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Cross polarization/magic angle spinning ^{13}C n.m.r. study of crosslinked polyesters

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The unsaturated polyesters derived from maleic anhydride and 2,2-di(4-hydroxypropoxyphenyl)propane were copolymerized with styrene in order to obtain the crosslinked materials. They were studied by means of high resolution ^{13}C n.m.r. in the solid state (CP/MAS). The structural changes upon crosslinking were followed by analysing proton spin-lattice relaxation time, T_1^{H} and spin-lattice relaxation time in the rotating frame, $T_{1\rho}^{\text{H}}$ vs crosslinking temperature and styrene content. With the assumption of spin diffusion among protons of the constituent components of the network, the $T_{1\rho}^{\text{H}}$ and T_1^{H} values were calculated using a model for linear additivity of relaxation rates. The theoretical values were considered as a measure of copolymer effect while the difference between calculated and experimental data were interpreted as being due to crosslinking effect. The results were discussed in terms of the adequacy of crosslinking. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Unsaturated polyesters are commonly prepared by polycondensation of maleic and/or phthalic anhydride with various diols. A three-dimensional network is formed by subsequent copolymerization with vinyl monomers, usually styrene. Mechanical and thermal behaviour of the final products depend both on the structure of unsaturated prepolymers and on the structure of a crosslinked network^{1,2}.

The presence of fumarate (*trans*) unsaturation sites plays an important role in determining the physical and chemical properties of the final crosslinked polyesters owing to a higher reactivity of the *trans* isomer in copolymerization with vinyl monomers. The properties of the cured resin are accounted for by the overall density of crosslinking (determined for a given polyester composition by the degree of double bond consumption and the average length of the crosslinking bridges).

In recent years n.m.r. has been extensively used to study the cured polyester resins of various compositions. Bergmark and Flodin³ found a correlation between ^{13}C spin-lattice relaxation time in the rotating frame, $T_{1\rho}^{\text{C}}$ and the curing temperature for a polyester derived from fumaric acid, adipic acid and 1,2-propylene glycol. High resolution solid state n.m.r. combined with dynamic mechanical spectroscopy was also employed to characterize the structure and dynamics of crosslinked polyesters prepared from maleic anhydride, 1,2-propylene glycol and diethylene glycol⁴. The sequence distribution of styrene crosslinks was studied by Paci *et al.* in polyesters obtained from maleic anhydride, phthalic acid, 1,2-propylene glycol and dipropylene glycol⁵ as well as by Bergmark and Flodin⁶ for fumaric acid/adipic acid/propylene glycol and fumaric acid/isophthalic acid/propylene glycol systems using the method developed by Birley *et al.* (maleic anhydride/terephthalic acid/propylene

glycol)⁷. The crosslinking process of unsaturated polyesters at different catalyst concentrations and temperatures was followed by measuring the changes in proton spin-lattice relaxation time, T_1^{H} using pulsed ^1H n.m.r.^{8,9}. The copolymer and crosslinking effects on glass transition were studied by Bellenger *et al.*^{10,11} for various maleate/phthalate polyesters and vinyl esters crosslinked with styrene.

The aim of this work was to find a relation between the conditions of copolymerization with styrene and a structure of the final crosslinked materials for polyester obtained from maleic anhydride and 2,2-di(4-hydroxypropoxyphenyl)propane.

EXPERIMENTAL

Materials

Unsaturated polyester (UPE) derived from maleic anhydride (MA) and 2,2-di(4-hydroxypropoxyphenyl)propane (PD, propoxylated dian, trademark Dianol 33; NZPO 'Rokita' Co., Poland) was prepared by the high-temperature (205°C) melt polycondensation. The details concerning the structure of PD-based polyester are given elsewhere¹². The polyester was found by ^1H n.m.r. to be predominantly fumarate (*ca.* 95%)¹³. Molecular mass of the studied polyester (calculated from acid number and determined by v.p.o.) corresponded to ~ 6 constituent repeat units. The polyester samples were dissolved in styrene (33, 42, 50 and 60 wt%; N.B. 5% of styrene was additionally incorporated, i.e. the amount which was found to be lost due to evaporation during preparation of the solutions, degassing and curing process) and the initiator consisting of 2% methyl ethyl ketone peroxide and 0.2% cobalt naphthenate promoter was added to the solutions. After degassing the systems were cured between glass plates for 24 h at ambient temperature

followed by postcuring for 24 h at 60, 100 and 150°C. All the samples were found to contain slight amounts of polystyrene and unreacted styrene as revealed by ^1H n.m.r. spectra of the solutions obtained after an overnight immersion of the powdered samples in CDCl_3 .

