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^{13}C solid-state n.m.r. study of styrene-crosslinked mixed polyesters

J. Grobelny

Centre for Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland

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Abstract

The styrene-crosslinked mixed polyesters derived from maleic anhydride, 2,2-di-(4-hydroxypropoxyphenyl)propane and 1,2-propylene glycol were studied by means of high-resolution ^{13}C n.m.r. in the solid state (CP/MAS). The proton spin–lattice relaxation time, T_1^{H} and spin–lattice relaxation time in the rotating frame, $T_{1\rho}^{\mathrm{H}}$ were determined and compared with corresponding values calculated for hypothetical mixed ester/styrene copolymers. The results, found to be consistent with T_g data, were interpreted in terms of the mixing, copolymer and crosslinking effects. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Unsaturated mixed polyesters; Crosslinking; ^{13}C CP/MAS nuclear magnetic resonance

1. Introduction

Unsaturated polyesters are defined as mixtures of heterochain prepolymers containing repeat ester groups and aliphatic unsaturation sites in the backbone, with a vinyl monomer. They are commonly prepared by polycondensation of maleic and/or phthalic anhydride with various diols followed by copolymerization with vinyl monomer, usually styrene, to form a three-dimensional crosslinked network [1–3]. Unsaturated polyesters are known to exhibit excellent physico-chemical properties. They can be easily processed and find a wide range of technological applications in many significant areas. Depending on the desired properties of a final product they are used as pure resins or in the form of mixtures with other polymers, fillers and additives.

Mechanical and thermal behaviour of the final products depend both on the composition of unsaturated prepolymers and on the structure of a crosslinked network. The most important structural parameters affecting the properties of unsaturated polyesters include the chemical composition, the degree of *cis–trans* isomerization and the extent of the double bond saturation via the addition of diol components leading to the chain branching. In addition, the properties of polyesters after curing are accounted for by the overall density of crosslinking (determined for a given average length of styrene crosslinking subchains by the unsaturated polyester composition and the degree of double bond consumption).

Bergmark and Flodin [4] measured the carbon spin–lattice relaxation times, $T_{1\rho}^{\mathrm{C}}$ 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 relaxation times with curing temperature to structural variations. The copolymer and crosslinking effects on glass transition temperature were studied by Cook and Delatycki [5] and by Bellenger et al. [6,7] for maleate/phthalate polyesters of various composition crosslinked with styrene. The influence of the amount of styrene on T_g was determined by Lucas et al. [8] in the case of unsaturated polyester derived from maleic anhydride, isophthalic acid, propylene glycol and dipropylene glycol, and the maximum T_g (135°C) was obtained for the samples with the initial ratio of styrene to polyester double bonds between 2 and 3. Takahashi [9] reported the dependence of T_g on the concentration of maleic anhydride, and explained the observation by the changes in crosslinking density.

Previous studies [10,11] concerned the influence of temperature and the amount of styrene as the crosslinking agent on the relaxation behaviour and glass transition temperature of a polyester prepared from maleic anhydride and 2,2-di-(4-hydroxypropoxyphenyl)propane (PD). In this work an attempt was made to determine the copolymer and crosslinking effects as well as that related to the presence of various diol components in styrene-crosslinked mixed polyesters.

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2. Experimental

2.1. Materials

Unsaturated mixed polyesters (UPE) derived from maleic anhydride (MA), propoxylated dian (PD) and 1,2-propylene glycol (PG) were prepared by the high-temperature (205°C) melt polycondensation using 1:1 molar ratio of the anhydride to the overall diol content. The samples, abbreviated as M*x*0*z* [12] differed in the mole fractions of PD(x) and PG(z) diols ($x + z = 6$; x and z being varied between 0 and 6). The structures of studied polyesters were verified by the previously proposed method based on solution-state ^{13}C n.m.r. measurements [12]. The polyester samples were dissolved in styrene, the weight fraction of styrene w_{st} corresponding in all cases to about 2 styrene units per 1 polyester double bond. The initiator consisted of 2% methyl ethyl ketone peroxide and 0.2% cobalt naphthenate promoter. After degassing, the systems were cured between glass plates for 24 h at ambient temperature followed by postcuring for 24 h at 100°C. The styrene-crosslinked polyesters will be designated as $Mxyz/l_{st}/t_{cl}$, where l_{st} is the average styrene sequence length, and t_{cl} is the curing temperature [10].

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.

2.2. Measurements

The ^{13}C spectra (500–1000 scans, 3–6 s repetition time) were taken using Hartmann–Hahn spin lock cross-polarization (CP) along with high power dipolar decoupling (DD) and magic angle sample spinning (MAS) [13,14]. The measurements were carried out at 20°C on a Varian VXR 300 spectrometer operating at the ^{13}C resonance frequency of 75 MHz, equipped with a Doty Scientific Co. (Columbia, SC) solids n.m.r. probe. In the present study the matched spin lock CP transfer employed ^{13}C and ^{1}H 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. About 200 mg of the powdered samples were compacted into Macor rotors with Kel-F end caps.

The proton spin–lattice relaxation times in the rotating frame, $T_{1\rho}^{H}$ and spin–lattice relaxation times for protons, T_1^H were measured by conventional methods [13–16]. The $T_{1\rho}^{H}$ values were calculated by analysing the decay of the carbon magnetization for long contact times in a cross-polarization experiment. The contact time τ_c was varied from 10 μs to 10 ms, and the changes in the intensity of carbon lines were fitted to the curves described by the following equation:

$$I = I_0\left[1 - \exp\left(\frac{-\tau_c}{T_{CH}}\right)\right]\exp\left(\frac{-\tau_c}{T_1^H}\right)$$

where T_{CH} is the cross-polarization relaxation time governed by the strength of the ^{1}H–^{13}C dipolar coupling.

