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Magic Angle Spinning-Cross Polarization ^{13}C NMR of Crosslinked Unsaturated Polyester Resins

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Summary. Magic Angle Spinning-Cross Polarization (MAS-CP) ^{13}C NMR spectra of four different unsatured resins reticulated with styrene have been measured.

Styrene crosslinks may be constituted essentially by dyads or may consist in $(\text{styrene})_n$ microdomains ($n \geqslant 2$), depending mainly upon the molar ratio of maleic acid residues in the original unsaturated polyester to styrene.

Also in the case of solid unsaturated resins the MAS-CP ^{13}CNMR technique promises to allow structural insights only very difficultly obtainable by more classical indirect means.

Introduction

Polyester resins of widespread technological applications are commonly prepared by mixing unsaturated polyesters and styrene in weight ratios to ensure nearly complete reaction of polyester double bonds when the resin is crosslinked by means of radical processes (cure). In fact, properties of the cured resins depend, among other things, on the degree of cure and also on the average lenght of the crosslinks made up of styrene residues. The sequence distribution of styrene moieties linking pairs of fumaric acid residues (presumably belonging always to different polyester chains) in a cured resin has been only recently examined (A.W.BIRLEY et al. 1981) by spectral analysis of the products resulting from complete alkaline hydrolysis of the resin (i.e.: styrene-fumarate copolymers). In addition, kinetic measurements of the cure of different resins suggest the existence of at least two different, distinguishable stages in the crosslinking process in qualitative agreement with the observations of A.W.BIRLEY et al. (1981). One stage would correspond to the bridging of polyester chain by a single styrene residue while the other would entail formation of polyester-$(\text{styrene})_n$-polyester microdomains ($n = 2 \div x$) in relative amounts depending on the initial molar ratio of reactants.

In our laboratory, in order to investigate more directly the structure of final products (cured resins), high resolu-

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tion MAS-CP ^{13}C NMR technique, particularly useful in the analysis of polymers in bulk has been employed. Four resins differing in maleic acid content and/or in styrene content have been considered.

Experimental

The composition of the four resins studied is given in TABLE I.

TABLE I

Polyester composition (moles of monomers) and relative amounts of styrene in the resins

Sample	Polyesters a)				Styrene b)	c)
	MA	PA	PG	DPG	%w/w	molar ratio
A	1.0	-	1.0	-	33.0	1.8
B	0.7	0.3	-	1.0	33.0	0.9
C	0.33	0.67	1.0	-	42.0	0.4
D	0.4	0.6	0.2	0.8	33.0	1.0

a) MA=maleic anhydride; PA=phthalic anhydride; PG=propyleneglycol; DPG=dipropyleneglycol.
b) weight ratio (%) of styrene to polyester
c) moles of olephinic bonds in the polyester over moles of styrene

Their synthesis has been already described elsewhere (M. PACI et al. 1981). Curing of these resins was carried out at 70°C for 10-12 hours and then at 100°C for 2 hours in the presence of 0.05% w/w of cobalt octoate as catalist and of 1% w/w of methylethylketone peroxide as initiator. The resulting solids were finely ground and the powders examined as such.

MAS-CP ^{13}C NMR spectra were recorded with a Bruker CXP-300 instrument operating at 75.46 MHz. Spinning side bands zeroing and resolution enhancement were performed with the aid of the Bruker Aspect 2000 software. A polystyrene sample has been used as reference for the assignement of the spectra.

Results and Discussion

The MAS-CP ^{13}C nmr spectra of the crosslinked resins listed in TABLE I are shown in FIG.1.

Assignment is acheived in straightforward manner on the basis of high resolution ^{13}C NMR spectra of the original poly-