High molecular weight polystyrene with $M_n = 68\,000$ (Merck, Germany) was used as a standard for the styrene constituent of a hypothetical linear random copolymer with ester.

Measurements

High-resolution solid-state ^{13}C n.m.r. experiments were performed at 20°C on a Varian VXR 300 spectrometer operating at the ^{13}C resonance frequency of 75 MHz. Hartmann-Hahn spin lock cross polarization (CP) along with high power dipolar decoupling (DD) and magic angle sample spinning (MAS) were used to obtain ^{13}C spectra from the solid state¹⁴⁻¹⁶. In the present study the matched spin lock CP transfer employed ^{13}C and ^1H magnetic fields of 20 kHz. Proton decoupling was provided at the strength of 55 kHz. The sample spinning at magic angle was carried out at rates between 5000 and 5500 Hz in a Doty Scientific Co. (Columbia, SC) solids n.m.r. probe. About 200 mg of the powdered samples were compacted into Macor rotors with Kel-F end caps. For all the polymers studied 500–1000 scans were accumulated with 3–6 s delay between pulse sequence repetitions.

The values of proton spin-lattice relaxation time in the rotating frame $T_{1\rho}^{\text{H}}$ were calculated by analysing the decay of the carbon magnetization for long contact times in a cross-polarization experiment^{17,18}. An alternative method involving a variable delay used prior to a fixed contact time¹⁸ was found to afford equivalent results. Spin-lattice relaxation times for protons, T_1^{H} were obtained from a $180^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence followed by simultaneous ^{13}C and ^1H spin lock and acquisition of the ^{13}C magnetization with ^1H decoupling¹⁶. The observed changes in relaxation times values vs sample composition and curing temperature were found to be highly reproducible. Chemical shifts relative to tetramethylsilane (TMS) were determined from the aromatic carbons line (132.1 ppm) of hexamethylbenzene (HMB) used as a standard.

RESULTS AND DISCUSSION

Figure 1 presents the ^{13}C n.m.r. spectra of the PD polyester before (A, B) and after copolymerization with 42 wt% of styrene at 100°C (D). The assignment of the resonance lines of unsaturated polyester in solid state (B) is straightforward as the chemical shifts are practically identical to those observed in solution (A)^{12,13}. The solid-state spectrum of polystyrene is also given for convenience (Figure 1c). Upon crosslinking, the spectra (D vs B) exhibit the changes associated with a formation of styrene bridges: the increase in intensity of the lines at about 42 ppm (CH_2 , CH), 128 ppm (*ortho*, *meta* and *para* aromatic carbons) and 144 ppm (*ipso* carbons) accompanied by the disappearance of the polyester 134 ppm line due to unsaturation sites and a downfield shift (from 164 to 172 ppm) of a resonance arising from the ester carbons. Such changes are known to result from the formation of a three-dimensional network of styrene-crosslinked polyesters³⁻⁵. In all the studied polyester samples obtained in different conditions residual fumarate (*trans*) unsaturation sites were found to be present.

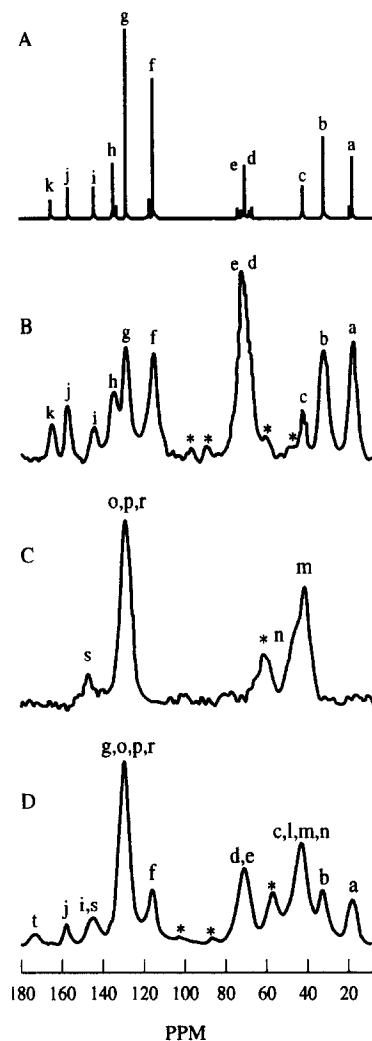


Figure 1 ^{13}C n.m.r. spectra of (A, B) PD-based unsaturated polyester (M600), (C) polystyrene and (D) PD-based polyester crosslinked at 100°C with 42 wt% of styrene (M600/3/100). (A) in CDCl_3 solution; (B–D) CP/MAS n.m.r. spectra obtained with 200 μs contact time. The spinning sidebands are denoted by asterisks. The assignments of the signals are given in Table 1