An alternative method was also used involving a variable delay τ (within the range of 50 μs to 10 ms) prior to a fixed contact time ($\tau_c = 200\ \mu$s). In such a case the data were fitted to the equation:

$$I = I_0\exp\left(\frac{-\tau}{T_{1\rho}^{H}}\right)$$

The two methods were found to give equivalent results.

Spin–lattice relaxation times for protons, T_1^H were obtained from a 180°–τ–90° pulse sequence followed by simultaneous 200 μs ^{13}C and ^{1}H spin lock and then acquisition of the ^{13}C magnetization with ^{1}H decoupling. The length of τ ranged from 0.1 to 10 s. The values of T_1^H were obtained by fitting the experimental data to the equation:

$$I = I_0\left[1 - 2\exp\left(\frac{-\tau}{T_1^H}\right)\right]$$

Chemical shifts relative to tetramethylsilane (TMS) were determined from the aromatic carbons line (132.1 ppm) of hexamethylbenzene (HMB) used as a standard.

Differential scanning calorimetry (d.s.c.) measurements were performed on the DuPont apparatus at 20 K/min. The glass transition temperatures were determined from the inflexion points.

The impact strength was determined by the method of Charpy. All the tests were carried out on five samples and averaged.

3. Results and discussion

Fig. 1 displays some typical ^{13}C CP/MAS n.m.r. spectra of the mixed unsaturated and styrene-crosslinked model polyesters prepared from maleic anhydride and various diols. The chemical shift assignment for polyester derived from PD is given elsewhere [10]. A replacement of some PD units by PG induces the expected changes in relative intensities of the signals due to extensive overlapping of the lines at about 17 ppm (CH_3), 70 ppm (OCH_2 and OCH), 134 ppm (fumarate unsaturation sites) and 164 ppm (ester carbons in the vicinity of double bonds). The spectra observed after curing exhibit the resonance lines characteristic for the three-dimensional network of styrene-crosslinked polyesters [4,17,18], i.e. 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 shift to higher frequencies (from 164 to 172 ppm) of a resonance arising from the ester carbons.

Representative behaviours of magnetization of individual carbons as a function of cross polarization contact time τ_c

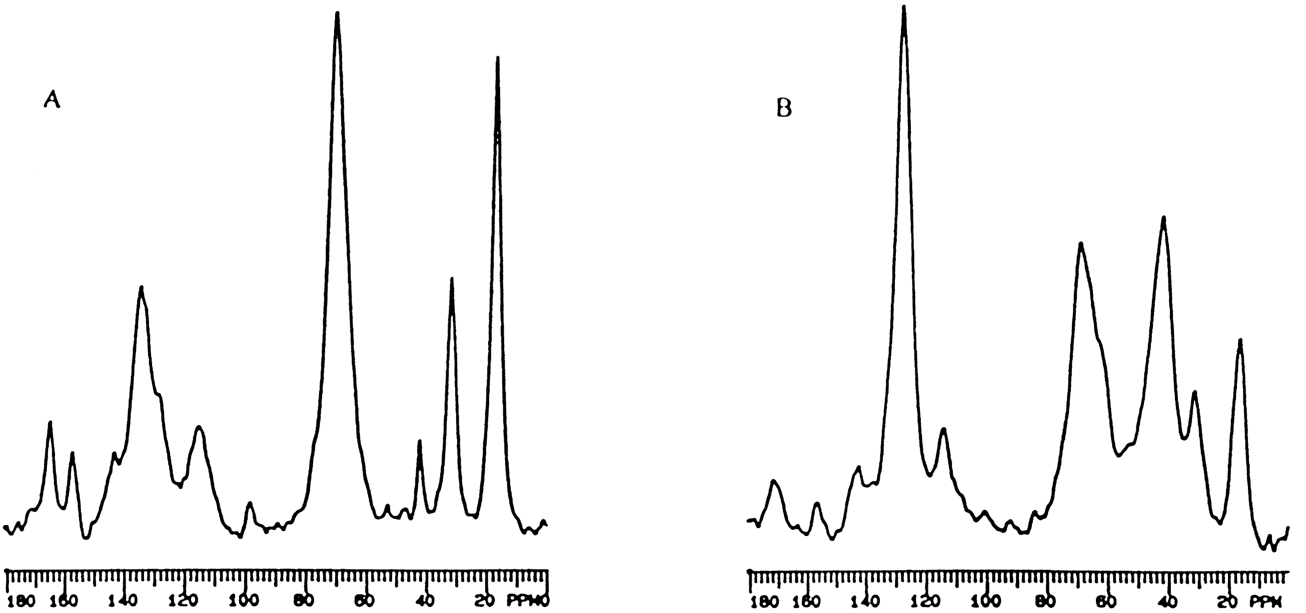

Fig. 1. Representative ^{13}C CP/MAS n.m.r. spectra of the mixed polyesters: (A) unsaturated PD/PG (M204); (B) crosslinked PD/PG (M204/2/100). Spectra were obtained with a CP contact time $\tau_c = 200$ μs.

are exemplified in Fig. 2. The long-time magnetizations determined for various carbon resonance lines of styrene-crosslinked PD/PG polyesters (including the composite ones) were found to exhibit monoexponential and uniform decays according to $T_{1\rho}^{H}$. The observation of the same relaxation times for all the protons shows the efficiency of spin diffusion [19–21] among protons of the polymer components indicating homogeneity of the PD/PG systems on a molecular level of several tens of ångstrom.

