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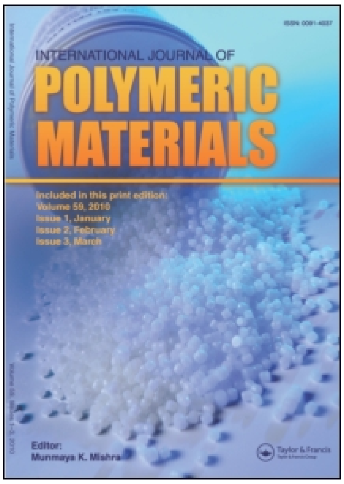

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Characterization of Cured Rubber Modified Polyester Resins by Nuclear Magnetic Resonance Methods

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The cure reaction of rubber-modified unsaturated polyester resins was investigated by ^{13}C-NMR of the hydrolysis products as function of the type and amount of rubber in the resin. A relation was found between the type of terminal groups present on the poly(butadiene) rubber and the length of polystyrene bridges cross-linking the polyester chains.

INTRODUCTION

Polyester resins can be obtained by radical copolymerization of an unsaturated polyester from maleic and phthalic anhydrides and glycol with styrene.

Parkyn *et al.*[1] reported that the properties of cured resins may be strongly influenced by the length of polystyrene bridges between the polyester chains. Moreover, we have found that the impact properties of such matrices may be significantly improved by the inclusion of suitable liquid rubbers such as polybutadiene which contains terminal groups that can react with the hydroxyl-end groups of polyesters.[2] The formation of a block copolymer (polyester-polybutadiene-polyester) is believed to be responsible of such improvements.

The aim of the work was to investigate the effects of the presence of rubbery modifiers upon the chemistry of the cure process. In order to elucidate the influence of rubber on the length of the styrene bridges between the polyester chains, we report in the present paper some results on the ^{12}C-NMR characterization of the hydrolysis products of cured rubber-reinforced polyester resins.

EXPERIMENTAL

The starting unsaturated polyester (PER) used in this work was kindly supplied by Molding system SpA (trace name H35 SNIATRON). The constituents are maleic anhydride, phthalic anhydride and 1,2-propane diol in 0.3:0.7:1 molar ratios. Styrene as a cross-linker was added to all polymers in amounts of 30% by weight. The catalyst used for the cure was methylethyl ketone peroxide (0.5% w/w) and Cobalt octoate as accelerator (0.015% w/w). The curing conditions were 3 hrs at 80°C.

One of the precursors (PBNCO) was prepared by treating hydroxyl-terminated polybutadiene (HTPB, Mw = 1350, average functionality slightly lower than 2, supplied by Polysciences) with an excess of 2,4-toluenediisocyanate (TDI) at 70°C for 10 minutes.[2] The precursor (PBNCO) was reacted with the starting polyester at 70°C for 30 minutes to get ABA type copolymers where A = PER and B = polybutadiene. The polymer obtained has urethane-like bonds between polybutadiene and polyester.

Two copolymers were prepared with 10 and 20% amounts in weight of PBNCO. For comparison purposes, a mechanical blend was prepared under the same conditions having 10% by weight of HTPB.

The samples used for proton and ^{13}C-NMR analysis were hydrolysis products of the styrene cured polyesters and of the blends (cured too) obtained with polybutadiene.

The hydrolysis was carried out by refluxing for 6 hours the powdered materials with KOH and ethylene glycol (6% w/w).[3] The hydrolysis yields the copolymers containing fumarate and styrene residues. The alkaline solution was acidified to pH = 4 to precipitate the styrene-fumarate copolymers. The solid material was washed with ethylene glycol and water mixtures and then with water up to a pH around 7. The precipitate was then dried under vacuum. Subsequently the polymer was treated with diazomethane to obtain an esterified product soluble in chloroform.

This procedure was slightly modified for the blends. Just before the esterification step with diazomethane, the obtained precipitates were washed several times with chloroform in order to wash away the polybutadiene components. The relative amounts of styrene and fumarate were determined via ^{1}H–NMR analysis.