They were observed indirectly by the existence of the low intensity 164 ppm signal due to ester carbons in the vicinity of double bonds indicating the copolymerization process to be incomplete. Table 1 summarizes the chemical shift assignments.

In order to study the influence of the styrene content and temperature on the structure of the crosslinked polyesters the values of the proton relaxation times were measured. The spin-lattice relaxation time (T_1^{H}) and rotating frame spin-lattice relaxation time ($T_{1\rho}^{\text{H}}$) are known to be sensitive to motions associated with frequencies in the MHz and kHz ranges, respectively¹⁴ and should provide information on the structural changes induced by different curing conditions. The relaxation times were determined for the polyester samples copolymerized and crosslinked at various temperatures ($t_{\text{cl}} = 20, 60, 100$ and 150°C) with 33, 42, 50 and 60 wt% of styrene corresponding to the average styrene sequence length, $l_{\text{st}} = 2, 3, 4$ and 6 styrene units per polyester double bond. According to the abbreviations previously used for the unsaturated polyesters¹² these samples will also be designated as M600/ $l_{\text{st}}/t_{\text{cl}}$.

The evolution of carbon magnetizations measured for

Table 1 ¹³C CP/MAS chemical shifts of the studied polymers (for the unsaturated polyester the values observed in CDCl₃ solution are given in brackets)

PD-based unsaturated polyester UPE(PD)		Polystyrene PS		PD-based polyester crosslinked with styrene UPE(PD)/PS	
Chemical shift (ppm)	Carbon	Chemical shift (ppm)	Carbon	Chemical shift (ppm)	Carbon
16.6 (16.6)	a			17.1	a
31.4 (31.0)	b			31.7	b
41.9 (41.7)	c	40.9	m, n	42.0	c, l, m, n
(69.8)	d				
70.3 (70.1)	d, e			70.0	d, e
	e				
114.2 (114.0)	f			114.5	f
127.8 (127.8)	g	128.0	o, p, r	128.1	g, o, p, r
133.7 (133.9)	h				
143.8 (143.6)	i	147.3	s	144.1	i, s
156.6 (156.3)	j			156.9	j
164.4 (164.4)	k			172.1	t

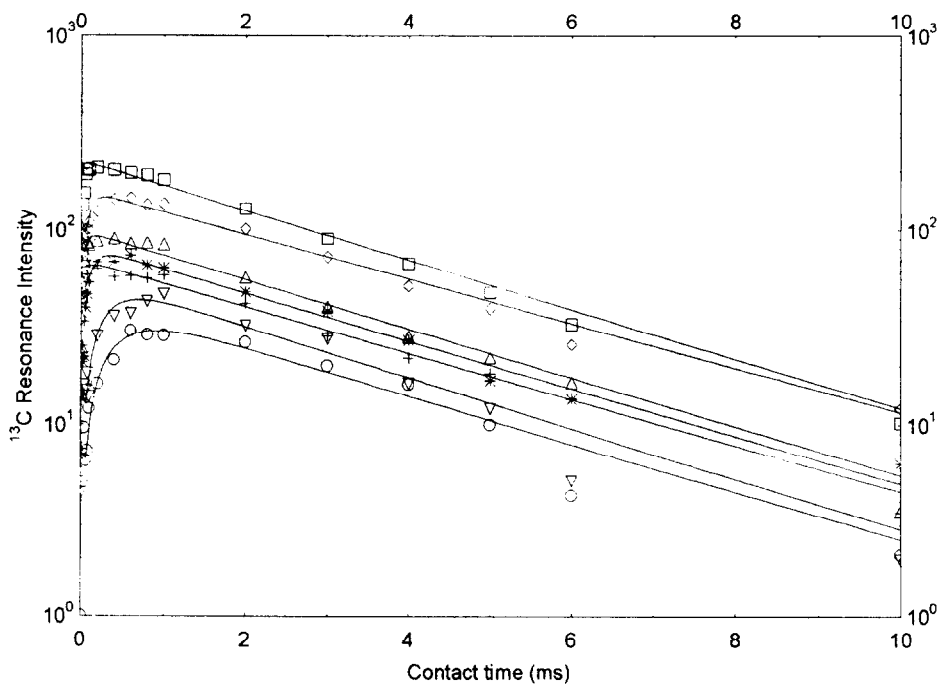
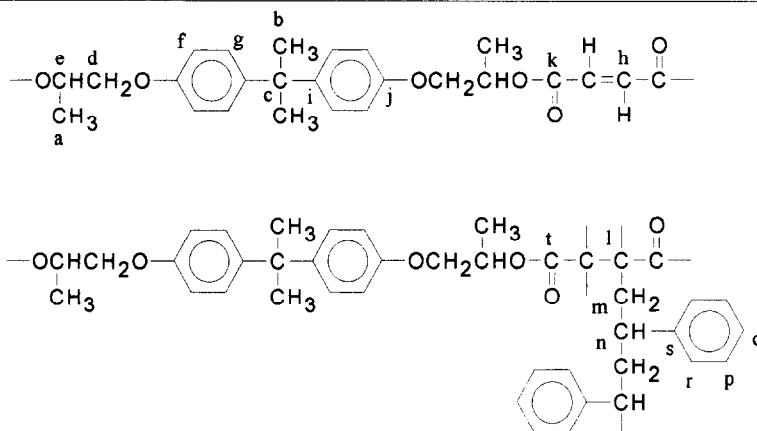


