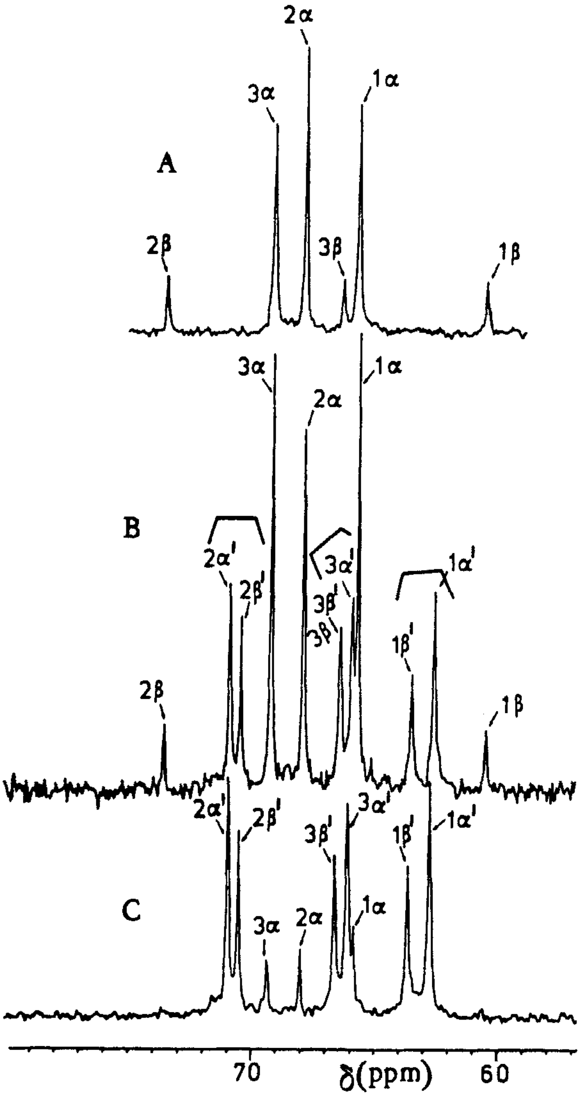


FIG. 4. ^{13}C-NMR spectra of initial and phthalic anhydride-modified vinyl ester resins. Expanded region, 60-80 ppm. (A) Vinyl ester resin. (B) Half-modification. (C) Full modification.

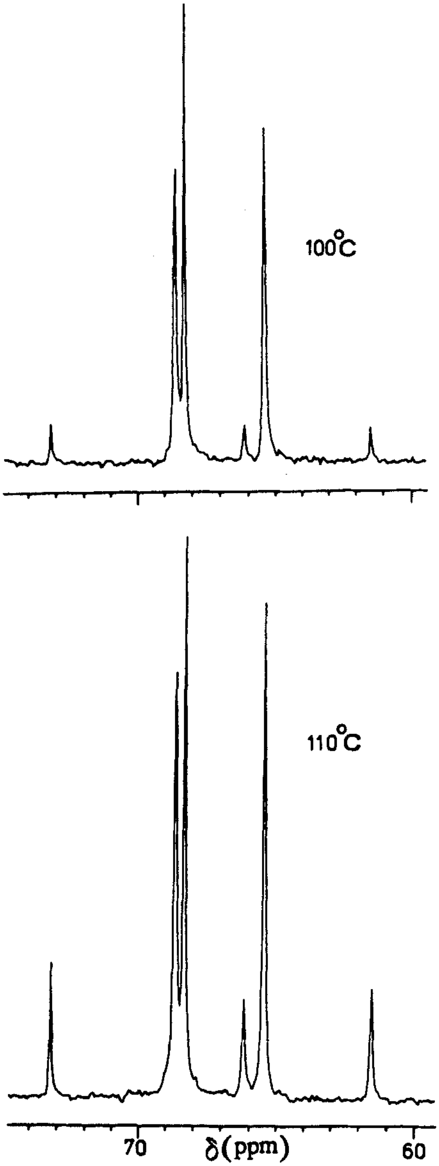


FIG. 5. ^{13}C-NMR spectra (20.13 MHz) of vinyl ester resin synthesized at different temperatures. Expanded region, 60-80 ppm.

