^{1}H n.m.r. relaxation of radiation induced crosslinking in polyester–styrene systems

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The structure and dynamics of a network formed by radiation induced crosslinking of polyesters based on 1,6-hexane diol and 1,2-propylene glycol and maleic anhydride (HDF and PGF, respectively) with styrene is studied by proton pulsed n.m.r. spectroscopy. The dependence of spin-lattice, T_1, and spin–spin, T_2, relaxation times on the structure of polyester chain, molar ratios of styrene to polyester unsaturations and the radiation doses are analysed in terms of network formation and structure, and their effect on molecular motion. Above the gel point, at temperatures above the glass transition, the presence of two T_2 components reflects the heterogeneity of the network structure in both resins. The glass transition temperature, determined from the T_2 relaxation measurements for PGF resins having molar ratio of styrene to polyester unsaturation (RU) up to 1.67:1 continuously decreases with the increasing styrene content. Generally, all the PGF-styrene mixtures have a higher degree of conversion of diol component than the styrene component. The largest shift in the glass transition to higher temperatures for HDF-styrene resins, which indicate the less mobile network, is found for resins with RU about 1:1. Glass transition temperatures also increase with increasing fumarate content as a consequence of better reactivity of styrene with the *trans* form. The shift in glass transition and the conversion data suggest a formation of different network structure in PGF- and HDF-based networks, which is a consequence of different chain structure. Parallel with the n.m.r. relaxation measurements the crosslink density was determined from the extracted gel phase or double bonds (fumaric and styrene) participating in the crosslinking process. Although the degree of *cis–trans* isomerization in the HDF series has an influence on the network formation, samples of both series having 50 mass per cent of styrene after irradiation with 3 kGy do not reach the gel point.

(Keywords: ^{1}H n.m.r. relaxation; radiation induced crosslinking; polyester of 1,2-propylene glycol and maleic anhydride/styrene; polyester of 1,6-hexane diol and maleic anhydride/styrene; crosslink density; glass transition)

INTRODUCTION

Commonly used unsaturated polyester resins are based on a heterochain polyester consisting of both saturated and unsaturated acids and a dialcohol. Cured resins are prepared by crosslinking unsaturated polyesters with styrene yielding a formation of three dimensional network.

Three component resins based on 1,2-propylene glycol are frequently used for commercial purposes. The indirect structural investigation of such networks was made by analysing the products of hydrolysis with ^{13}C n.m.r.[1,2]. A ^{13}C n.m.r. study of cured polyester in the solid state was also recently reported[3]. The crosslinking reactions were temperature and peroxide initiated. However, radiation induced crosslinking of such systems had not yet been thoroughly studied. In the previous work the dielectric and mechanical relaxation techniques were used to study the final properties of the resulting network[4,5].

The understanding of the network structure in terms of regions possessing different molecular motion is of particular interest. N.m.r. relaxation studies have provided considerable insight into the nature of molecular motions in polymers[6]. It has also been demonstrated that pulsed n.m.r., as a nondestructive technique, can be very valuable for assessing radiation effects in macromolecules[7,8].

The spin lattice relaxation time, T_1, associated with short-range motions in the polymer chain appears to be less sensitive to the radiation dose until very high crosslink densities are reached[9]. On the other hand, the spin–spin relaxation time, T_2, connected with the long range low frequency cooperative motions is largely affected by the presence of intermolecular couplings such as crosslinks or entanglements[10–12]. Therefore, T_2 is very sensitive to the formation of a network. Charlesby *et al.*[10] have demonstrated the relationship between crosslink density and T_2 by analysing a double exponential decay of the spin–spin relaxation above the gel point[10–12].

In this work the T_1 and T_2 relaxation times were used to investigate the effects of radiation induced crosslinking of two-component model polyester–styrene systems based on polyesters of 1,2-propylene glycol and 1,6-hexane diol with maleic anhydride. The presence of long linear aliphatic dialcohol enables the synthesis of polyesters with various fumarate content[13]. In contrast, the reaction of maleic anhydride with 1,2-propylene glycol results in a polyester with almost completely isomerized fumaric units[14], which should be more reactive compared with the maleic *cis* form. The emphasis was placed on the analysis of the crosslink density and

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Table 1 Reaction temperatures, fumarate contents, maleate/fumarate ratio (M/F) and molecular mass (M_n) of polyesters based on 1,6-hexane diol (HDF)

Sample	Reaction temperature (°C)	Fumarate content (%)	M/F	M_n
HDF-18	140	18	4.4	1.1×10^3
HDF-28	160	28	2.6	1.3×10^3
HDF-55	180	55	0.8	2.0×10^3

network heterogeneity in terms of two T_2 components, their relation to the extracted sol and gel phase, and how this correlation depends on the polyester structure, styrene content and irradiation dose. The glass transition temperature, T_g, determined from the n.m.r. measurements is compared with the overall reacted double bonds involved in the crosslinking.

EXPERIMENTAL

The unsaturated polyesters based on 1,2-propylene glycol (PGF) were prepared by condensation of equivalent amounts of PG and maleic anhydride in a melt at 220°C under nitrogen gas[14]. The molecular mass of a polyester (PGF) was $M_n = 3 \times 10^3$ and the fumarate content was 96% (maleate to fumarate ratio, M/F = 0.04).

The unsaturated polyesters based on 1,6-hexane diol (HDF) were prepared by condensation of equivalent amounts of HD and maleic anhydride in a melt at 140, 160 and 180°C, respectively. The fumarate content, determined by the high resolution ^{1}H n.m.r., is found to depend on the reaction temperature (*Table 1*). The details of the polyester synthesis and structure were described earlier[13].

Polyesters were mixed with 20, 30, 40 and 50 mass per cent of styrene yielding molar ratios of styrene to polyester unsaturated double bonds (RU) for PGF series of 0.42:1, 0.71:1, 1.11:1 and 1.67:1, respectively. For the HDF series RU values are 0.52:1, 0.90:1, 1.38:1 and 2.07:1, respectively. The mixtures were crosslinked by γ-radiation of a ^{60}Co source at 40°C. The total doses were 3, 6 and 9 kGy, respectively. The absence of free radicals in the resins is checked by e.s.r. prior to n.m.r. measurements.

The degree of conversion and the gel phase were analysed by conventional extraction with benzene in a Soxhlet apparatus for six days. The unreacted styrene monomer was quantitatively determined spectrophotometrically in the extract. The absence of polystyrene was confirmed by the precipitation with methanol.