The average values of the proton rotating-frame spin–lattice, $T_{1\rho}^{H}$ and spin–lattice, T_1^{H} relaxation times versus composition of unsaturated and crosslinked PD/PG

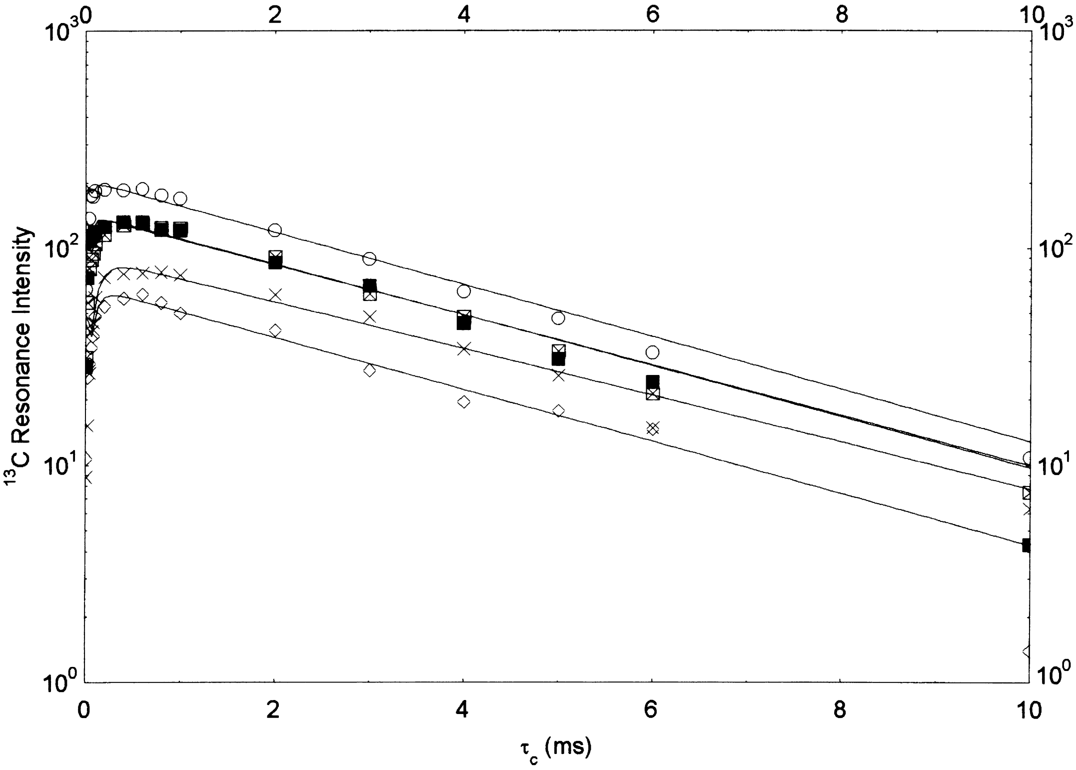

Fig. 2. The evolution of carbon magnetization measured from different resonance signals versus cross-polarization contact time for the styrene-crosslinked PD/PG (M204/2/100) polyester.

Table 1
The proton rotating frame spin–lattice relaxation times ($T_{1\rho}^{\mathrm{H}}$) versus composition of the mixed PD/PG polyesters

Mx0z	a_{PD}	$d_{\mathrm{cl}}^{\mathrm{calcd}}$ (mol/kg)	$T_{1\rho}^{\mathrm{H,\,PD/PG,\,exp.}}$ (ms)	$T_{1\rho}^{\mathrm{H,\,PD/PG,\,calcd}}$ (ms)	$T_{1\rho}^{\mathrm{H,\,(PD/PG)/PS}}$ (ms)	$\Delta T_{1\rho}^{\mathrm{H}}$(co.e.) (ms)	$T_{1\rho}^{\mathrm{H,\,(PD/PG)/PS,\,exp.}}$ (ms)	$\Delta T_{1\rho}^{\mathrm{H}}$(cl.e.) (ms)
M006	0.00	2.76		0.5	1.1	0.6	4.0	2.9
M105	0.17	2.44	0.7	0.8	1.3	0.5		
M204	0.33	2.20	0.8	1.1	1.5	0.4	3.7	2.2
M303	0.50	2.00	1.7	1.6	1.8	0.2		
M402	0.67	1.85	2.5	2.2	2.2	0.0	3.6	1.4
M501	0.83	1.71		2.9	2.6	−0.3		
M600	1.00	1.58	3.9		3.1	−0.8	3.5	0.4

polyesters are presented in Tables 1 and 2. These experimental values can reasonably be expected to result from a combination of various effects. The influence of incorporating PG diol units into unsaturated PD-based polyester (and vice versa) on the relaxation behaviour can be referred to as the mutual mixing effects. The changes induced by copolymerization with styrene can be considered as the copolymer effect. Finally, the crosslinking effect resulting from the reduced molecular mobility is expected to operate in the cured systems.

The experimental values of the relaxation times measured for unsaturated PD/PG polyesters and respective crosslinked polymers were fitted to the curves derived from the linear additivity model for relaxation [20,22,23], adapted to the studied systems. In Eqs. (1)–(5) k and k^0 denote, respectively, the proton spin–lattice $\left(T_1^{\mathrm{H}}\right)^{-1}$ or rotating frame spin–lattice $\left(T_{1\rho}^{\mathrm{H}}\right)^{-1}$ relaxation rates of a given multicomponent system, and those of the individual components. Taking into account the number of protons in the repeat units of PD- and PG-based polyesters, we obtain:

$$k_{\mathrm{PD/PG}} = \frac{7a_{\mathrm{PD}}k_{\mathrm{PD}}^0 + 2\left(1-a_{\mathrm{PD}}\right)k_{\mathrm{PG}}^0}{5a_{\mathrm{PD}}+2} \tag{1}$$

where a_{PD} is the mole fraction of PD in the overall diol content. In Eq. (1) the previously measured relaxation times ($T_{1\rho}^{\mathrm{H,\,PD}} = 3.9$ ms, $T_1^{\mathrm{H,\,PD}} = 0.64$ s) [10] and the experimental values of $k_{\mathrm{PD/PG}}$ were used in order to determine $T_{1\rho}^{\mathrm{H}}$ (0.5 ms) and T_1^{H} (4.0 s) for unsaturated PG-based polyester (Fig. 3).