Figure 2 The evolution of carbon magnetization vs cross polarization contact time for PD-based polyester crosslinked at 100°C with 42 wt% of styrene (M600/3/100) measured from different resonance lines: *, 31 ppm; ◇, 40 ppm; △, 70 ppm; +, 114 ppm; □, 128 ppm; ▽, 144 ppm; ○, 157 ppm

Table 2 The proton rotating frame spin-lattice relaxation times ($T_{1\rho}^H$) vs crosslinking temperature and the UPE(PD)/PS network composition

Styrene weight fraction, w_{st}	Average styrene sequence length, l_{st}	$T_{1\rho}^{H,cop}$ (ms)	$t_{cl} = 60^\circ\text{C}$		$t_{cl} = 100^\circ\text{C}$		$t_{cl} = 150^\circ\text{C}$	
			$T_{1\rho}^H$ (ms)	$\Delta T_{1\rho}^H = T_{1\rho}^H - T_{1\rho}^{H,cop}$ (ms)	$T_{1\rho}^H$ (ms)	$\Delta T_{1\rho}^H = T_{1\rho}^H - T_{1\rho}^{H,cop}$ (ms)	$T_{1\rho}^H$ (ms)	$\Delta T_{1\rho}^H = T_{1\rho}^H - T_{1\rho}^{H,cop}$ (ms)
0.33	2	3.10	3.3	0.20	3.5	0.40	3.4	0.30
0.42	3	2.95	3.3	0.35	3.7	0.75	3.4	0.45
0.50	4	2.85	3.1	0.25	3.2	0.35	3.2	0.35
0.60	6	2.70	2.8	0.10	2.8	0.10	2.9	0.20

$T_{1\rho}^{H,cop}$ is the proton rotating-frame spin-lattice relaxation time for a hypothetical UPE(PD)/PS copolymer calculated on the basis of the linear additivity model

different carbons as a function of proton-carbon contact time is displayed in Figure 2 for the UPE(PD)/PS system obtained with 42 wt% of styrene at 100°C (M600/3/100). The long-time magnetizations measured from different carbon resonance lines (including the composite signals) exhibit monoexponential decays according to $T_{1\rho}^H$. The data were fitted to the curves described by the following equation which characterizes the behaviour of the carbon magnetization as a function of the contact time, t_c ¹⁷:

$$M_C = M_{0C}[1 - \exp(-t_c/T_{CH})] \exp(-t_c/T_{1\rho}^H) \quad (1)$$

where T_{CH} is the cross polarization relaxation time.