The proton relaxation times were measured on a CPS-2 Spin Lock Ltd pulsed n.m.r. spectrometer operating at a resonant frequency of 60 MHz. Spin–lattice relaxation time was measured by using a conventional 180°–τ–90° pulse sequence; spin–spin relaxation time was computed from the free induction decay (FID) following a 90° pulse. Larger values of T_2 were determined by the Carr–Purcell spin–echo pulse sequence[15]. The non-exponential spin–spin relaxation time of the polyester resins is described by a double exponential function of the form:

$$I(t)/I(0) = f \times e^{-t/T_{2L}} + (1-f) \times e^{-t/T_{2S}}$$

where $I(0)$ and $I(t)$ are signal intensities at time zero and t, respectively; T_{2L} and T_{2S} are the long and short transverse relaxation times, respectively, and f is the fraction of protons relaxing with T_{2L}. Multiple T_2 components were resolved from the semi-logarithmic presentation of the FID intensity[16–18].

RESULTS AND DISCUSSION

Unirradiated polyester–styrene mixtures

In order to follow the effect of styrene concentration on the segmental mobility of HDF and PGF resins the T_1 and T_2 relaxation times for unirradiated mixtures are measured. The relaxation times T_1 and T_2 for PGF–styrene mixtures as a function of temperature are shown in *Figure 1*. The temperature of measurements did not exceed 80°C in order to minimize the observed thermally activated crosslinking during the equilibration and measurement above 80°C. It can be seen that the relaxation times strongly depend on the styrene concentration. The low temperature T_1 minimum appears at approximately the same temperature (−90°C) while the depth of the minimum changes with the styrene concentration. This minimum is attributed to the 1,2-propylene glycol methyl group reorientation, analogously to the reorientation of methyl group in polypropylene[19]. At higher styrene concentration the T_1 relaxation time increases because of the long T_1 of pure styrene component, and the minimum can not be resolved.

The high temperature T_1 minima are attributed to the general molecular motion associated with the phase transition. The high temperature minimum of pure PGF polyester appears above 80°C. With the increase of styrene concentration the T_1 minima are shifted to lower temperatures. Such a lowering of high temperature minima is expected because the styrene acts as a solvent

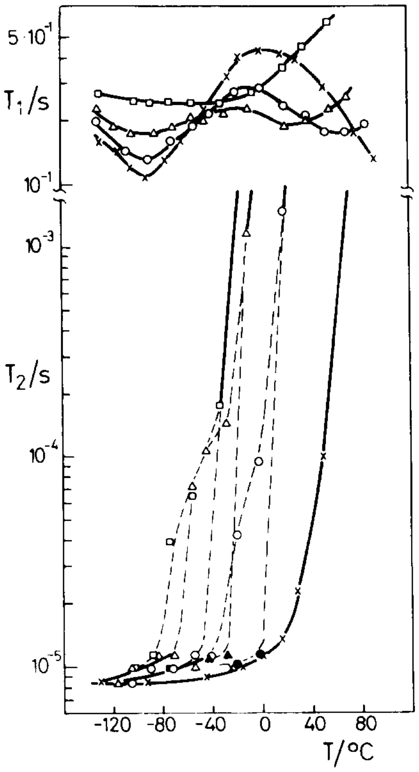

Figure 1 Temperature dependence of relaxation times T_1 and T_2 for unirradiated PGF resins with RU 0:1 (×); 0.42:1 (○); 0.71:1 (△) and 1.67:1 (□). Filled symbols represent the T_{2S} component

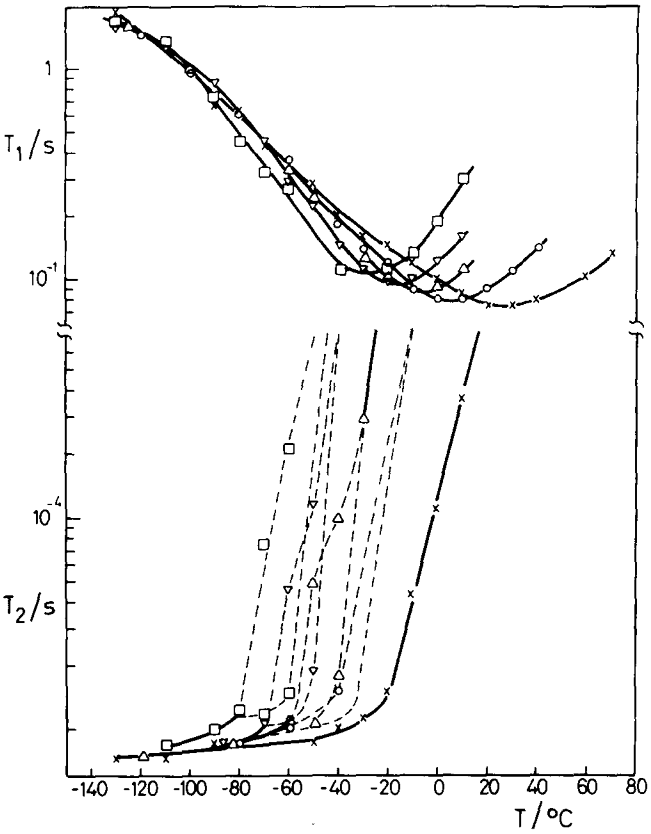

Figure 2 Temperature dependence of relaxation times T_1 and T_2 for unirradiated HDF-18 with RU 0:1 (×); 0.52:1 (○); 0.89:1 (△); 1.38:1 (▽) and 2.07:1 (□)

for polyester chains. At highest styrene content (50 mass per cent) the low and high temperature minima are merged giving rise to a very broad and shallow minimum. Although the T_1 relaxation is sensitive to the change in segmental motions below the glass transition, T_g, as well as to the dynamics of phase transition, it is not sensitive to the microheterogeneity at the molecular level due to the effect of spin diffusion[6].

The T_2 curves, which are more sensitive to the general molecular motion, exhibit in a certain narrow temperature range (around the phase transition) double exponential decay with short, T_{2S}, and long, T_{2L}, components, respectively. The presence of two components suggests the existence of microheterogeneity as a consequence of nonmiscibility on the segmental scale. Some segments of the polyester are not plasticized by the styrene monomer.

With the increasing styrene concentration the appearance of T_{2L} component is approaching a phase transition of pure styrene. After a short temperature interval (about 35°C) the two T_2 components can not be resolved, partly because of a relatively small difference between the components (of the order of 10 μs) and because of the inhomogeneity of the magnetic field.