The copolymer effect, i.e. the influence of copolymerizing PD/PG polyester with styrene, was calculated from the following equation:

$$k_{\mathrm{(PD/PG)/PS}} = \frac{\left(5a_{\mathrm{PD}}+2\right)M_{\mathrm{st}}\left(1-w_{\mathrm{st}}\right)k_{\mathrm{PD/PG}} + 2M_{\mathrm{PD/PG}}^{\mathrm{ru}}w_{\mathrm{st}}k_{\mathrm{PS}}^0}{\left(5a_{\mathrm{PD}}+2\right)M_{\mathrm{st}} + \left[2M_{\mathrm{PD/PG}}^{\mathrm{ru}} - \left(5a_{\mathrm{PD}}+2\right)M_{\mathrm{st}}\right]w_{\mathrm{st}}} \tag{2}$$

where $M_{\mathrm{PD}}^{\mathrm{ru}} = 424$ g/mol and $M_{\mathrm{PG}}^{\mathrm{ru}} = 156$ g/mol are, respectively, the molecular weights of the repeat units of PD- and PG-based polyesters, M_{st} is the molecular weight of styrene, and

$$M_{\mathrm{PD/PG}}^{\mathrm{ru}} = a_{\mathrm{PD}}M_{\mathrm{PD}}^{\mathrm{ru}} + \left(1-a_{\mathrm{PD}}\right)M_{\mathrm{PG}}^{\mathrm{ru}}$$

When

$$w_{\mathrm{st}} = \frac{l_{\mathrm{st}}M_{\mathrm{st}}}{\left(M_{\mathrm{PD/PG}}^{\mathrm{ru}} + l_{\mathrm{st}}M_{\mathrm{st}}\right)}$$

corresponds to $l_{\mathrm{st}} = 2$, Eq. (2) becomes:

$$k_{\mathrm{(PD/PG)/PS}} = \frac{\left(5a_{\mathrm{PD}}+2\right)k_{\mathrm{PD/PG}} + 4k_{\mathrm{PS}}^0}{5a_{\mathrm{PD}}+6} \tag{3}$$

Alternatively, if the $k_{\mathrm{PD/PG}}$ of the mixed polyester were not known, Eqs. (2) and (3) could be expressed in terms of the k_{PD}^0 and k_{PG}^0 values, measured separately for individual polyesters derived from one kind of each diol:

$$k_{\mathrm{(PD/PG)/PS}} = \frac{7a_{\mathrm{PD}}M_{\mathrm{st}}\left(1-w_{\mathrm{st}}\right)k_{\mathrm{PD}}^0 + 2\left(1-a_{\mathrm{PD}}\right)M_{\mathrm{st}}\left(1-w_{\mathrm{st}}\right)k_{\mathrm{PG}}^0 + 2M_{\mathrm{PD/PG}}^{\mathrm{ru}}w_{\mathrm{st}}k_{\mathrm{PS}}^0}{\left(5a_{\mathrm{PD}}+2\right)M_{\mathrm{st}} + \left[2M_{\mathrm{PD/PG}}^{\mathrm{ru}} - \left(5a_{\mathrm{PD}}+2\right)M_{\mathrm{st}}\right]w_{\mathrm{st}}} \tag{4}$$

Table 2
The proton spin–lattice relaxation times (T_1^{H}) versus composition of the mixed PD/PG polyesters

Mx0z	a_{PD}	$d_{\mathrm{cl}}^{\mathrm{calcd}}$ (mol/kg)	$T_1^{\mathrm{H,\,PD/PG,\,exp.}}$ (s)	$T_1^{\mathrm{H,\,PD/PG,\,calcd}}$ (s)	$T_1^{\mathrm{H,\,(PD/PG)/PS}}$ (s)	ΔT_1^{H}(co.e.) (s)	$T_1^{\mathrm{H,\,(PD/PG)/PS,\,exp.}}$ (s)	ΔT_1^{H}(cl.e.) (s)
M006	0.00	2.76		4.00	2.59	−1.41	1.50	−1.09
M105	0.17	2.44	1.30	1.27	1.67	0.40		
M204	0.33	2.20	0.80	0.92	1.33	0.41	0.96	−0.37
M303	0.50	2.00	0.75	0.79	1.13	0.34		
M402	0.67	1.85	0.65	0.72	1.00	0.28	0.80	−0.20
M501	0.83	1.71		0.67	0.92	0.25		
M600	1.00	1.58	0.64		0.86	0.22	0.70	−0.16

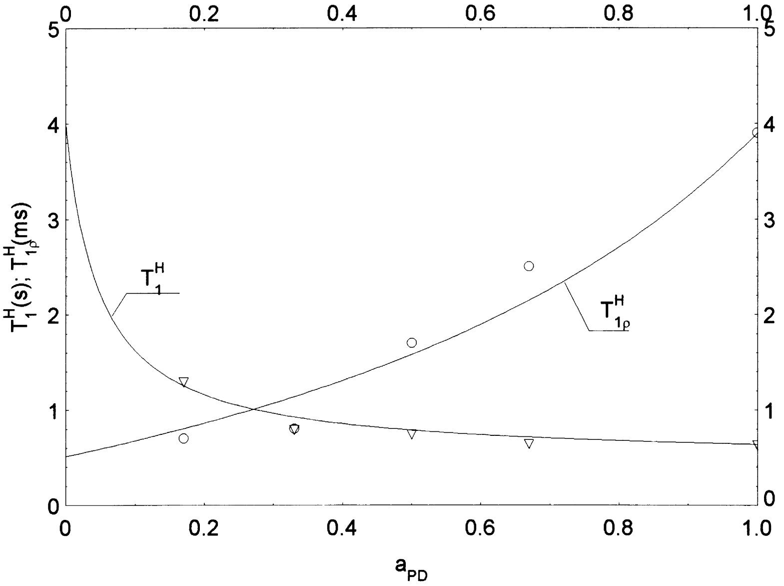

Fig. 3. The variations in $T_{1\rho}^{\mathrm{H}}$ and T_1^{H} with the mole fraction of PD for PD/PG unsaturated polyesters.