All the protons were found to share a common T_1^H and $T_{1\rho}^H$ values within the experimental error. The observation of the same relaxation times shows that proton spin diffusion among the constituent components is efficient over the distance of $\sim 200 \text{ \AA}$ corresponding to T_1^H and $\sim 20 \text{ \AA}$ for $T_{1\rho}^H$ thus indicating a homogeneity of the studied systems on a molecular level¹⁸⁻²¹. The average values of proton relaxation times are listed in Table 2. (N.B. A presence of polystyrene and unreacted styrene—see Experimental—and a consequent slight reduction in styrene content involved in the formation of the network was found to exert no measurable influence on the relaxation.)

A structure of the studied networks can be roughly thought of as a system composed of chemically linked linear polymers (polyester and polystyrene) or as a system of mutually connected macromolecules of linear random ester/styrene copolymer. In either approach the constituent repeat unit consists of a fragment of polyester chain between two successive crosslinking sites and a short block of PS.

The changes in the proton relaxation times induced by the reaction with styrene were calculated from the linear additivity model without specifying the proton relaxation sites^{19,20} adapted here tentatively for the case of a three-dimensional network:

$$k_{PD/PS} = \frac{N_H^{PD}}{N_H^{PD} + N_H^{PS}} k_{PD}^0 + \frac{N_H^{PS}}{N_H^{PD} + N_H^{PS}} k_{PS}^0 \quad (2)$$

where N_H^{PD} and N_H^{PS} are the numbers of protons of PD and PS bridge in the constituent repeat unit of the network; and k, k^0 are the proton spin-lattice $(T_1^H)^{-1}$ or spin-lattice in the rotating frame, $(T_{1\rho}^H)^{-1}$ relaxation rates of the whole system and of the constituent components, respectively.

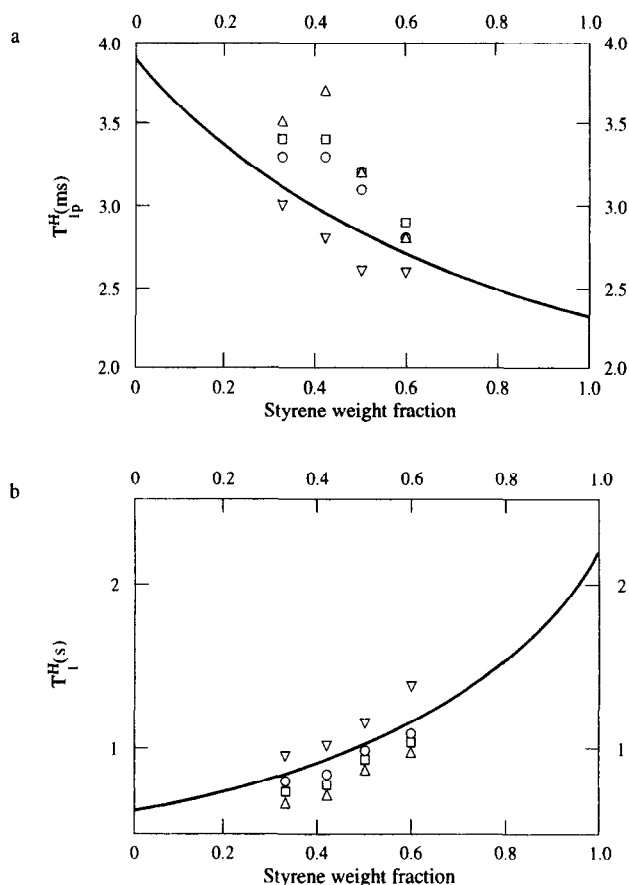


Figure 3 The variations in (a) $T_{1\rho}^H$ and (b) T_1^H with the content of styrene for PD-based polyester crosslinked at different temperatures (∇ , $t_{cl} = 20$; \circ , $t_{cl} = 60$; \triangle , $t_{cl} = 100$; and \square , $t_{cl} = 150^\circ\text{C}$). The solid lines represent the values calculated from equations (3) and (4)

In terms of the styrene weight fraction, w_{st} the relaxation times can be described by the following equations:

$$T_{1\rho}^H = \frac{(6.6 + 1.1w_{st})T_{1\rho}^{H,PD}T_{1\rho}^{H,PS}}{6.6(1 - w_{st})T_{1\rho}^{H,PS} + 7.7w_{st}T_{1\rho}^{H,PD}} \quad (3)$$

$$T_1^H = \frac{(6.6 + 1.1w_{st})T_1^{H,PD}T_1^{H,PS}}{6.6(1 - w_{st})T_1^{H,PS} + 7.7w_{st}T_1^{H,PD}} \quad (4)$$

In the calculations the experimental values determined separately for the PD-based polyester ($T_{1\rho}^{H,PD}$ and $T_1^{H,PD}$) and polystyrene ($T_{1\rho}^{H,PS}$ and $T_1^{H,PS}$) were applied: $T_{1\rho}^{H,PD} = 0.64 \text{ s}$; $T_{1\rho}^{H,PD} = 3.9 \text{ ms}$; $T_1^{H,PS} = 2.2 \text{ s}$; $T_{1\rho}^{H,PS} = 2.3 \text{ ms}$.