The temperature dependence of T_1 and T_2 for the HDF-18 polyester with different styrene content in the temperature range from −130 to 80°C is shown in *Figure 2*. The T_1 minima are associated with the phase transition. With the increase of styrene concentration the T_2 minima are shifted to lower temperatures due to the plasticization effect of the styrene monomer. The HDF-28 and HDF-55 exhibit analogous behaviour.

The T_2 relaxation times for all HDF mixtures, regardless of their styrene content, exhibit near the phase transition two-component FID consisting of a short (T_{2S}) and long (T_{2L}) component, respectively, which is explained analogously as for the PGF resins. However, the difference between two T_2 components is not very pronounced (of the order of 10 μs). The mixtures of the fumarate rich HDF-55 resin exhibit phase separation in a broader temperature interval in the vicinity of the glass transition, T_g. Furthermore, it is not possible to determine correctly the phase transition for the mixture having the highest styrene content. As compared with the HDF-18 mixtures, HDF-55–styrene systems with the same amount of styrene exhibit considerably larger shifts of T_g towards lower temperatures. This effect may be understood in terms of better compatibility of styrene with fumaric units compared with maleic units. The fact that the *trans* units have a higher flexibility than the *cis* units should also be considered in interpreting larger shifts of T_g (ref. 20). It should be mentioned that the FID curves depend on the heating and cooling rates throughout the temperature region of the phase transition.

Irradiated polyester–styrene mixtures

Figure 3 shows the temperature dependence of T_1 relaxation time for irradiated PGF–styrene mixtures with RU 0.42:1 and 1.67:1, respectively. General features of the curves are determined both by the styrene content and radiation dose. Resins with lower styrene content (20 mass per cent), irradiated with a 3 kGy exhibit longer T_1 times compared with the uncured PGF resin (*Figure 3a*). However, there is a very small difference in T_1 vs. temperature curves for the resins irradiated with 6 and 9 kGy, respectively. The positions of low temperature minima are not perceptibly changed by crosslink density, and the slopes of the curve in that region are approximately independent of the radiation dose. It appears that the crosslink density has a little influence on the methyl group rotation at low styrene

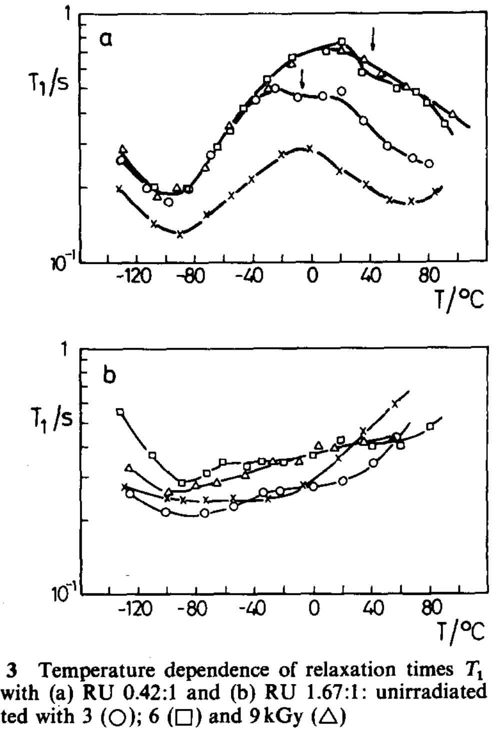

Figure 3 Temperature dependence of relaxation times T_1 for PGF resins with (a) RU 0.42:1 and (b) RU 1.67:1: unirradiated (×) and irradiated with 3 (○); 6 (□) and 9 kGy (△)

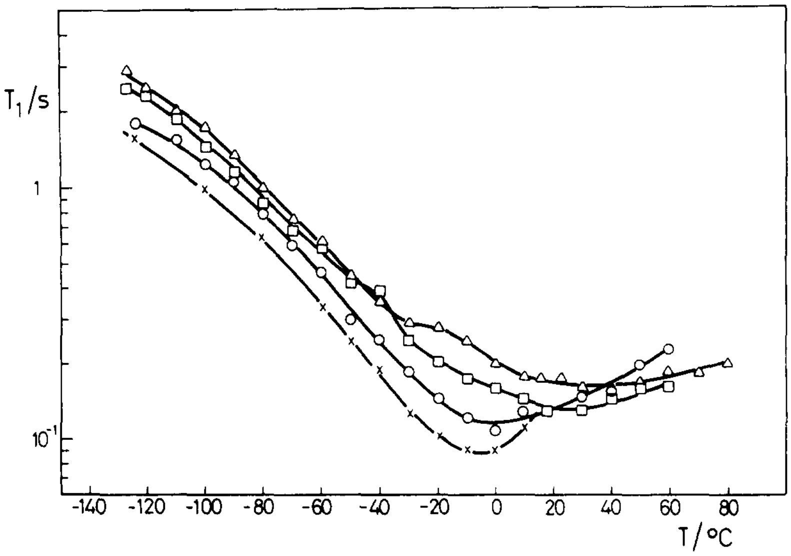

Figure 4 Temperature dependence of relaxation times T_1 for HDF-18 0.89:1 resin unirradiated (×) and irradiated with 3 (○); 6 (□) and 9 kGy (△)

concentration. Similar behaviour has been observed in the crosslinked polypropylene[19] and other polymer systems[21]. The T_1 vs. temperature behaviour suggests a shift of high temperature minima for all the irradiated samples above 80°C. The shapes of T_1 curves display a weak bend between -20 and $+40$°C depending on the radiation dose (indicated with arrows in *Figure 3a*). As this bend is not present in the unirradiated resins it may relate to the styrene crosslinks in the network.

The temperature dependence of T_1 for PGF resins with 50 mass per cent of styrene differs markedly from those with lower styrene concentrations (*Figure 3b*). The low temperature minimum is very shallow at lower radiation dose. The fact that this minimum is more pronounced at higher radiation doses may be a consequence of the decreased concentration of styrene component and the formation of styrene crosslinks.