and for $l_{\mathrm{st}} = 2$:

$$k_{\mathrm{(PD/PG)/PS}} = \frac{7a_{\mathrm{PD}}k_{\mathrm{PD}}^0 + 2(1 - a_{\mathrm{PD}})k_{\mathrm{PG}}^0 + 4k_{\mathrm{PS}}^0}{5a_{\mathrm{PD}} + 6} \tag{5}$$

In Eqs. (2)–(5) k_{PS}^0 stands for the inverse relaxation times of polystyrene [10]: $T_{1\rho}^{\mathrm{H,PS}} = 2.3$ ms; $T_1^{\mathrm{H,PS}} = 2.2$ s).

The above equations enable the calculation of the relaxation time values for the hypothetical linear copolymer of mixed PD/PG polyester with styrene (Fig. 4; Tables 1 and 2). These values when compared with corresponding unsaturated polymer express the changes induced by copolymerization with styrene. The differences $\Delta 1/k(\mathrm{co.e.}) = 1/k^{\mathrm{(PD/PG)/PS}} - 1/k^{\mathrm{PD/PG}}$ can thus be regarded as the copolymer effect. Therefore the differences $\Delta 1/k(\mathrm{cl.e.}) = 1/k^{\mathrm{(PD/PG)/PS,exp.}} - 1/k^{\mathrm{(PD/PG)/PS}}$ between the experimental and calculated values can reasonably be expected to result exclusively from the crosslinking effect. The copolymer and crosslinking effects as a function of theoretical crosslinking density d_{cl}[1] are presented in Fig. 5.

The relaxation behaviours of the unsaturated and crosslinked PD/PG polyesters were found to be consistent with the T_g data obtained by d.s.c. [Fig. 6(a); Table 3]. The same three effects, mentioned above, operating in the system can be discerned.

Considering the mixing effect, a good correlation was found between the experimental T_g values of unsaturated PD/PG polyesters and those calculated from the relevant equation [24]:

$$\frac{1}{T_g^{\mathrm{PD/PG}}} = \frac{1}{T_g^{\mathrm{PD}}}w_{\mathrm{PD}} + \frac{1}{T_g^{\mathrm{PG}}}(1 - w_{\mathrm{PD}}) \tag{6}$$

where $T_g^{\mathrm{PD}} = 331$ K and $T_g^{\mathrm{PG}} = 268$ K, designate, respectively, the experimentally determined values for PD- and PG-based fumarate polyester, while w_{PD} stands for the weight fraction of PD in the overall diol content.

The theoretical values which can be assumed to be due to the copolymer effect were derived from the equation:

$$\frac{1}{T_g^{\mathrm{(PD/PG)/PS}}} = \frac{1}{T_g^{\mathrm{PD/PG}}}(1 - w_{\mathrm{st}}) + \frac{1}{T_g^{\mathrm{PS}}}w_{\mathrm{st}} \tag{7}$$

where $T_g^{\mathrm{PD/PG}}$ are the values determined from Eq. (6) for PD/PG unsaturated polyesters with various contents of

Table 3
Glass transition temperatures (T_g) versus composition of the mixed PD/PG polyesters

M*x*0*z*	a_{PD}	$d_{\mathrm{cl}}^{\mathrm{calcd}}$ (mol/kg)	$T_g^{\mathrm{PD/PG,\,exp.}}$ (K)	$T_g^{\mathrm{PD/PG,\,calcd}}$ (K)	$T_g^{\mathrm{(PD/PG)/PS}}$ (K)	ΔT_g(co.e.) (K)	$T_g^{\mathrm{(PD/PG)/PS,\,exp.}}$ (K)	ΔT_g(cl.e.) (K)
M006	0.00	2.76	268		321	53	436	115
M105	0.17	2.44	293	287	327	40		
M204	0.33	2.20	302	301	332	31	441	109
M303	0.50	2.00		311	336	25		
M402	0.67	1.85	322	319	339	20	405	66
M501	0.83	1.71		326	342	16		
M600	1.00	1.58	331		345	14	410	65

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[1] $d_{\mathrm{cl}} = 10^3/M_{\mathrm{cl}}^{\mathrm{ru}}$, where $M_{\mathrm{cl}}^{\mathrm{ru}} = a_{\mathrm{PD}}M_{\mathrm{PD}}^{\mathrm{ru}} + (1 - a_{\mathrm{PD}})M_{\mathrm{PG}}^{\mathrm{ru}} + l_{\mathrm{st}}M_{\mathrm{st}}$ is the molecular weight of the (PD/PG)/PS copolymer repeat unit between two successive crosslinks.