The variations in $T_{1\rho}^{\text{H}}$ and T_1^{H} with the content of styrene are displayed in *Figures 3a* and *b*. The solid lines represent the theoretical relaxation time values derived from equations (3) and (4) and refer to a hypothetical linear copolymer of styrene and PD-based fumarate ester. They are thus assumed to illustrate the 'pure' copolymer effect. For the samples obtained at $t_{\text{cl}} = 60, 100$ and 150°C the experimental values of $T_{1\rho}^{\text{H}}$ appear to be higher while T_1^{H} to be lower than corresponding theoretical values. Such behaviour may be ascribed to the enhanced rigidity of the system resulting from the formation of the three-dimensional network. In order to eliminate the copolymer effect related to the changes in overall composition, the differences between the experimental and theoretical values were calculated. These differences, designated as $\Delta T_{1\rho}^{\text{H}}$ and ΔT_1^{H} , may be considered as arising exclusively from the crosslinking

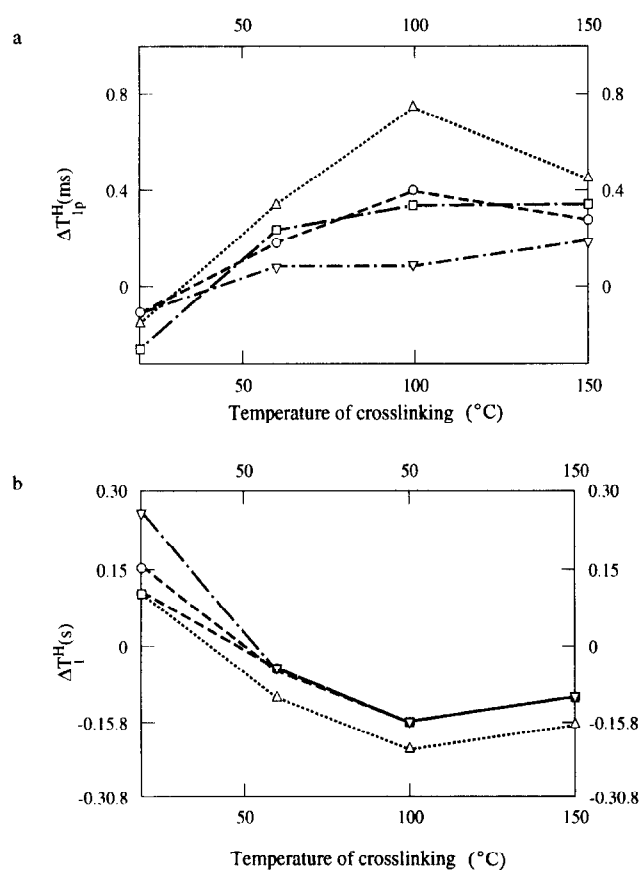


Figure 4 The variations in (a) $\Delta T_{1\rho}^{\text{H}}$ and (b) ΔT_1^{H} with the crosslinking temperature for PD-based polyester crosslinked with different amounts of styrene (\circ , $w_{\text{st}} = 0.33$; Δ , $w_{\text{st}} = 0.42$; \square , $w_{\text{st}} = 0.50$; and ∇ , $w_{\text{st}} = 0.60$)

effect (including a disappearance of the polyester double bonds) and their magnitudes as a measure of the overall crosslinking density and reduced molecular mobility (*Figures 4a* and *b*, *Tables 2* and *3*).

For the samples prepared at $t_{\text{cl}} = 20^\circ\text{C}$ (M600/ $l_{\text{st}}/20$) the experimental relaxation time values relative to the calculated curves reflect the poor crosslinking and high flexibility expected in the case of room temperature curing. With ageing time these values were observed to approach and then to exceed the theoretical curves which indicates an improvement of the crosslinked structure and a consequent increased contribution of the crosslinking effect.

