Study of irradiated polymers using double-modulation electron spin resonance and size exclusion chromatography

Srećko Valić, Boris Rakvin, Franjo Ranogajec and Zorica Veksli*
Ruđer Bošković Institute, POB 1016, 41001 Zagreb, Croatia

and Zlatka Grubišić-Gallot
Institut Charles Sadron, CRM-EAHP, CNRS-ULP, 6 rue Boussingault, 67083 Strasbourg Cedex, France
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Irradiated polymers such as polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(α-methylstyrene) (PαMS) have been studied using size exclusion chromatography and double-modulation electron spin resonance (d.m.e.s.r.). Size exclusion chromatography coupled on-line with low-angle laser light scattering and viscometry have demonstrated that PS irradiated in the solid state gives only slight increases of molecular weight and viscosity with increasing dose. When irradiated in solution, the results confirm the existence of a highly crosslinked and heterogeneous PS matrix. PMMA and PαMS undergo degradation at the same doses. The d.m.e.s.r. spectra of a spin probe in the slow-motion region have been used to investigate the heterogeneity of the polymer matrix introduced by changes in crosslinking or by degradation. Discrete molecular motions of a spin probe above the internal probe transition (≈ 190 K) are very sensitive to local matrix density and to side-chain relaxation modes. The d.m.e.s.r. spectra indicate clearly a bimodal motion of spin probes located in regions of two considerably different crosslink densities of the PS matrix irradiated in solution.

(Keywords: size exclusion chromatography; spin probe; double-modulation electron spin resonance; γ-irradiation; polystyrene; poly(methyl methacrylate); poly(α-methylstyrene); matrix heterogeneity)

INTRODUCTION

The properties of glassy polymers are known to be influenced by molecular motion and by the density of molecular packing or free volume. The free-volume concept has been very useful in explaining some macroscopic properties. In recent years, several physical techniques using photochromic probes and electron spin resonance (e.s.r.) spin probes have been applied to estimate mobility and free volume in glassy polymers of different network heterogeneities[1–5]. The double-modulation electron spin resonance (d.m.e.s.r.) spectroscopy spin-probe method monitors slow molecular motions (rotational correlation times, $\tau_R \geqslant 10^{-6}$ s) characteristic of polymers below T_g, the glass transition temperature[6].

In this study, d.m.e.s.r. is used to determine local density changes and non-cooperative segmental or side-group motions at lower temperatures as functions of irradiation dose. It is known that drastic changes in polymer properties may be introduced by ionizing radiation[7–9]. The most important modifications observed in irradiated polymers are crosslinking and degradation. In this work polystyrene (PS) ($G_C \approx 0.02$–0.1) is chosen as a crosslinking type of polymer, and poly(methyl methacrylate) (PMMA) ($G_S \approx 1.8$–2.3) and poly(α-methylstyrene) (PαMS) ($G_S \approx 0.39$) as degrading types[9]. (The G_C value is defined as the number of crosslinks per 100 eV, G_S as the number of chain scissions per 100 eV and G_R as the number of free radicals per 100 eV of absorbed energy.)

Size exclusion chromatography (s.e.c.) coupled with viscometry and low-angle laser light scattering (l.a.l.l.s.) have provided evidence of degradation or crosslinking phenomena induced by γ-irradiation.

EXPERIMENTAL

Sample preparation

Polystyrene (PS), poly(α-methylstyrene) (PαMS) and poly(methyl methacrylate) (PMMA) samples were synthesized at the Charles Sadron Institute. The polymers were irradiated using a ^{60}Co γ-source in vacuum at room temperature with a dose rate of 10 kGy h^{-1}. The total doses were 200, 300 and 400 kGy, respectively. The second set of experiments were performed on PS and PαMS solutions in cyclohexane ($c = 0.1$ g cm^{-3}) under the same conditions. Once the desired radiation dose was obtained, the samples were annealed at 333 K until the free radicals disappeared. PS and PαMS were precipitated from cyclohexane solution using methanol and the filtrate dried under vacuum at 363 K.