The effect of crosslinking induced by different radiation doses in the HDF-18 resin containing 30% of styrene on the T_1 relaxation is shown in *Figure 4*. All other irradiated HDF polyester–styrene mixtures exhibit similar T_1 vs. temperature behaviour. The T_1 minima are shifted to higher temperatures with the increasing radiation dose and are broadened considerably. However, the difference in the minima of the curves corresponding to 6 and 9 kGy, respectively, can be hardly seen. A similar behaviour is observed in some other polymer systems[22]. The T_1 minima are shallower and broader for the irradiated samples than for the unirradiated mixtures suggesting a broad distribution of correlation times[21]. Because of the complex T_1 relaxation curve for the irradiated mixtures, it is difficult to predict any suitable model to assess the function for the distribution of correlation times. The broadening is a typical manifestation of the gel phase formation. On the low temperature slope of the T_1 minima for each curve a small bend is observed. Its position and intensity is influenced by the styrene concentration and by the radiation dose. The intensity of the bend (or poorly resolved minimum) increases with the styrene concentration. Analogously to the PGF resins, this bend can be assigned to the relaxation of styrene component.

In the case of a complex heterogeneous system such as cured resin, the spin–spin relaxation data, connected with a low-frequency motion, can provide more information about the crosslinked matrix. The analysis of a complex T_2 relaxation enables one to correlate the crosslink density of a network with the glass transition temperature, T_g, and the mobile fraction with the sol phase[16]. Since the molecular mass of both resins is about 3000 (in the sol phase), i.e. below the limit at which T_2 becomes influenced by the chain entanglements, the short T_2 component is ascribed to the motional restriction predominantly induced by the chain crosslinks[12].

The temperature dependence of T_2 for PGF resins with different RU irradiated with various doses is shown in *Figure 5*. The abrupt increase of T_2 times, associated with the general motion, T_g, depends on the radiation dose and styrene content. At the same applied dose this change is shifted to higher temperatures as the styrene content decreases. Contrary to the T_2 values for unirradiated resins, which continuously increase with increasing temperature (in the measured range), resins with lower styrene content irradiated with larger doses exhibit a tendency to approach a constant value (plateau) with the rise of temperature. This behaviour was previously observed in various crosslinked polymers. The effect has been ascribed by several authors to a non-zero averaging of dipolar coupling due to the anisotropic motions between crosslinks[23–25]. However, the plateau can not be completely detected due to the limitation of high temperature range. At temperatures above 80°C, in some cases T_2 values slowly decrease indicating further motional restrictions as a consequence of thermally induced crosslinking.

The general feature of T_2 vs. temperature curves for irradiated PGF–styrene mixtures is an appearance of two phase systems above the glasss transition. The exception is PGF containing 50% of styrene irradiated with 3 kGy where two T_2 times coexist only in a short temperature interval, similar to the unirradiated system. It appears that the dose of 3 kGy is not sufficient to induce the network formation for the particular styrene concentration. According to Folland and Charlesby[16] the T_2 is unaffected by crosslinking until the gel point is reached. The existence of regions within the sample,

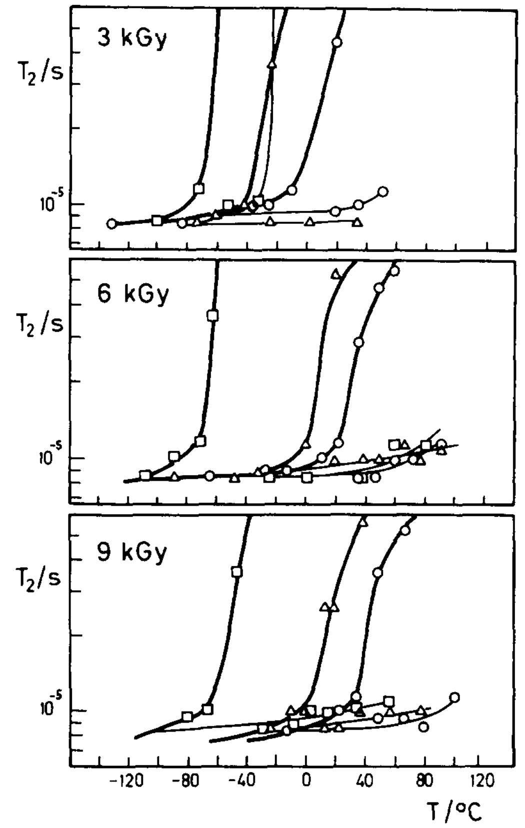

Figure 5 Temperature dependence of relaxation times T_2 for PGF resins with RU 0.42:1 (○); 0.71:1 (△) and 1.67:1 (□) irradiated with 3, 6 and 9 kGy. The thick and thin lines represent the long and short T_2 components, respectively. The T_2 curves have been truncated

which have formed a crosslinked network of considerably restricted translational motion, would result in a distinctly shorter T_2 component.

The T_2 vs. temperature curves for irradiated HDF-18 mixtures are shown in *Figure 6*. At low radiation dose (3 kGy) the T_2 patterns are similar to those of the unirradiated sample. Apparently the dose of 3 kGy seems to be too low to reach the gel point regardless of the styrene concentration. At the dose of 6 kGy the T_2 transitions are shifted to higher temperatures. However, above a certain temperature interval only a single component of FID is observed, corresponding to the long T_2 relaxation time. This suggests the existence of a certain degree of crosslinking, yet insufficient to impose significant restriction on the chain motion. Finally, at the dose of 9 kGy the presence of two T_2 relaxation times above the phase transition is observed for all the samples in the measured temperature interval, except for the mixture with 50% of styrene. The longer T_2 component approaches a constant value (plateau region) in the measured temperature range. The amount of this component depends on the radiation dose and styrene concentration. Mixtures with 20 and 30% of styrene exhibit similar nonuniformity in terms of the proportion of T_{2S} and T_{2L}, which may lead to the conclusion that similar density of the network structure has been formed.

In addition, these two mixtures irradiated with 9 kGy appear to contribute to the optimal crosslink density or restrictive effect on the translational mobility of the chains in the gel and, hence, to the highest glass transition. At styrene concentrations higher than 30% the mobility increases rapidly at the same radiation dose. This behaviour may be explained in the following manner. At high styrene concentrations when most of the fumarate groups have reacted with styrene the possibility for styrene molecules to react with each other, as well as with fumarate units, is increased. Thus, the intermolecular styrene crosslinks will be longer, yielding a lowering of the general transition as a consequence of reduced density and increased translational mobility[26,27].