Samples were examined by ^{13}C NMR with a Varian XL-200 MHz instrument operating at 50 MHz and by ^{1}H-NMR with a Bruker WH-270 MHz machine. Both instruments are located at the "Centro Interdipartimentale di Metodologie Chimico-Fisiche" of the University of Naples. In particular, ^{12}C-spectra were obtained using 10 mm sample tube and $CDCL_3$ solution (10% w/v). Experimental conditions were optimized in order to allow full recovery of magnetization between pulses. Typical delay times were of the order of 3 seconds and the number of scans varied between 44000 and 50000.

Three standard copolymers were prepared from diethyl fumarate and styrene for comparison following the procedure described by Birley *et al.*[3] They were prepared from a feed containing 91%, 57% and 11% of styrene in order to have long and short styrene sequences. In fact under the conditions chosen for polymerization monomer reactivity ratios of styrene and diethyl fumarate are 0.3 and 0.07 respectively.

RESULTS AND DISCUSSION

The starting polymers had the following general formulas:

$$\mathrm{HOCO{-}\Phi{-}[{-}O{-}CH(CH_3){-}CH_2{-}O{-}CO{-}\Phi{-}CO{-}O{-}}$$
$$\mathrm{CH(CH_3){-}CH_2{-}O{-}CO{-}CH{=}CH{-}CO{-}]_{\mathit{n}}{-}O{-}}$$
$$\mathrm{{-}CH(CH_3){-}CH_2{-}OH}$$

PER

where Φ = *o*-phenylene

The hydroxyl-terminated polybutadiene undergoes the following reaction with TDI:

HO—PB—OH + 2 OCN—R—NCO →
HTPB TDI
OCN—R—NH—CO—O—PB—O—CO—NH—R—NCO
PBNCO

where R = methyl-1,3-phenylene.

The subsequent reaction between PBNCO and the large excess of PER, as shown by our previous work,[2] leads preferentially to formation of triblock copolymers as reported below:

HOOC—PER—O—CO—NH—R—NH—CO—O—PB—O—
—CO—NH—R—NH—CO—O—PER—COOH
A—B—A Triblock copolymer

The alkaline hydrolysis of cured specimens causes the breakage of ester linkages along the polyester chains, leaving the fumarate-(styrene)$_n$-fumarate copolymers. The resulting material was carefully extracted with $CHCl_3$ in order to get a clean copolymer. This procedure was repeated several times especially in the case of blends as the presence of polybutadiene would interfere in the ^{13}C-NMR analysis. In fact the resonances of polybutadiene unsaturated carbons occur around 140 ppm where the important C1 styrene signals appear.

^{1}H NMR spectra were used to estimate the fumarate-styrene ratios in the polymers obtained from the hydrolysis and in the copolymers used for comparison.

The proton spectra show resonances that demonstrate the isomerization of maleate to fumarate. This is revealed by the appearance of a CH resonance around 6.9 ppm in agreement with literature data.[3] The styrene-fumarate ratios determined for the hydrolysis products from the areas of aromatic and aliphatic regions give (Table I) values of 1.0, 0.9, 0.8 and 1.0. Such data refer to neat polyester, cured polyesters plus PBNCO 10% and 20% by weight and to a mechanical mixture PER/HTPB of 10% polybutadiene respectively. More detailed structural information is obtained from the ^{13}C-NMR spectra of the various polymers used in this work. We have used the standard copolymers at various styrene-fumarate

TABLE I

^{13}C NMR chemical shifts (δ/ppm) of investigated materials

Carb. Atoms	A)	B)	C)	D)
$COOCH_3$	173.7–171.7	173.1–172.3	173.9–172.4	173.9–172.3
Cl styrene	144.1	145.4–142.6	143.9–142.8	145
Cl styrene	140.8–138.5	140.2–138.4	140.9–138.7	140.6–138.9
C_2–C_6	128.1, 127.1 126.6	128.1, 127.1	126.9, 126.6	128.1, 127.3 126.7
CH fumaric	53.7	52	52	52
CH_3O ester	51.4	51.3	51.4	51.4
CH styrene	43.1	43.1	43.0	43.0
CH_2 styrene	40.4	40.5	—	40.4