All the polymer samples were studied before and after γ-irradiation using s.e.c. coupled with viscometry and l.a.l.l.s. More precisely, the s.e.c. experiments were carried out using tetrahydrofuran and a Waters 150C

* To whom correspondence should be addressed

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Table 1 Molecular weight, polydispersity index and intrinsic viscosity of irradiated polymers

Sample	Dose (kGy)	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n	$[\eta]$ (ml g^{-1})	$[\eta]^a$ (ml g^{-1})
PS	0	99	92	1.07	45	44
PS	200	111	103	1.08	48	48
PS	400	134	116	1.15	54	55
PS in solution	200	324	158	2.04	65	101
PS in solution	300	1521	361	4.21	91	300
PMMA	0	74	73	1.02	31	29
PMMA	200	39	28	1.35	21	19
PMMA	400	28	22	1.30	15	15
PαMS	0	140	133	1.05	59	
PαMS	200	121	109	1.11	46	
PαMS	300	117	102	1.14	40	
PαMS	400	108	84	1.28	37	
PαMS in solution	200	93	49	1.90	34	

[a] Calculated from $[\eta] = 1.41 \times 10^{-2} M^{0.7}$ for PS and from $[\eta] = 1.28 \times 10^{-2} M^{0.69}$ for PMMA

chromatograph with a five-column set (PLgel 10 μm), the exclusion limits being 10^6, 10^5, 10^4, 10^3 and 500 Å, on-line with a 'home-made' continuous viscometer and a Chromatix CMX-100 photometer[10]. Molecular weights, molecular-weight distributions and viscosities at the given total doses are listed in *Table 1*. The original polymers have a very narrow molecular-weight distribution.

The spin-probed samples were prepared by dissolving the polymers in benzene solutions of perdeuterated 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy probe (MSD Isotopes). The spin-probe concentration was less than 0.03 wt%. The solvent was slowly evaporated at 308 K and the samples were annealed under vacuum at 363 K.

D.m.e.s.r. measurements

The d.m.e.s.r. spectra were recorded on a Varian E-109 X-band spectrometer equipped with an additional modulation coil and a Wavetek radiofrequency generator as a second frequency source. The experimental details are described in previous papers[6,11].

Recent experiments have confirmed that the d.m.e.s.r. full linewidth at half-intensity, Δ (in frequency units), is related to $(T_1\pi)$ under the condition that $T_1 \gg T_2$, where T_1 is the spin–lattice relaxation time and T_2 is the spin–spin relaxation time[12,13]. In our experiments, the temperature dependence of the d.m.e.s.r. linewidth, presented as $(\Delta\pi)^{-1}$ vs. inverse temperature, was measured. The linewidth $(\Delta\pi)^{-1}$ is related to the rotational correlation time of the standard sample[14] (deuterated spin probe in a glycerol/water matrix). One finds that:

$$\tau_R \approx 4.5(\Delta\pi)^{-1} \quad (1)$$

This relation, derived from d.m.e.s.r. linewidths in the slow-motion region, gives a simple approach to the τ_R values of Hwang *et al.*[15] for the jump model.

RESULTS AND DISCUSSION

Irradiated PS

PS samples irradiated in the solid state show a slight increase in molecular weight (M_w, M_n) and intrinsic viscosity with increasing irradiation dose (*Table 1*). In other words, we observe predominantly the crosslinking of a small number of macromolecules, in agreement with the values of the calculated and measured viscosities.

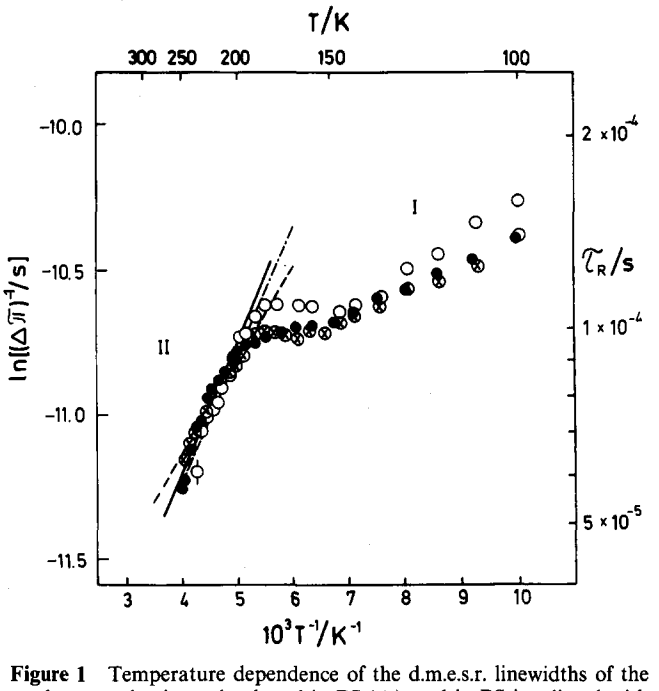

Figure 1 Temperature dependence of the d.m.e.s.r. linewidths of the perdeuterated spin probe doped in PS (○), and in PS irradiated with 200 kGy (●) and 400 kGy (⊗). On the right-hand vertical scale τ_R denotes calibrated values according to equation (1)