Furthermore, the molecular mobility and T_g do not depend only on the styrene concentration, but also on the polyester chain configuration. Since the maleic units are less reactive than the fumaric ones, their increased concentration would decrease the reactivity of the whole resin. For the resin containing highest fumarate content (HDF-55) a gel point is reached in the measured temperature range for all applied radiation doses and styrene concentrations, except for the sample with highest styrene concentration irradiated with 3 kGy. At higher doses, samples with 20 and 30% of styrene exhibit very low fraction of the mobile phase (T_{2L} component) associated with a shift of the glass transition to higher temperatures. In order to underline the importance of the chain configuration in the final structure and crosslink density the T_2 relaxation times for three resins containing 30% of styrene and different M/F ratio are shown in *Figure 7*. While the resin with low fumarate content irradiated with 3 and 6 kGy is still below the gel point, resins with higher fumarate content exhibit considerable change in the proportions of the two T_2 components. According to the T_{2S} component, motional restriction

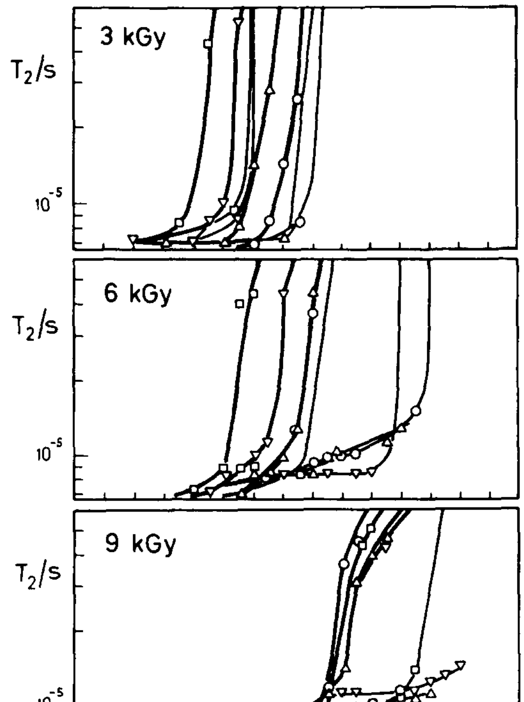

Figure 6 Temperature dependence of relaxation times T_2 for HDF-18 resins with RU 0.52:1 (○); 0.89:1 (△); 1.38:1 (▽) and 2.07:1 (□) irradiated with 3, 6 and 9 kGy. The thick and thin lines represent the long and short T_2 components, respectively. The T_2 curves have been truncated

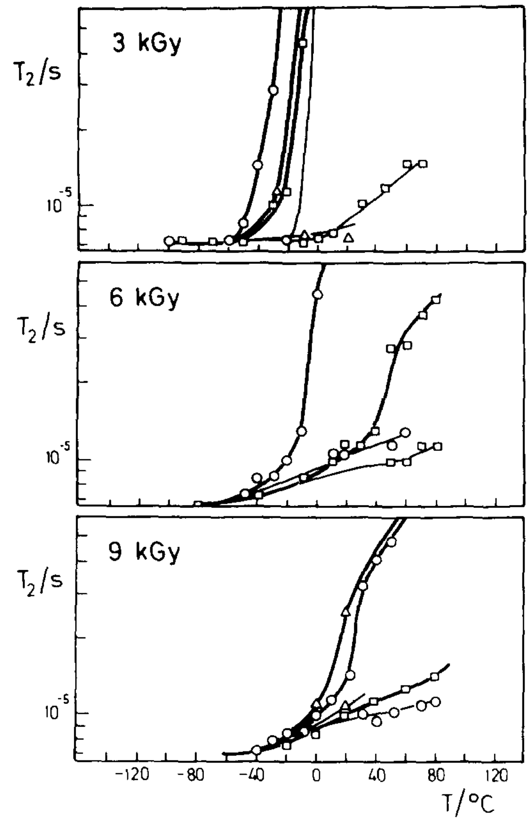

Figure 7 Temperature dependence of relaxation times T_2 for resins with RU 0.89:1 irradiated with 3, 6 and 9 kGy: (○) HDF-18; (△) HDF-28 and (□) HDF-55. The thick and thin lines represent the long and short T_2 component, respectively, The T_2 curves have been truncated

induced by the network formation increases with the increased content of fumarate units, resulting in a shift of the glass transition to higher temperatures.

After the n.m.r. measurements have been completed at 80°C and the samples cooled to room temperature, the repeated measurements showed a shift of the T_2 transition for several degrees to higher temperatures as a consequence of thermally activated crosslinking. Therefore, a small amount of thermally induced crosslinks at higher temperatures contributes to the overall crosslink density.

The glass transition temperature for samples where the gel point has been achieved is determined as the temperature where the long component, T_{2L}, appears. At lower radiation doses, prior to the gel point, where most of the samples exhibit two T_2 components in a narrow temperature region, the average value of the two temperatures corresponding to the appearance of abrupt changes in T_2 was taken as a measure of T_g. The glass transition temperature for irradiated PGF and HDF resins are listed in *Tables 2* and *3*, respectively. The values of T_g for PGF resins are shifted to higher temperatures with the increased radiation doses. However, contrary to the irradiated HDF resins, where the highest T_g is observed for the system with RU approximately 1:1 (*Table 3*), PGF resins display continuous increase in T_g with decreasing styrene concentration. Better compatibility of styrene with PGF containing 96% of fumaric units has been already shown through the significant lowering of T_g for unirradiated resins, as compared with the HDF resins. The T_g behaviour for irradiated PGF resins shows that in this system the effect of styrene as a solvent on T_g is more pronounced than its effect as a crosslinking agent.

The best agreement between the calculated, $T_{g(\mathrm{calc})}$, and measured values for the glass transition of irradiated polyesters was obtained with the modified Fox–Loshaek equation[28,29], which is primarily valid for crosslinked homopolymers and it is independent of the chemical structure of the network and the crosslink distribution. Taking into account that the styrene and fumaric units have a tendency towards alternating copolymerization[30] the modified Fox–Loshaek relation $T_g = T_g^0 + K\rho'$ is used, where ρ' is the overall number of double bonds participating (fumaric and styrene double bonds) in the reaction per unit mass and K is 2.8 for the HDF-55 resin. From the extraction experiments and ^{13}C n.m.r. analysis of the sol phase it is found that all the reacted double bonds are present in the gel phase. According to the extraction and n.m.r. T_2 data, at low radiation doses there is no gel phase present. The data shown on *Table 3* indicate quite a good agreement between predicted and measured glass transition temperature for the HDF-55 resin, except for the sample with lowest styrene concentration. The reason could be a very low ρ' value in a rather large amount of the gel phase compared with the higher styrene concentrations.

At low doses T_g increases with increasing RU, while at higher doses there is a maximum T_g at the RU about 1:1. It should be mentioned that the HDF-55 mixtures have approximately similar conversion ratios for both reactants. It is slightly higher for the styrene component in the samples with lower styrene concentration and slightly higher for the HDF-55 component in the samples with lower HDF-55 concentration.