A) Fumarate-styrene copolymer from neat PER
B) Fumarate-styrene copolymer from PER/PBNCO 90/10 w/w
C) Fumarate-styrene copolymer from PER/PBNCO 80/20 w/w
D) Fumarate-styrene copolymer from PER/HTPB 90/10 w/w

ratios for the identification of the resonances and their assignment in terms of styrene sequences. Chemical shifts and assignments are reported in Table I. Expansions of the spectra showing the aromatic Cl resonances are reported in Figure 1. These resonances appear in the region between 138–146 ppm.[3] They are known[4] to yield information on styrene stereoregularity; in particular it has been found[5] that in the Cl region there are three major components corresponding to iso, syndio and heterotactic sequences covering a spectral range of 2.5 ppm. In styrene homopolymers these components are further split into more resonances that have been assigned to stereosequence distributions up to heptads.[6] In the case of our styrene copolymers the Cl resonances are more widespread and cover a range of 8 ppm. On the basis of literature data[3] it is possible to assign the resonances at lower field (centered at 145 ppm) to polystyrene sequences while the resonances centered at 138 ppm can be attributed to styrene groups adjacent to fumarate units. Both groups of resonances are fairly broadened by configurational effects and degree of polymerization.

The standards we have synthesized show two groups of signals that are roughly centered at 140 and 143 ppm. The group around 140 ppm can be further divided in two broad components, one at 139.3 and the other at 140 ppm. The former is attributed to monomeric units, the latter to diads and *n*-ads 3. Similarly the

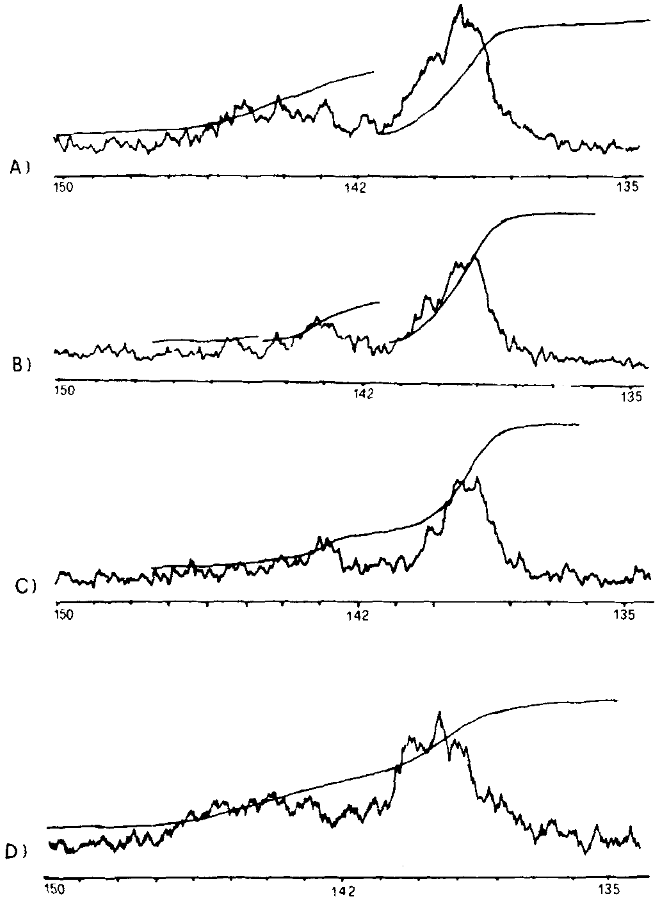

FIGURE 1 Proton decoupled natural abundance ^{13}C NMR spectra of fumarate-styrene copolymer obtained from hydrolysis of: A) PER 100%; B) PER/PBNCO 90/10; C) PER/PBNCO 80/20; D) PER/HTPB 90/10.

group centered at 143 ppm has several components that are assigned to dyads and *n*-ads with *n*3. These resonances are particularly evident in the copolymer obtained with a 57% by weight styrene feed (Figure 2) and are on the other hand rather similar to those of the hydrolyzed polymers (Figure 1).