The heterogeneity of the crosslinked matrix was analysed by the d.m.e.s.r. technique. The temperature dependence of the d.m.e.s.r. linewidths, $(\Delta\pi)^{-1}$, of the perdeuterated spin probe dispersed in PS irradiated with different doses is shown in *Figure 1*. Two distinct regions of molecular motions are observed for all the PS samples. The crossover points, which mark the intrinsic transition of the specific spin-probe molecule, are between 190 and 200 K[6,14]. The sharp linewidth broadening above 200 K reflects the temperature-increased mobility of the spin-

probe skeleton. In this temperature interval the host matrix structure and dynamics make a dominant contribution to the d.m.e.s.r. linewidth broadening. The change of free volume and its distribution in a PS matrix irradiated with 200 kGy seem to have a negligible influence on the spin-probe motion. This result may be explained by the very small change of polydispersity (from 1.07 to 1.08) for non-irradiated PS and PS irradiated with 200 kGy (*Table 1*). However, the linewidth broadening decreases with increase of irradiation dose (400 kGy) in the same temperature interval. The lower linewidth broadening indicates a restricted rotational motion of the spin-probe molecules. The corresponding activation energies are listed in *Table 2*.

It should be noted that the probe molecules are statistically distributed in the polymer matrix and the probe distribution will depend on the free-volume environments at different positions in the matrix. Thus, some probe molecules will be trapped in regions with higher crosslink density or smaller free volume. These probes will experience restricted rotational motion and consequently give rise to a slower linewidth broadening. The spin probes embedded in regions of lower density will contribute to a faster linewidth broadening. If so, then at any instant spin probes will experience a certain distribution of free volume. Therefore, we may expect that the detected d.m.e.s.r. spectrum reflects a distribution of correlation times for spin probes embedded in an irradiated PS matrix (*Figure 2a*, spectrum I).

According to the s.e.c. experiments, M_w of PS irradiated with 400 kGy in the solid state is increased by only 35% and the polydispersity from 1.07 to 1.15 (*Table 1*). Obviously, in the solid state there is only a low degree of branching. However, when PS is irradiated in cyclohexane solution, the molecular weight and polydispersity index increase very strongly. This is illustrated in *Figure 2b*. In addition the intrinsic viscosity is much lower than that of the corresponding linear sample[16]. This result suggests a high degree of branching and confirms the existence of very significant crosslinking of the polystyrene chains.

The d.m.e.s.r. spectra of this highly crosslinked PS matrix between 250 and 260 K display a complex feature that cannot easily be resolved at present (*Figure 2a*, spectrum II). The calculated rotational correlation times reveal two relaxation processes above

Table 2 Activation energies of spin-probe motion in polymers

Sample	Dose (kGy)	E_a (kJ mol^{-1}) Region II	Region III
PS	0	3.7	
PS	200	3.9	
PS	400	2.7	
PS in solution	200	4.2	
PS in solution	300	3.7	8.6
PMMA	0	1.8	6.7
PMMA	200	1.4	5.3
PMMA	400	0.6	4.3
PαMS	0	4.3	
PαMS	200	4.7	
PαMS	300	5.4	
PαMS	400	6.3	
PαMS in solution	200	9.0	