It follows from the plots (*Figures 4a* and *b*) that for a given crosslinking temperature the crosslinking effect vs styrene weight fraction tends to go through a maximum. Likewise, a maximum is observed for a given w_{st} vs t_{cl} . Such behaviour may be explained by considering various possible structures differing in the crosslinking density (*Figure 5*). It seems that at a given temperature, t_{cl} the increase in w_{st} results in a decreasing amount of polyester double bonds and an increase in the crosslinking density, d_{cl} . Further increase in w_{st} leads to an elongation of styrene bridges; l_{st} with no considerable enhancement in double bond consumption, thus lowering d_{cl} . In turn, for a given styrene weight fraction, the increase in crosslinking temperature induces an increase in double bond consumption (high d_{cl}). However, at the highest temperatures an enhanced rate of termination reaction⁶ (via disproportionation) of the growing styrene chain results in an increase in the concentration of the styrene chain ends which leads to reduced d_{cl} and enhanced molecular mobility. Obviously, also the concentration of polyester chain ends varies with the changes in styrene content thus affecting mobility of the system. In consequence, there exist optimum conditions (curing temperature and styrene content) in which the most dense structure of the highest overall crosslinking density is obtained. Various contributions of different structures presented schematically in *Figure 5* may be considered to account for the overall rigidity and crosslinking density and thus for the observed changes in the relaxation times. The crosslinking effect ($\Delta T_{1\rho}^{\text{H}}$ and ΔT_1^{H}) was found to be most pronounced for the sample M600/3/100 cured at 100°C with 42 wt% of styrene.

These observations are in agreement with the findings of Bergmark and Flodin³. The authors measured the carbon spin-lattice relaxation times, $T_{1\rho}^{\text{C}}$ as a function of the curing temperature for the styrene-crosslinked polyester prepared from fumaric acid, adipic acid and propylene glycol. They found the relaxation time maximum corresponding to the most complete crosslinking reaction at around 85°C and ascribed the changes in

Table 3 The proton spin-lattice relaxation times (T_1^{H}) vs crosslinking temperature and the UPE(PD)/PS network composition

Styrene weight fraction, w_{st}	Average styrene sequence length, l_{st}	$T_1^{\text{H,cop}}$ (s)	$t_{\text{cl}} = 60^\circ\text{C}$			$t_{\text{cl}} = 100^\circ\text{C}$		$t_{\text{cl}} = 150^\circ\text{C}$	
			T_1^{H} (s)	$\Delta T_1^{\text{H}} = T_1^{\text{H}} - T_1^{\text{H,cop}}$ (s)	T_1^{H} (s)	$\Delta T_1^{\text{H}} = T_1^{\text{H}} - T_1^{\text{H,cop}}$ (s)	T_1^{H} (s)	$\Delta T_1^{\text{H}} = T_1^{\text{H}} - T_1^{\text{H,cop}}$ (s)	
0.33	2	0.85	0.80	-0.05	0.70	-0.15	0.75	-0.10	
0.42	3	0.95	0.85	-0.10	0.75	-0.20	0.80	-0.15	
0.50	4	1.05	1.00	-0.05	0.90	-0.15	0.95	-0.10	
0.60	6	1.15	1.10	-0.05	1.00	-0.15	1.05	-0.10	

$T_1^{\text{H,cop}}$ is the proton spin-lattice relaxation time for a hypothetical UPE(PD)/PS copolymer calculated on the basis of the linear additivity model