Table 2 Glass transition temperatures, T_g, of irradiated PGF resins determined from T_2 relaxation measurements

RU	Radiation dose (kGy)	T_g
0.42:1	3	0
	6	25
	9	37
0.71:1	3	−35
	6	5
	9	14
1.67:1	3	−75
	6	−70
	9	−57

Table 3 Glass transition temperatures of irradiated HDF resins determined from T_2 relaxation measurements, T_g(obs), and from the modified Fox–Loshaek equation, T_g(calc)

Styrene %	Radiation dose (kGy)	HDF-18	HDF-55	
		T_g (°C) (obs)	T_g (°C) (obs)	T_g (°C)(calc)
20	3	−25	−10	
	6	−15	15	64
	9	13	50	81
30	3	−44	−18	
	6	−11	42	51
	9	25	85	87
40	3	−61	−30	
	6	−28	50	44
	9	24	90	82
50	3	−83	−55	
	6	−57	32	27
	9	20	72	73

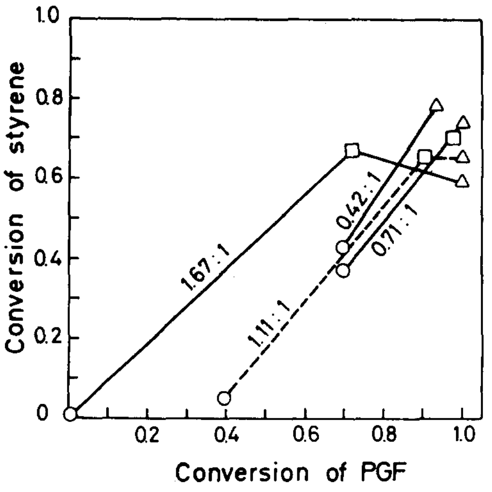

Figure 8 Conversion of styrene monomer plotted against the conversion of PGF resin at different RU after irradiation with 3 (○); 6 (□) and 9 kGy (△)

However, by using $K=0.7$, which gives the best fit, the calculated T_g values for PGF are generally higher than the observed ones, particularly for the samples with larger styrene content (RU = 1.67:1).

The results of conversion measurements (*Figure 8*) indicate that PGF resins with RU higher than 0.42:1 after radiation with 9 kGy show almost quantitative conversion of fumaric units. However, there is a continuous decrease of styrene conversion with increasing RU. Since the conversion of fumaric units in samples with RU equal or higher than 0.71:1 is almost complete, it is reasonable to expect that the additional styrene concentration contributes to a formation of longer styrene crosslinks[31], although styrene and fumaric units have a tendency to form primarily alternating copolymers[30]. In this case a smaller crosslink density and lowering of glass transition temperature can be expected.

The number of double bonds involved in the crosslinking reaction is calculated on the basis of the conversion of both components. Since the loss of double bonds is not observed in the sol phase it is assumed that all the double bonds involved in the reaction process are in the gel phase. The number of reacted double bonds (in moles) per unit mass, ρ', for each component is determined from the extraction data (*Table 4*). However, from the extraction data it is not possible to calculate the number of reacted fumaric double bonds in a polyester chain (which consists of approximately 10 repeating units). Thus, the ρ' for PGF resins is given in terms of moles/mass of repeating structural unit rather than mole/mass of polyester. The overall number of reacted double bonds, as well as the double bonds of components, exhibit relatively a large increase with the radiation dose up to 6 kGy. Further radiation (9 kGy) results in small increase of ρ' for PGF component and the whole resin, although the styrene component in resins with RU higher than 1:1 shows a decrease in reacted double bonds. At the same time, the conversion of PGF component in resins with RU higher than 0.71:1 is 100% (at the dose 6 kGy resins with RU close to 1:1 have about 95% conversion of PGF).

The overall reacted double bonds, ρ', decrease proportionally with the increase of styrene content (except for the sample irradiated with 3 kGy with RU 0.42:1 and 0.71:1). The gel fraction as a function of ρ' for samples irradiated with 6 and 9 kGy, respectively, also increases with very small change of ρ'. Therefore, it can be expected that the larger gel fraction will not contribute considerably to the increase in T_g.

The increase of reacted styrene in PGF resins with RU higher than 1:1 irradiated with 9 kGy is very small compared with resins irradiated with 6 kGy. The results in *Figure 8* which indicate slightly lower styrene conversion in PGF resin with 50% of styrene irradiated at 9 kGy as compared with the sample irradiated at 6 kGy (54% vs. 67%) are probably due to the incomplete extraction (styrene clustered in the network) and experimental errors during the determination of styrene content with the extraction and spectrophotometric experiments.

Although both types of resins have analogous behaviour of the gel fraction (highest gel content for samples irradiated with 6 and 9 kGy at RU about 1:1), a shift in T_g generally follows the amount of reacted double bonds. All the PGF–styrene mixtures have higher degree of conversion of diol component than the styrene component, which is not the case for (all) HDF-styrene samples. The conversion data suggest a formation of different network structure in PGF and HDF based networks.

Figure 9 shows the gel-fraction vs. the number of the participating double bonds per unit mass, ρ', for HDF-55 resin with different styrene concentrations and radiation doses. According to the extraction experiments there is no three-dimensional network (insoluble part) present in the irradiated HDF-55 with 40% of styrene. However, a slight decrease in the T_{2L} component compared with the unirradiated sample suggests a certain partial crosslinking of the polyester chains.