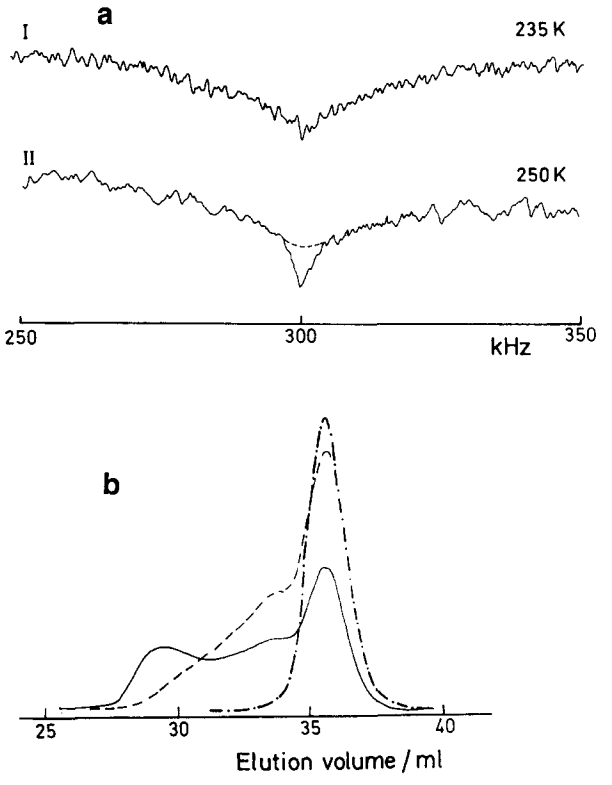

Figure 2 (a) D.m.e.s.r. spectra of spin probe doped in (I) PS irradiated with 200 kGy and (II) PS irradiated with 400 kGy in cyclohexane solution. All spectra are recorded with the magnetic field centred on the central nitrogen hyperfine line at a maximal signal intensity. The second modulation frequency ($\omega_2/2\pi$) was swept in the range from 250 to 350 kHz. The broken curve on spectrum II indicates possible decomposition of the two spin-probe populations. (b) S.e.c. chromatograms of non-irradiated PS (–·–·–), and PS irradiated in cyclohexane solution with 200 kGy (– – – –) and 300 kGy (———)

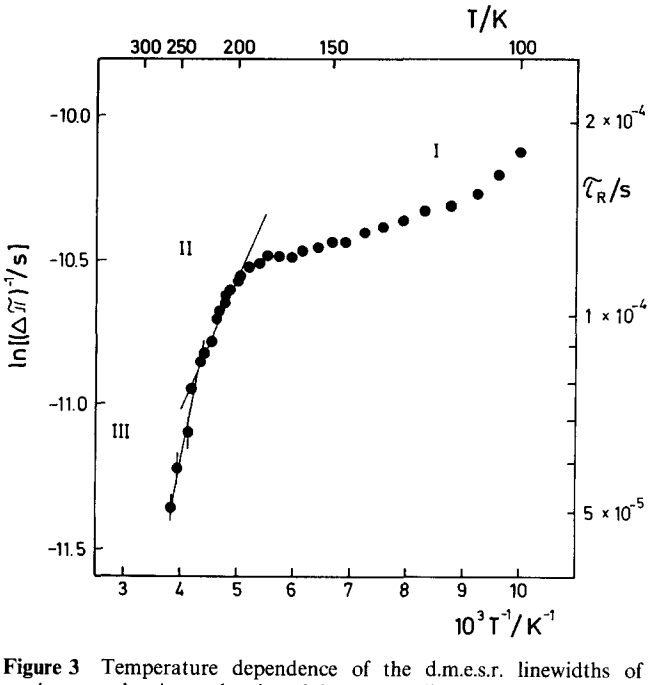

Figure 3 Temperature dependence of the d.m.e.s.r. linewidths of perdeuterated spin probe doped in PS irradiated with 300 kGy in cyclohexane solution

200 K (*Figure 3*). As the temperature of the measurements is far below the glass transition temperature of PS, the relaxation processes marked as II and III could not be connected with the segmental mobility of polymer chains.

Furthermore, a probable influence of phenyl ring flipping as a highly restricted form of rotation on the spin-probe motion is also ruled out in this temperature interval[17].

Present results suggest that a PS matrix irradiated in solution has a very different density fluctuation or free-volume size distribution than a PS matrix irradiated in the solid state. Considering the shape of the d.m.e.s.r. spectra and polydispersity (*Figures 2a* II and *2b*), the two motions above 200 K shown in *Figure 3* may be explained as a distribution of spin probes in two regions of considerably different crosslink density. The lines associated with probe molecules located in highly crosslinked regions will undergo restricted motion and show a slower linewidth broadening than those placed in less dense regions. Thus, the experimental spectrum to a good approximation can be described as a superposition of two distinct populations of spin-probe mobilities. At lower temperatures, the d.m.e.s.r. spectra will be dominated by the contribution of more restricted motions, while, at higher temperatures, fast tumbling probes and broadened lines will prevail.

It is known that the crosslinking efficiency in PS solution depends on solvent and polymer concentration[8]. The much higher crosslinking efficiency in cyclohexane solution could be explained by an increase of the overall polymer radical concentration, through hydrogen abstraction on polystyrene chains by reactive radicals formed by the radiolysis of cyclohexane ($G_R \approx 6.5$). Since the temperature of irradiation was slightly below the Θ temperature of cyclohexane/polystyrene, crosslinking could be favoured by the local aggregation of polymer chains. The consequence is a highly heterogeneous crosslinked network, as observed in our experiments.