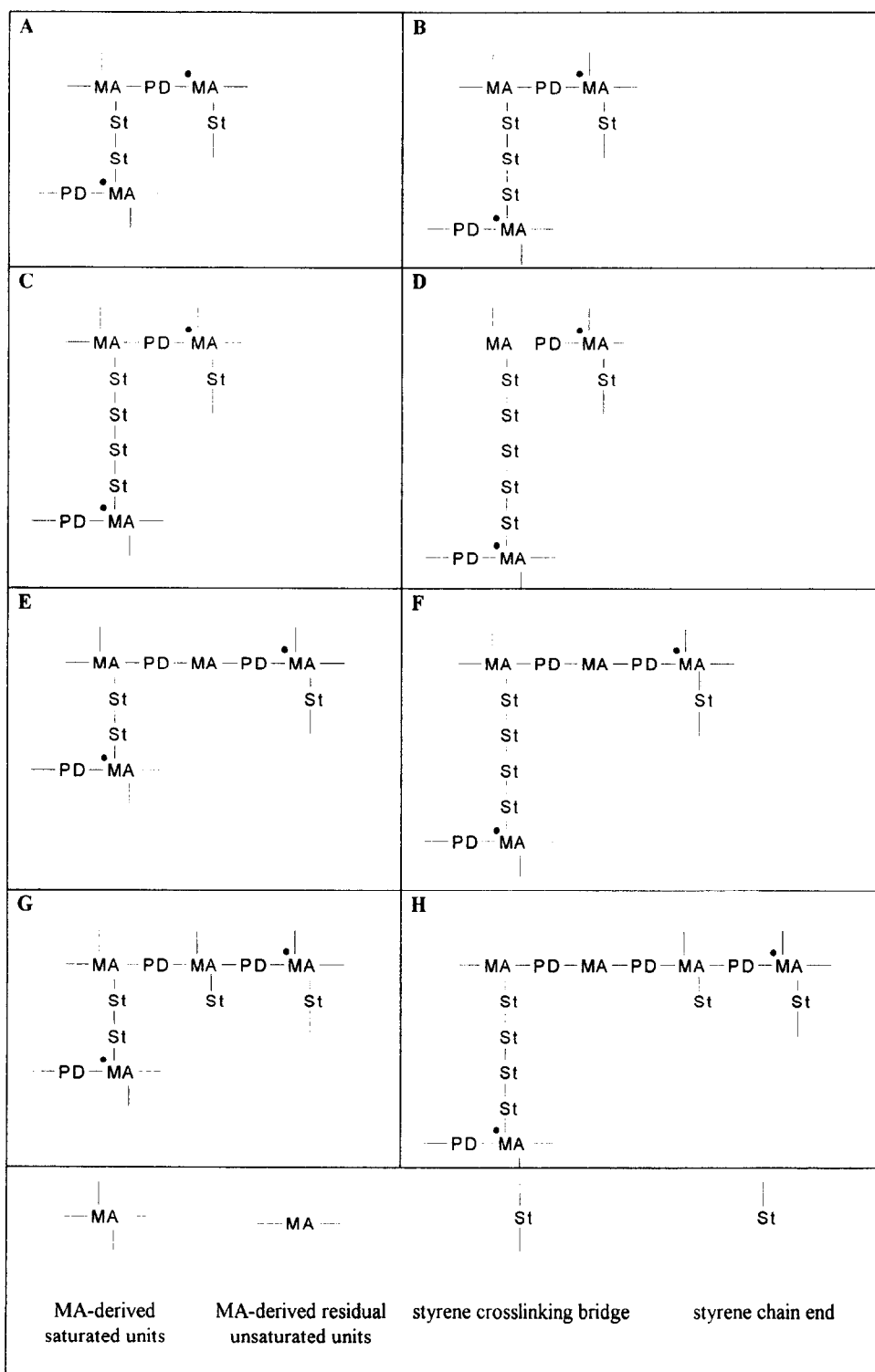


Figure 5 Various possible structures with corresponding calculated values of crosslinking density d_{cl} (mol kg^{-1}) ($d_{cl} = 10^3/M_{cl}$, where M_{cl} is the molecular mass of the copolymer repeat unit between two successive crosslinks marked by the filled dots); (A) 1.58, (B) 1.36, (C) 1.19, (D) 1.06, (E) 0.95, (F) 0.79, (G) 0.86, (H) 0.73

relaxation times with curing temperature to structural variations.

The relaxation behaviour of the studied systems was found to be consistent with changes in glass transition temperature and the maximum in T_g was observed for the same curing temperature and overall composition²².

CONCLUSIONS

An intimate correlation was found between the conditions

of the reaction of PD-based unsaturated polyester with styrene and the structure of the resulting crosslinked material. Optimum conditions favouring a formation of the most 'perfect' structure can be established. Both the temperature and the amount of styrene used were observed to affect the proton relaxation times of the studied systems. The differences in relaxation behaviour may be ascribed to the variations in the structure and molecular mobility of the three-dimensional network. An attempt was made to separate the crosslinking effect from the copolymer effect.

The extent of the crosslinking effect (governed by the amount of residual unsaturation sites, the length of styrene subchains and the concentration of styrene and polyester chain ends) can be determined by subtracting the calculated values of relaxation times related exclusively to the composition (the copolymer effect) from the experimental values resulting from the combined copolymer and crosslinking effects.

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