In both HDF-55 2.07:1 and 0.52:1 samples irradiated with 6 kGy half of the initial styrene has reacted during the crosslinking and the ρ' values are approximately the same. The resin HDF-55 1:1 irradiated with 9 kGy exhibits the highest shift in T_g. Although the resins with two extreme RU (0.52:1 and 2.07:1) have the same gel fraction (about 0.8), the T_g for the resin with RU 2.07:1 is about 20° higher than the corresponding T_g of the resin

Table 4 Gel content and moles of reacted double bonds per unit mass for styrene, $\rho'(\mathrm{ST})$, PGF component, $\rho'(\mathrm{PGF})$ and for the PGF resin, ρ'

RU	Radiation dose (kGy)	Gel (%)	$\rho'(\mathrm{ST}) \times 10^4$ ($\mathrm{mol\,g^{-1}}$)	$\rho'(\mathrm{PGF}) \times 10^4$ ($\mathrm{mol\,g^{-1}}$)	$\rho' \times 10^4$ ($\mathrm{mol\,g^{-1}}$)
0.42:1	0	0.0	19.2	45.9	65.1
	3	64.0	8.2	31.7	39.9
	6	85.5			
	9	90.4	15.0	42.7	57.7
0.71:1	0	0.0	28.8	40.2	69.0
	3	60.0	10.6	27.7	38.3
	6	89.4	20.2	39.4	59.6
	9	99.8	21.3	40.2	61.5
1.11:1	0	0.0	38.4	34.4	72.8
	3	25.5	1.9	13.4	14.3
	6	81.0	25.3	31.3	56.6
	9	94.4	24.9	34.4	59.3
1.67:1	0	0.0	48.0	28.7	76.7
	3	0.0	0.0	0.0	0.0
	6	69.5	32.2	20.7	52.9
	9	76.4	25.9	28.7	54.6

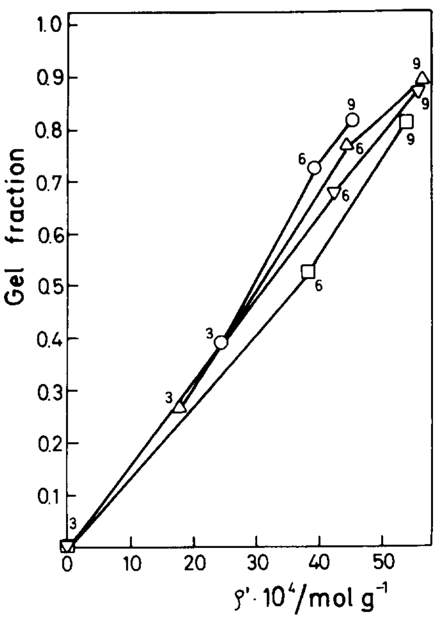

Figure 9 Gel fraction determined from the extraction measurements as a function of reacted double bonds (ρ') for HDF-55 mixtures with RU 0.52:1 (○); 0.89:1 (△); 1.38:1 (▽) and 2.07:1 (□) irradiated with 3, 6 and 9 kGy, respectively. The numbers at the curves denote radiation doses

with RU 0.52:1. This difference can be explained with the larger number of reacted double bonds (ρ').

According to the n.m.r. measurements PGF resins, regardless of the radiation dose and styrene content, exhibit a larger fraction of mobile phase compared with the sol fraction (*Figure 10a*). For example, PGF with RU 0.71:1 irradiated with 9 kGy has no sol fraction while the amount of n.m.r. mobile fraction is about 40%. Thus, although the material is gelled, the mobility of some polymer chains in the gel remains unaltered on the microscopic level. The higher amount of mobile component compared with the sol phase and small shifts in T_g may be explained in terms of lower network density and plasticizing effect of the unreacted styrene.

The molecular mobility and T_g do not depend only on the styrene concentration, maleic–fumaric isomerization, but also on the polyester chain configuration. Although the PGF resins have a higher *cis–trans* isomerization (about 93%) compared with HDF resins (up to 55%) the difference in chain configuration of polyesters results in a lower crosslink density of PGF resins. The asymmetric glycol unit imposes a steric hindrance and, regardless of the high fumarate content of PGF resins, a lower crosslink density will be formed. Consequently, it is concluded that the network formation, its structure and mobility is determined by the microstructure of the polyester chain in the two described polyester–styrene systems at the same styrene concentration and radiation dose.

The sol fractions determined by extraction were compared with the mobile fraction (associated with T_{2L} component; *Figure 10b*) for HDF-55 resin with different RU and radiation doses. There is a good agreement betwen the two parameters. Some exceptions, such as HDF-55 1.38:1 irradiated with 3 kGy which contains about 30% of restricted component (T_{2S}) but has no gel phase could be explained by the partly crosslinked polyester chains, still insufficient to form an insoluble network. The other exception is HDF-55 0.52:1 irradiated with 6 kGy which low T_g has already been discussed. An additional explanation of the highly mobile fraction compared with the low sol fraction is probably the network of lower crosslink density and plasticizing effect of the unreacted styrene on some chain segments as in the case of PGF resins. Longer chain segments between the crosslinks resulting in larger amplitudes of motion contribute to the mobile fraction. Thus, the mobile fraction is not exclusively related to the sol fraction. In addition, a reason for the difference between the two parameters should also be looked for in the nature of the spin–spin relaxation, which is sensitive to the short time scale microscopic behaviour, and the extraction method, which is a long time scale technique.

In order to examine the influence of the sol phase on the mobile component and molecular dynamics of the network, the HDF-28 resin containing 30% of styrene was measured after the extraction process. It was confirmed that the fraction of the material relaxing with T_{2L} component is partly related to the sol phase, while the T_{2S} component corresponds to the network material. *Figure 11* shows T_1 and T_2 relaxation curves for sample HDF-28 0.89:1 irradiated with 3 and 9 kGy, respectively, prior to and after the extraction. Since the sample irradiated with 9 kGy has 90% of the gel fraction, the T_1

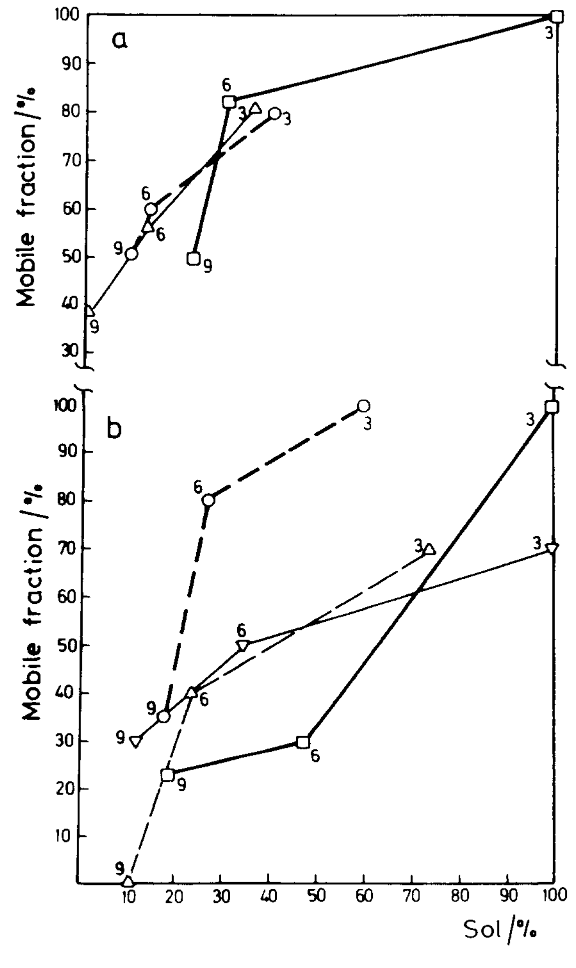

Figure 10 N.m.r. mobile fraction (T_{2L} component) at 80°C vs. the sol fraction for (a) PGF resins with RU 0.42:1 (○); 0.71:1 (△) and 1.67:1 (□) irradiated with 3, 6 and 9 kGy, respectively; (b) HDF-55 mixtures with RU 0.52:1 (○); 0.89:1 (△); 1.38:1 (▽) and 2.07:1 (□) irradiated with 3, 6 and 9 kGy, respectively. The numbers at the curves denote radiation doses