Irradiated PMMA

Contrary to PS, PMMA degrades under irradiation, leading to a reduction in average molecular weight[7-9] and intrinsic viscosity with increasing radiation dose (*Table 1*). The degradation, as a dominant process, is confirmed by the very good agreement between the values of intrinsic viscosity of PMMA[16] and those determined from the s.e.c. experiments. The spin-probe motion in the irradiated PMMA matrix reveals three relaxation processes as in the case of a non-irradiated sample[6] (*Figure 4*). According to our previous experiments with the perdeuterated spin probe and the theoretical explanation[6,14], only a smooth change of the d.m.e.s.r. linewidth in region I can be expected. The existence of a small minimum at ~150 K was explained as a coupling of CD_3 motion of the spin probe with motionally active ester side-chain groups at low temperature. The two discrete motions above 190 K, when the spin probe begins to rotate, are connected with spin-probe motions influenced by the high-frequency motion of the side-chain groups. The relaxation process defined as region II is mainly affected by the ester side-chain CH_3 motion, while the process in region III, which becomes active above 240 K, is dominated by the α-CH_3 motion[6,18,19]. In irradiated PMMA a difference appears in linewidth broadening in regions II and III, depending on the irradiation dose. The lower d.m.e.s.r. linewidth broadening or a decrease of the apparent activation energy (*Table 2*) for both relaxation processes with increase of irradiation dose can be explained by two effects. One effect is main-chain scission. As shown in *Table 1* the molecular weight of PMMA decreases with

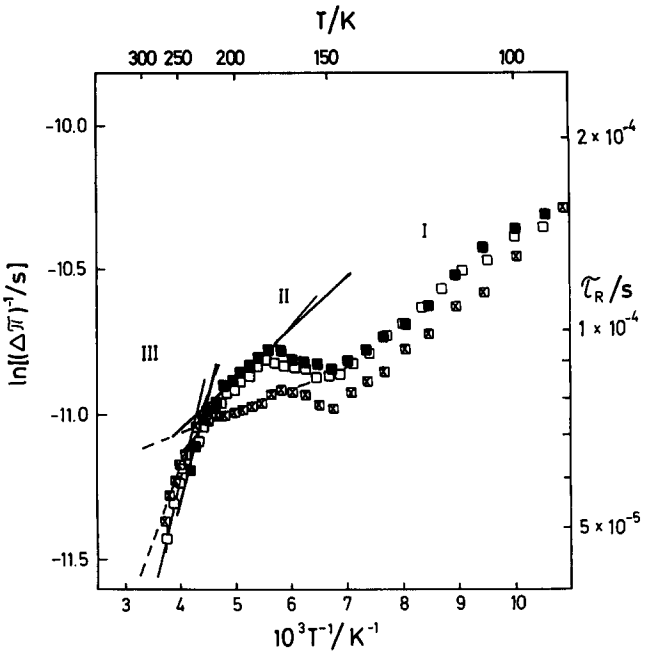

Figure 4 Temperature dependence of the d.m.e.s.r. linewidths of perdeuterated spin probe doped in PMMA (□), and in PMMA irradiated with 200 kGy (■) and 400 kGy (⊠)

increase of irradiation dose. A very pronounced decrease in molecular weight affects the local density distribution and increases the free volume[20]. The second effect is the simultaneous rupture of the side-chains[21]. The composition of the gaseous products suggests that the methyl ester groups are more labile than the methyl branches. C=C double bonds form during the radiolysis of PMMA, and CO and CH_2O are the main radiolytic products. Thus, the intramolecular conversion of side-chain radicals lowers the concentration of ester CH_3 groups and brings about a restricted mobility of the remaining CH_3 group attached to the C=C bond.

If the high-frequency motions of α-CH_3 and ester side-chain CH_3 groups, respectively, have a prevailing influence on spin-probe tumbling above the internal probe transition in a matrix of higher local density[6], a slower overall motion of the spin probe in the degraded matrix can be expected. Spin probes dispersed at sites of lower local density or larger free volume will experience weaker coupling with the polymer side-chain groups.