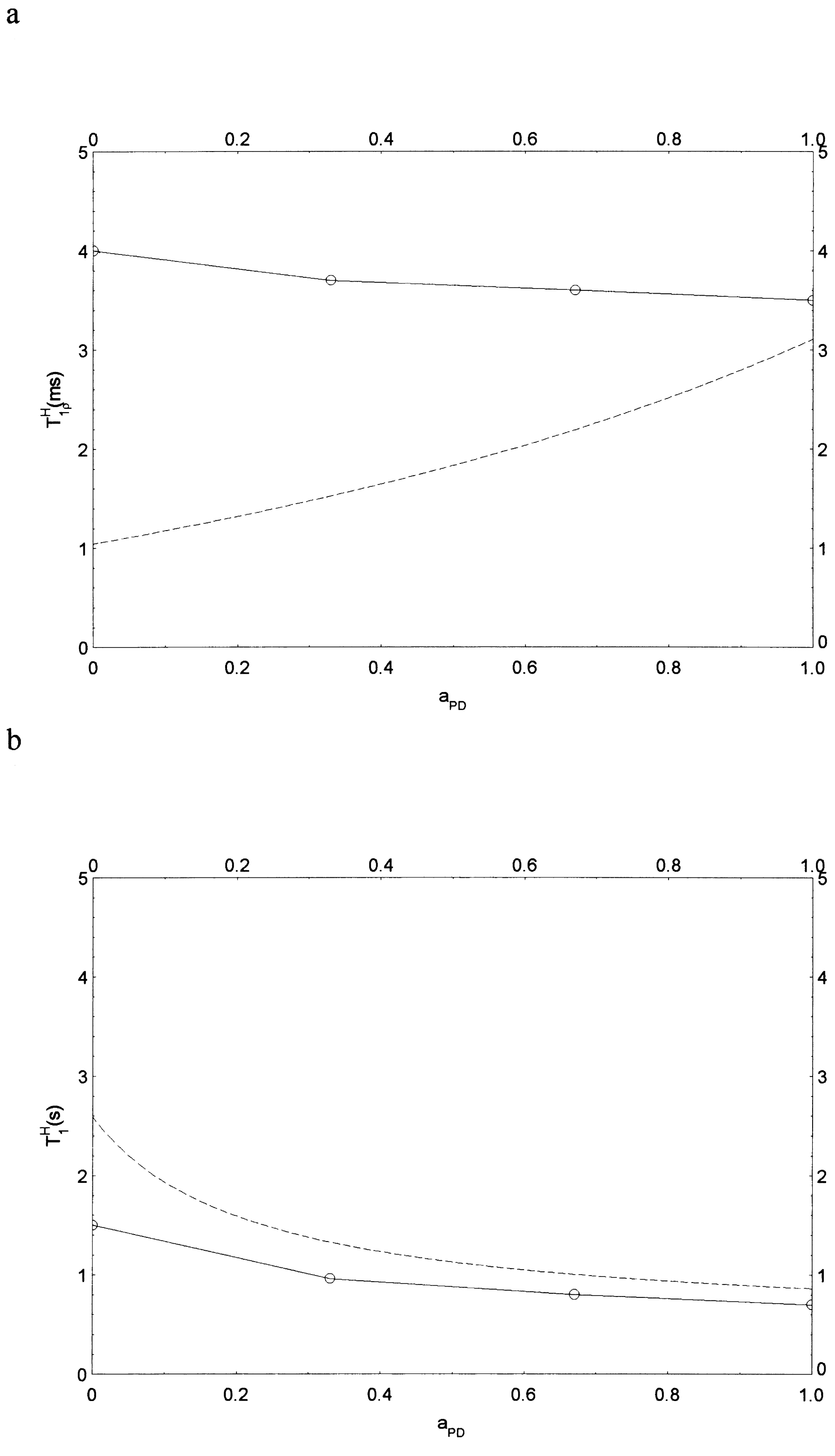

Fig. 4. The variations in (a) $T^{H}_{1\rho}$ and (b) T^{H}_{1} with the mole fraction of PD for (—○—) styrene-crosslinked PD/PG polyesters and (- - -) hypothetical PD/PG-styrene copolymers.