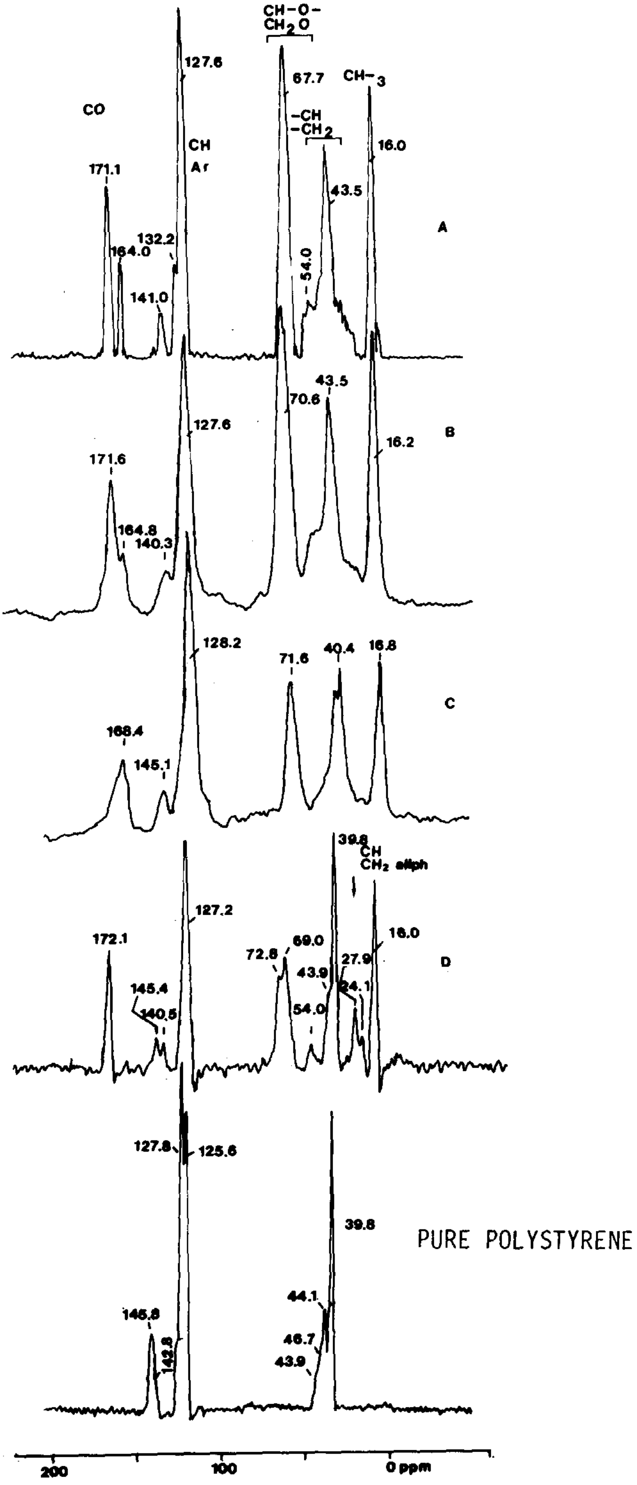

FIG. 1. MAS-CP 75.46 MHz ^{13}C spectra of the cross-linked samples referenced in TABLE I
Chemical shifts are reported in ppm

ester samples in $CDCl_3$ solutions (M. PACI et al. 1981). Pure polystyrene was used to assign the 40.0 ppm resonance due to the methylene and methine carbon atoms in the $(styrene)_n$ bridges of the cured resins. The latter resonance is absent, or at least is very weak, in the spectrum of samples A having the highest MA residues/styrene molar ratio (TABLE I). Moreover, for the same sample the 43.5 ppm resonance exhibits a large multiplicity denoting a distribution of chemical environments around aliphatic moieties.

On the contrary, for sample B with the lowest MA residues/styrene molar ratio, a peak at 40 ppm is clearly developed, thus indicating that substantial amounts of relatively long $(styrene)_n$ bridges should be present in this cured resin.

The predominant type of sequencing of styrene residues in the crosslinked products can be further evidenced considering the resonances of the quaternary carbon atoms belonging to styrene. In fact, the 139-142 ppm peaks would characterize a dyad sequence distribution while the 144 ppm one may evidence n-ads sequences (A.W.BIRLEY et al. 1981). In our case, samples A and B display resonances at 141 and 140.3 ppm, and sample C shows a peak centered at 145.1 ppm. Sample D shows two peaks of nearly the same intensity at 145,4 and 140,5 ppm.

In conclusion, in a cured sample prepared from a resin with a molar ratio of MA residue to styrene higher than 1 the dyad distribution is predominant while for lower molar ratios the n-ads distribution would prevail. In the latter case,however, we cannot exclude the presence also of styrene dyads: in fact, in the spectrum of sample C in particular, the 140 ppm region is nearly completely overlapped with the broad resonance at 128 ppm due to the ring carbons of styrene and of the phthalic residues.

In sample D, on the other hand, both peaks are observed so indicating that even at 1:1 (MA residues/styrene) molar ratio, $(styrene)_n$ bridges are present in the cured resin.This is in agreement with the presence of a strong peak at 39.8 ppm which, as already stated above,would indicate relatively large amounts of $(styrene)_n$ microdomains.

For resin D in particular, peaks at 27.9 and 24.1 ppm would then be assigned to the CH_2 groups of the tetrahydrophthalic residues in the polyester chains.

Finally, the signals of carbonyl groups have different positions and shapes depending mainly on the polyester composition. For sample A two different signals are observed at 171 and 164 ppm.Such large splitting cannot be due to differences arising from carbonyl groups enchainment <u>via</u> -CH- or <u>via</u> CH_2- groups of the propylene glycol moieties.

Most probably the two resonances are due to carbonyl groups of unreacted and of crosslinked MA residues respective ly (in the other spectra carbonyl resonances are crowded because of the presence of phthalic residues too). Results reported here strongly suggest that MAS-CP ^{13}C NMR spectroscopy of cured resins is a unique structural probe for such otherwise rather intractable materials, deserving further detailed studies.

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