On these grounds the hydrolysis product of the 100% polyester (to which no polybutadiene was added) exhibits a sequence

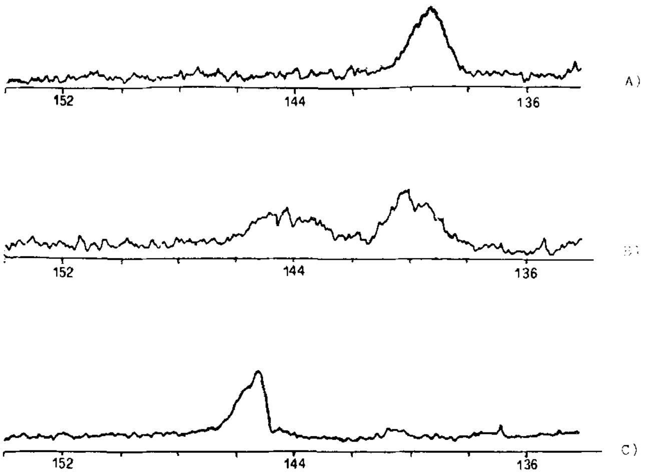

FIGURE 2 Proton decoupled natural abundance ^{13}C-NRM spectra of standard copolymer of styrene and diethylfumarate A) 91% styrene in feed, B) 57% styrene in feed, C) 11% styrene in feed.

distribution of styrene with a predominance of monomeric units and dyads (next to fumarate units). In fact the relative area of the first group of signals centered at 140 ppm is 0.64 versus 0.36 of the second group centered at 144 ppm which is representative of dyads and *n*-ads (not directly bound to fumarate units). When PBNCO is added and blends are formed, the relative integrals for the resonances centered at 140 ppm give higher values of 0.73 and 0.78 for the blends with 10% and 20% of polybutadiene respectively.

A logical extension of these measurements would be a further estimate of the ratio between styrene monomeric units and higher order *n*-ads (next to fumarate units; region 139–141 ppm, Figure 1). Unfortunately the resonances are rather broad and only the overall integral of this region is meaningful. Nevertheless a visual inspection of Figure 1 in the region 139–140 reveals that going from spectrum A to C the observed area increase can be attributed to the high-field component (centered at 139.3 ppm and attributed mostly to monomeric units). This conclusion is on the other hand supported by the concomitant area reduction of the resonances in the

TABLE II

Code and composition of investigated materials and relative areas* of the signals centered at 140 ppm.

Sample code area*	Rubber content (wt%)	Relative integral
PER	0	0.64
PER/HTPB 90/10	10	0.64
PER/PBNCO 90/10	10	0.73
PER/PBNCO 80/20	20	0.78

* The areas are calculated from the ratio of the signal centered at 140 ppm over the signals covering the range 140–144 ppm. Data refer to hydrolyzed materials.

region 142–147 ppm attributed to dyads and *n*-ads with *n*3. Therefore it is fairly evident that the addition of polybutadiene stabilizes short styrene units in the cured polyesters.

We have also examined the polymer obtained from a mechanical mixture of polybutadiene HTPB (10%) and polyester (90%). The results are summarized in Table II and show that the ratio of long styrene sequences does not change when compared to pure polyester.

In particular the relative integral of the high-field area is 0.64 which is essentially similar to that measured for the pure polyester copolymerized with styrene.

These results agree well with a separate study on the viscosity-gelation time relationship which is at present being carried on. Actually, it is found that the presence of HTPB in a mechanical blend scarcely affects the induction time which occurs in polyester resins before gelation. On the contrary, the presence of PBNCO (either 10% or 20% by weight of the feed) even at room temperature causes a significant shortening of the induction period, together with an increase in the viscosity of the medium, and before the addition of the catalyst. Such phenomena can be attributed to the formation of the block copolymers ABA of moderately elevated molecular weight with induce some thickening of the reacting mixture. At the same time, as it is well established in literature,[7] the increase in viscosity causes the gelation to occur earlier, so leading to shorter bridges between the chains.

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