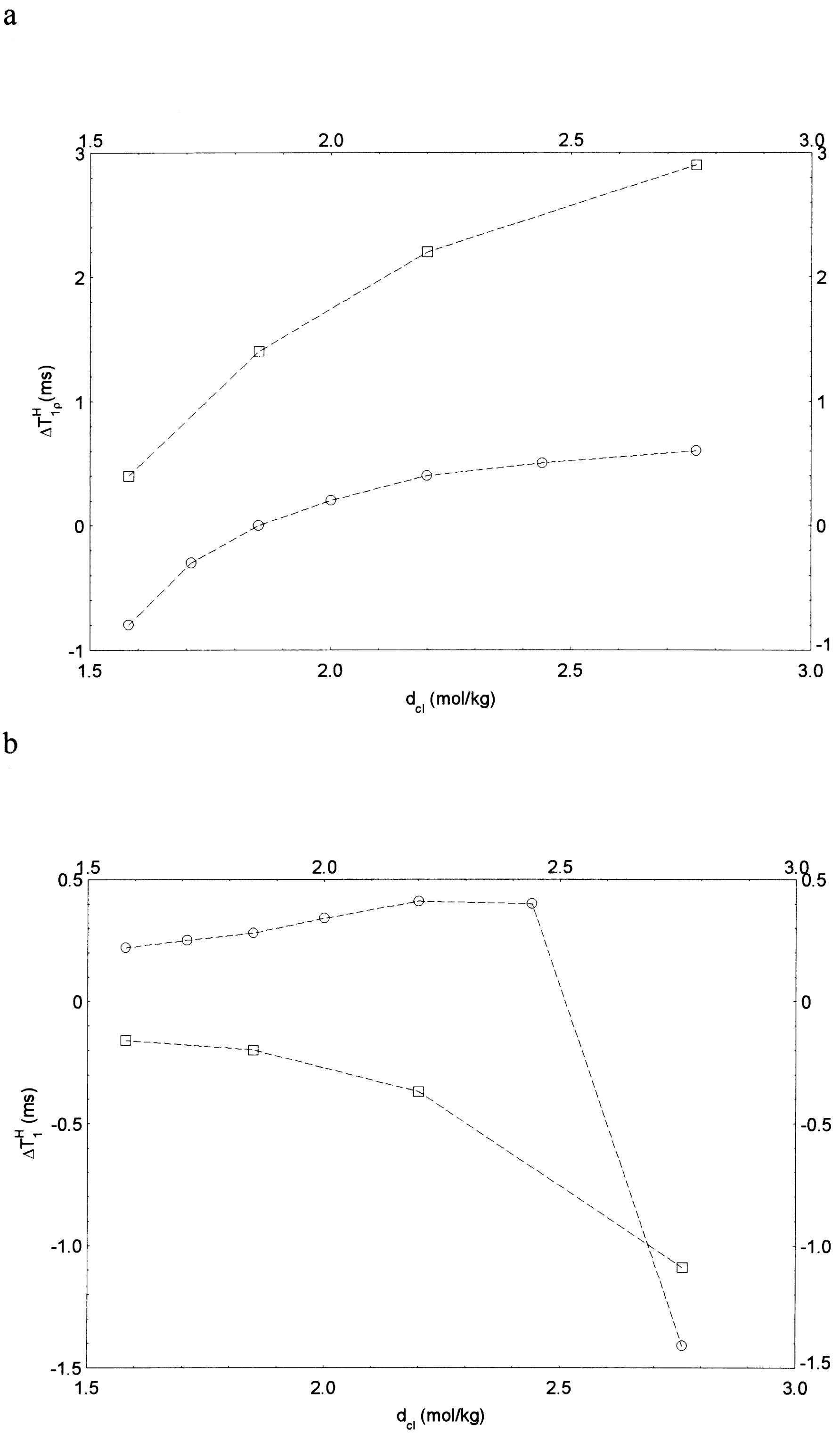

Fig. 5. The copolymer effect (○) and crosslinking effect (□): (a) $\Delta T_{1\rho}^{\mathrm{H}}$ and (b) $\Delta T_{1}^{\mathrm{H}}$ versus crosslinking density of styrene-crosslinked PD/PG polyesters.

the two diols, and $T_{\mathrm{g}}^{\mathrm{PS}} = 378\,\mathrm{K}$ is the glass transition temperature of polystyrene [12].

The differences $\Delta T_{\mathrm{g}}(\mathrm{co.e.}) = T_{\mathrm{g}}^{(\mathrm{PD/PG})/\mathrm{PS}} - T_{\mathrm{g}}^{\mathrm{PD/PG}}$ may be thought of as the composition-dependent copolymer effect, whereas $\Delta T_{\mathrm{g}}(\mathrm{cl.e.}) = T_{\mathrm{g}}^{(\mathrm{PD/PG})/\mathrm{PS,\,exp.}} - T_{\mathrm{g}}^{(\mathrm{PD/PG})/\mathrm{PS}}$ can be considered as a measure of the crosslinking effect [Fig. 6(b); Table 3].

For a given polyester composition the crosslinking effect, $\Delta T_{1\rho}^{\mathrm{H}}(\mathrm{cl.e.})$, $\Delta T_{1}^{\mathrm{H}}(\mathrm{cl.e.})$ or $\Delta T_{\mathrm{g}}(\mathrm{cl.e.})$, reflects exclusively the network stiffening. It is worth noting that the extent of the