Irradiated PαMS

The γ-irradiation of PαMS in the solid state and in cyclohexane solution results in chain scission (*Table 1*). Irradiated PαMS doped with the spin probe shows a similar minimum at ≈150 K to the non-irradiated sample (*Figure 5*), which is explained as a possible interaction between α-CH_3 motion and CD_3 groups of the probe[6]. The PαMS matrix structure makes a dominant contribution to the d.m.e.s.r. linewidth in the measured temperature interval above ~200 K. The linewidth broadening is faster at higher doses. The largest change in molecular weight and polydispersity is, however, observed in PαMS irradiated in solution (*Table 1*). This results in even faster linewidth broadening or a higher corresponding activation energy (*Table 2*).

The spin probe dispersed in either a PαMS or a PMMA matrix can be coupled to the high-frequency side-chain motion[3] and, depending both on the local density or free

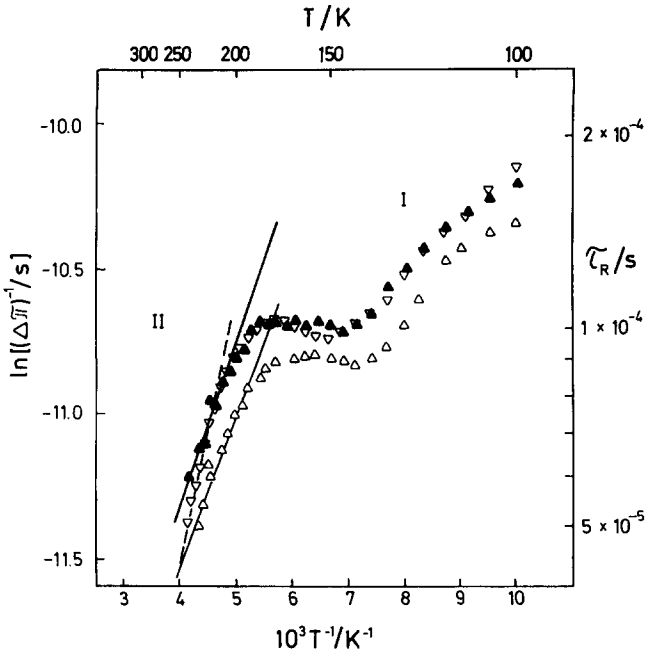

Figure 5 Temperature dependence of the d.m.e.s.r. linewidths of perdeuterated spin probe doped in PαMS (△), and in PαMS irradiated with 200 kGy (▲) and 400 kGy (▽)

volume and the mode and type of side-group motion, will undergo faster or slower motion. It should be kept in mind that the chain structures of PαMS and PMMA and the effects of irradiation are different. This may cause different local distributions of free volume regions in which the motion of spin probes takes place, and consequently different interactions between the side-groups and probe molecules. The proposed mechanism[22] of PαMS degradation suggests that the CH_3 end-groups formed in the course of degradation are immobilized by the double bond. As chain scission is increased at higher doses, the spin-probe motion may be enhanced by an increase of free volume if the coupling with α-CH_3 groups in PαMS has no prevailing influence. At present it is not possible without a complete d.m.e.s.r. lineshape analysis to estimate the contribution of both effects on spin-probe motions.

CONCLUSIONS

Size exclusion chromatography coupled on-line with low-angle laser light scattering and viscometry are very accurate and a convenient way to explore the molecular weights, polydispersities and viscosities of polymers exposed to γ-irradiation. PS irradiated in the solid state shows only a slight increase of molecular weight and viscosity with increasing dose. For irradiation in solution, the data confirm the existence of considerable crosslinking. Contrary to PS, PMMA and PαMS show the degradation of polymer chains at the same doses.

The influence of irradiation effects on the polymer matrix homogeneity was studied by d.m.e.s.r. The d.m.e.s.r. spectra of the spin probe above the internal probe transition have been shown to be very sensitive to any change of the host polymer matrix. These changes are connected with variations in free volume and local side-chain motions in the slow-motion region.

In the highly crosslinked PS matrix, irradiated in solution, the d.m.e.s.r. spectra have demonstrated the superposition of two rotational correlation times identified with the spin probes located in regions of considerably different crosslink densities.

Two discrete molecular motions of the spin probe in PMMA above 190 K ascribed to the side-chain motions and the corresponding effective activation energies decrease with increasing irradiation dose. This behaviour is attributed to a weaker interaction of side-chain motions with the spin probe embedded in a matrix of larger free volumes and a smaller concentration of methyl ester groups as a consequence of side-chain rupture.

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