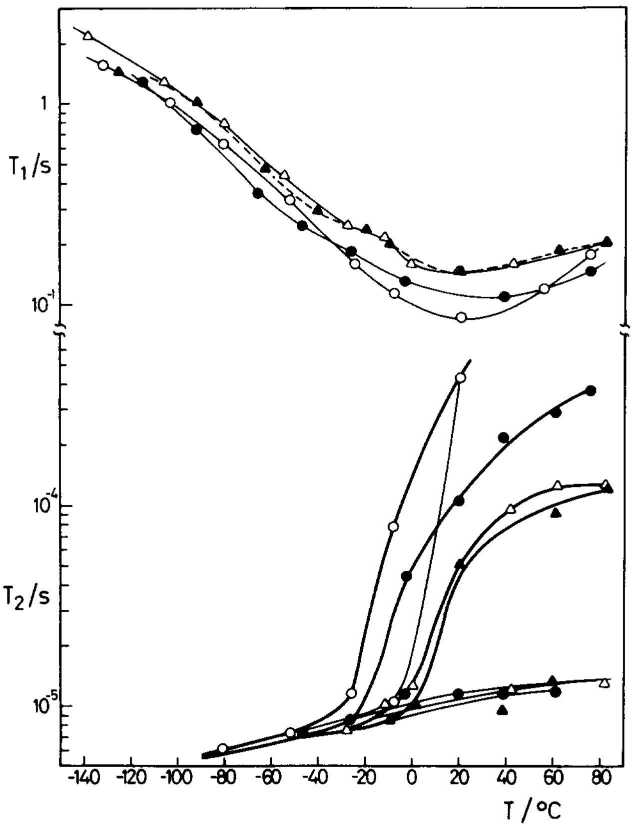

Figure 11 Temperature dependence of relaxation times T_1 and T_2 for HDF-28 with RU 0.89:1 irradiated with 3 (○) and 9 kGy (△). Open symbols represent the measurement prior to the extraction and filled symbols are the relaxation times after the extraction process

curves remain practically unchanged, while the abrupt change in T_2 for the extracted sample is shifted for *c.* 5° to higher temperatures. However, a weak bend at lower slope of T_1 minima is still present. It is obvious that this bend arises from the styrene crosslinks and not from the styrene in the sol phase or homopolymer. Taking into account the low G_R value for styrene[32] it is reasonable to expect that the radiation homopolymerization of styrene in the mixture can be neglected at the given RU. This is supported by the experimental fact that no styrene homopolymer was detected in the sol fraction after prolonged extraction of crosslinked samples.

Because the sample irradiated with 3 kGy has a sol fraction of about 70%, the shape of relaxation curves before and after the extraction are considerably different. The T_1 minima and T_2 abrupt change are shifted to higher temperatures and the fraction of mobile component is lower for the extracted sample than for the unextracted one. However, the gel phase still exhibits two T_2 components indicating that parts of a network which give rise to the T_{2L} component can not be extracted, contrary to some homopolymers where the sol fraction is in a good agreement with the n.m.r. T_{2L} component[16]. Two component systems such as unsaturated resins exhibit more complex behaviour. Thus, the network is considered to be inhomogeneous in terms of local crosslink density distribution. Such an inhomogeneity of the polyester network with short and long T_2 components has already been observed[18].

Table 5 Activation energies (E_a) for glass transition of crosslinked HDF resins calculated from the BPP (A) and VJGM (B) theories

Sample	RU	Radiation dose (kGy)	E_a (kJ mol^{-1}) (A)	E_a (kJ mol^{-1}) (B)
HDF-18	0.52:1	3	12.7	19.7
		6	9.3	19.8
		9	8.8	18.3
HDF-18	0.89:1	3	11.9	25.6
		6	9.8	22.3
		9	9.1	19.4
HDF-18	2.07:1	3	12.7	
		6	11.5	
		9	7.2	
HDF-55	0.52:1	3	13.1	22.9
		6	8.9	20.0
		9	10.3	19.3
HDF-55	0.89:1	3	9.8	18.9
		6	8.0	16.6
		9	8.0	12.1
HDF-55	2.07:1	3	12.1	
		6	9.1	
		9	8.6	

The temperature dependence of the T_1 relaxation time enables one to calculate apparent activation energies, E_a, for the detected processes. A number of models and corresponding spectral density functions, $J(\omega)$, have been proposed for polymer systems[6]. Although the simple Bloembergen–Purcell–Pound (BPP) theory[33] which assumes a single correlation time is not generally valid for complex molecules, the E_a calculated from the BPP theory is a useful qualitative approximation. Furthermore, due to the restriction of the experimental temperature range to 80°C it is not possible to detect the T_1 vs. temperature curve in a wider temperature range around the minima which could be simulated with the appropriate functions. A well expressed high temperature minimum in the measured temperature range is detected only for the HDF resins. The E_a for crosslinked resins calculated from the low temperature slope of the T_1 vs. V curve are listed in *Table 5*. The application of Valeur–Monnerie diamond lattice model (VJGM)[34] yields similar qualitative data, with the E_a values in the range from about 16 to 25 kJ/mole (*Table 5*)[35]. In both cases the energies of activation for the glass transition decrease with increasing radiation dose, i.e. with increasing degree of crosslinking. This behaviour, generally observed for crosslinked polymers, could be explained by considering the large distances between polymer chains in the network which provides more space for segmental motion[19].

As a general conclusion, we have shown how n.m.r. relaxation measurements and extraction data could be correlated in order to provide useful information about radiation crosslinked polyester–styrene systems depending on the chain structure, radiation dose and styrene concentration.

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