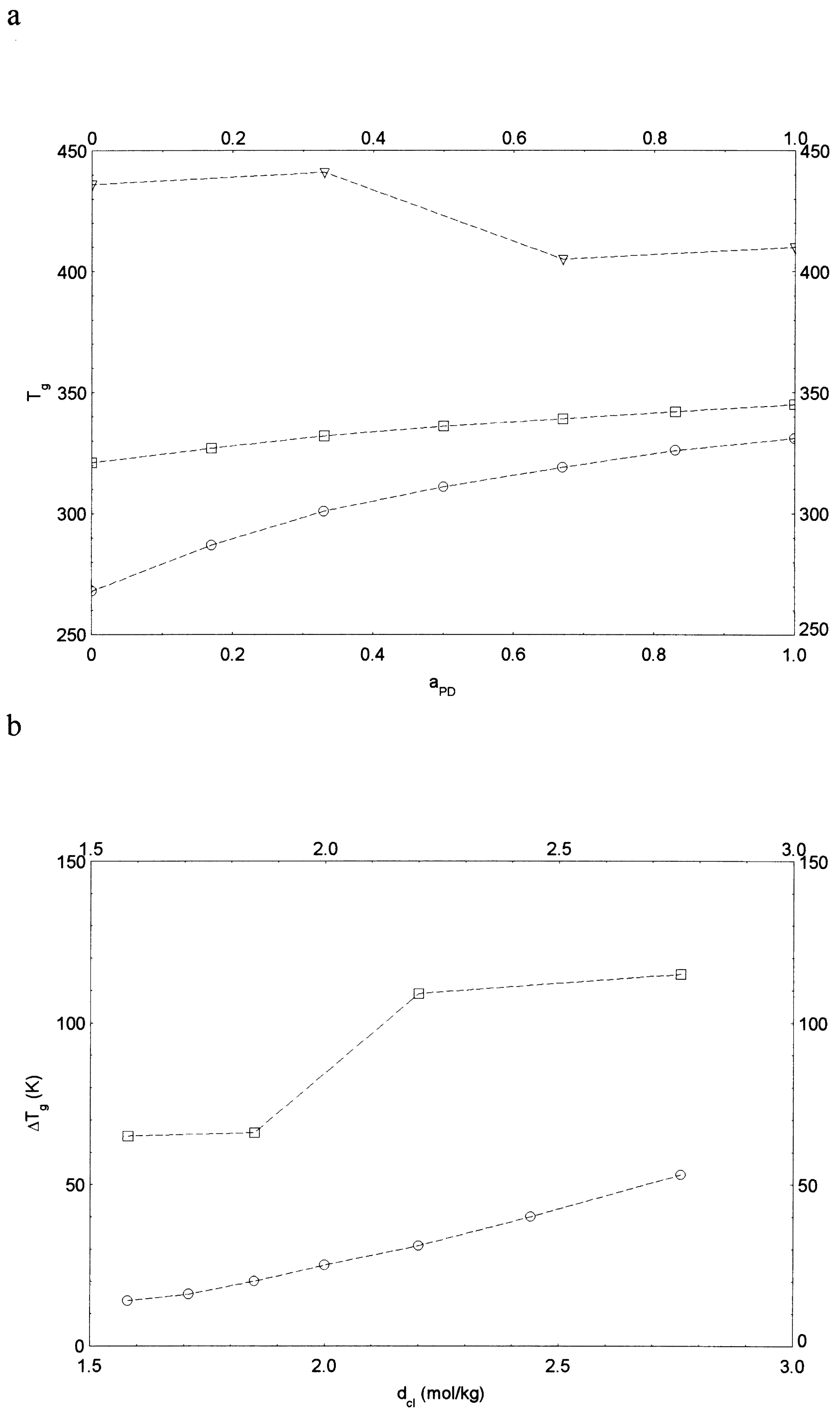

Fig. 6. The variations in (a) T_g with the mole fraction of PD for (○) unsaturated PD/PG polyesters, (□) hypothetical PD/PG-styrene copolymers and (▽) styrene-crosslinked PD/PG polyesters, and in (b) ΔT_g versus crosslinking density of styrene-crosslinked PD/PG polyesters: the copolymer effect (○) and crosslinking effect (□).

crosslinking effect determined both by n.m.r. and d.s.c. for the (PD/PG)/PS polyesters with constant average length of the styrene subchains increases with lowering PD content, i.e. in order of increasing density of crosslinking d_{cl}. These observations confirm a validity of the proposed approach in extracting the effect resulting exclusively from the enhancement in rigidity of unsaturated polyesters upon curing.

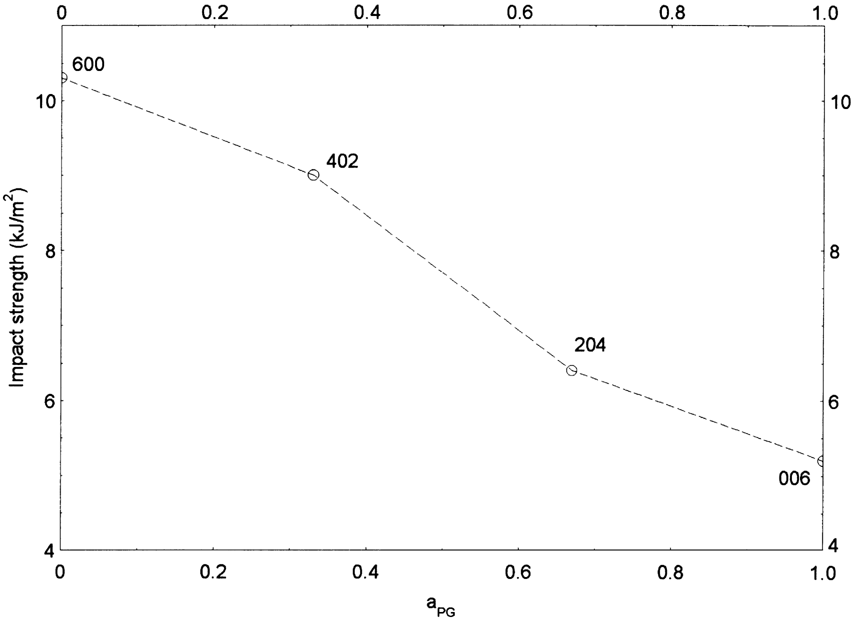

Fig. 7. Impact strength of the styrene-crosslinked PD/PG polyesters versus composition.

The evaluation of the extent of crosslinking effect may be useful in determining the relationship between the structure of mixed unsaturated polyesters and thermal and mechanical properties of subsequently cured materials. These properties are known to be influenced among others by diol components used and their relative amounts. Enhanced hardness, flexural and compressive strength are provided by 1,3-propylene glycol. A presence of propoxylated dian units improves in addition the heat, chemical and weathering resistance.

The impact strength of the investigated systems may be directly related to the crosslinking density and molecular mobility (Fig. 7). The rotating frame spin–lattice relaxation times are known to be sensitive to molecular motions in the mid-kilohertz (10–100 kHz) region. In turn, an agreement between the frequencies of such motions and the frequencies characteristic of impact strength phenomena may be considered as a measure of the ability to dissipate the energy of the impact [25]. Thus, if the differences in $\Delta T_{1\rho}^{\mathrm{H}}$ values may indeed be correlated with the overall network rigidity, the reduced crosslinking effect should result in the increased impact strength. In fact, the impact strength as well as the ultimate elongation were found to be higher for polyesters with enlarged distance between successive crosslinks.

4. Conclusions

A composition of the mixed unsaturated polyesters was found to influence the overall relaxation behaviour of the subsequently crosslinked systems. An attempt was made to eliminate the influence of variable contents of diol constituents (mixing effect) and that related to the formation of copolymer with styrene (copolymer effect). The extent of the crosslinking effect under fixed curing conditions (i.e. for a given styrene sequence length and curing temperature) may be attributed exclusively to the changes in crosslinking density controlled by the variations in the unsaturated prepolymer composition. The n.m.r. results were found to be in agreement with the T_g values obtained from d.s.c. measurements as well as with some mechanical properties.

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