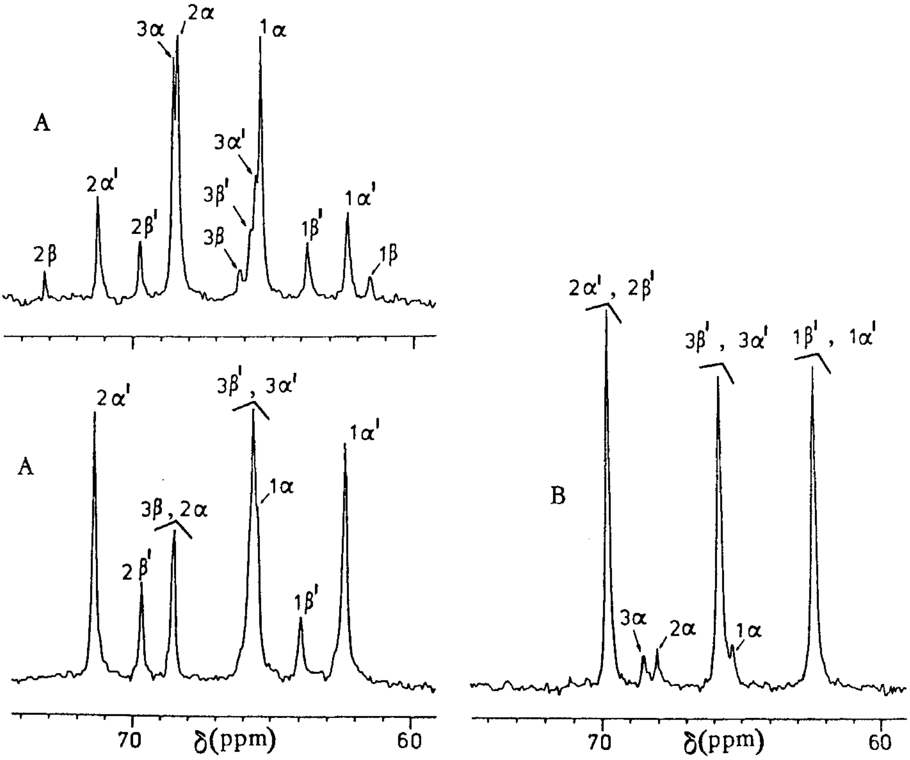


FIG. 6. ^{13}C-NMR spectra of maleic and succinic anhydride-modified vinyl ester resins. Expanded region, 60-80 ppm. (A) Maleic anhydride modification. (B) Succinic anhydride modification.

TABLE 4. ^{13}C-NMR Assignments of α- and β-Isomers of Anhydride-Modified Vinyl Ester Resins (60-80 ppm region)

Sample	1α'	2α'	3α'	1β'	2β'	3β'
PR_2	62.7	71.0	66.1	63.6	70.5	66.6
MR_2	62.4	71.4	65.5	63.9	69.7	65.7
SR_2	62.4	69.8	65.8	62.4	69.8	65.8

ACKNOWLEDGMENT

Dr B. S. Rao thanks the French Government for the award of a postdoctoral fellowship to support this work.

REFERENCES

[1] D. H. Swisher and D. C. Garms, U.S. Patent 3,564,074 (1971).
[2] J. W. Jernigan, C. R. Bearden, and D. W. Pennington, 22nd SPI Reinforced Plastics/Composites Conference, 1967, Paper 80D.
[3] R. F. Stavinova and J. D. Macrae, 27th SPI Reinforced Plastics/Composites Conference, 1972, Paper 2-E.
[4] B. S. Rao, P. J. Madec, and E. Maréchal, *Polym. Bull.*, *16*, 153 (1986).

Received July 9, 1986