E.p.r. study of spin-labelled glycidyl methacrylate–ethylene dimethacrylate and styrene–divinylbenzene suspension copolymers in the swollen state

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Reactive groups of homogeneous or macroporous copolymers glycidyl methacrylate–ethylene dimethacrylate and styrene-divinylbenzene containing different amounts of crosslinking agents have been modified in the reaction with an amino derivative of stable nitroxide. The spin-labelled copolymers thus formed were swollen in thermodynamically good or bad solvents and studied by the electron paramagnetic resonance (e.p.r.) method. Two types of spin labels were found in the majority of these copolymers at suitable temperatures and their concentrations were determined. According to our interpretation, the spin labels subjected to rapid rotational diffusion belong to the modified groups localized on chains attached to the inner surface of macroporous copolymers while the spin labels subjected to the very slow rotational diffusion belong to the modified groups localized inside highly crosslinked globules forming the inner structure of the macroporous copolymers. In the less highly crosslinked homogeneous copolymers the modified groups carrying the spin labels subjected to very slow and rapid rotational diffusion are localized in, respectively, the more crosslinked and less crosslinked domains of the polymer beads.

(**Keywords: styrene/divinylbenzene; suspension polymerization; electron paramagnetic resonance**)

INTRODUCTION

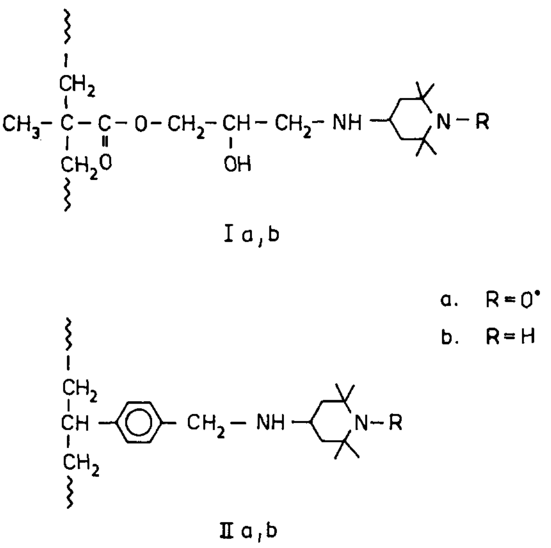
Homogeneous and macroporous suspension glycidyl methacrylate–ethylene dimethacrylate (GMA–EDMA) copolymers are reactive polymers which are used as chromatographic sorbents, polymeric reagents and carriers of catalytic or other species bound to these copolymers via the highly reactive oxirane groups[1,2]. Concentration, accessibility and localization of the reactive groups in the polymer particles are important parameters characterizing such carriers. Suitable derivatives of sterically hindered nitroxides may be relatively easily and selectively reacted with the oxirane groups of GMA–EDMA copolymers or with chloromethylated groups of styrene–divinylbenzene (ST–DVB) copolymers. The amount of the modified reactive groups Ia or IIa (*Scheme 1*) in the spin-labelled copolymers thus formed represents that of the reactive groups capable of reacting with a suitable low molecular weight compound and, together with the rotational mobility of the nitroxide spin label may in principle be determined in the e.p.r. study of these copolymers[3]. Information concerning the character and localization of the modified reactive groups in the copolymers may then be deduced from the rotational mobility of the spin labels.

Regen[4–6] found in e.p.r. studies of spin-labelled homogeneous ST–DVB copolymers containing different amounts of the crosslinking agent (1–12% DVB) an inverse proportionality between the correlation time characterizing the rotational mobility of the spin labels in the swollen copolymers and the swelling ratio (swollen volume/dry volume) of the particular copolymer in the solvent used. In this paper we present results obtained in an e.p.r. study of spin-labelled homogeneous or macroporous GMA–EDMA or ST–DVB copolymers swollen in thermodynamically good or bad solvents, and we compare our results with the reported data.

EXPERIMENTAL

Materials

Macroporous GMA–EDMA copolymers (GM) were prepared by suspension polymerization using the method described previously[7]. To obtain homogeneous GMA–



Scheme 1

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Table 1 Composition and properties of copolymers

Sample	Crosslinking agent content (wt%)	Mean size of polymer particles (μm)	Specific surface area ($m^2 g^{-1}$)	Porosity (%)	Active groups concentration[a] c_A (mmol g^{-1})
GX-2.5	2.5	100	0	31.5	5.2
GX-7.5	7.5	120	0	23.9	5.7
GX-25	25	220	0.1	3.1	5.0
GM-40	40	220	69.4	65.2	4.2
GM-85	85	220	266.4	70.5	1.1
GM-95	95	220	410.4	70.0	0.5
SX-1	1	70	0	71.7	2.3
SX-2	2	70	0.4	64.7	2.7
SM-10	10	800	11.6	47.1	2.9
SM-60	60	3	200.0	57.3	1.6

[a] Concentration of oxirane groups in GX and GM copolymers determined by i.r. spectroscopy and chlorine concentration in the chloromethylated SX and SM copolymers

EDMA copolymers (GX), 30 g of dispersed phase composed of GMA and EDMA without any porogenic solvent and 0.06 g 2,2′-azo-bis(4,4-dimethyl-2-methoxy)-valeronitrile (initiator) were stirred in 100 ml of a 0.1% aqueous solution of poly(vinyl alcohol) (Polyviol W 25/140, Wacker-Chemie, FRG) with 20 g saccharose added. The polymerization proceeded at 323 K for 16 h under otherwise identical conditions[7].

Homogeneous (SX-1) and macroporous (SM-10 and SM-60) ST–DVB copolymers, where the number denotes the percentage of pure DVB in the monomer mixture, were purchased from the Research Institute of Synthetic Resins and Lacquers, Pardubice, Czechoslovakia. They were chloromethylated using chloromethyl methyl ether and $SnCl_4$ as a catalyst. SX-2 is a commercial chloromethylated ST–DVB (Merrifield resin, Fluka, Switzerland).

The specific surface area of copolymers was determined by the nitrogen dynamic desorption method with a Quantasorb apparatus[8]. Porosity was determined from benzene regain in copolymer spherical particles by the centrifugation technique[9]. Infra-red (i.r.) spectra of GMA–EDMA copolymers were quantitatively measured in KBr pellets with a PE 577 spectrometer. Concentrations of oxirane groups in these copolymers (c_A) were determined using the 910 cm^{-1} band corrected for nonspecific contributions of EDMA[10]. The characteristics of all copolymers studied are summarized in *Table 1*. All solvents used were purified by standard procedures.

Spin-labelling of copolymers

The nucleophilic displacement reaction of oxirane group in GMA–EDMA[11] or of the chloromethylated group in ST–DVB[12] with the amino group of the nitroxide was used for spin-labelling of the polymers. Polymer beads (0.1 g) were swollen for 24 h in a sufficient volume of the solvent, 0.2–0.9 ml benzene or hexane, according to the swelling ratio of the copolymer in the given solvent. The required amount of the nitroxide solution, 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl (Fluka, Switzerland) in 2,2,6,6-tetramethyl-4-aminopiperidine (Fluka, Switzerland), was then added to obtain a twofold molar excess of amine groups with respect to the concentration of active groups (c_A) in the particular copolymer. The optimum concentrations of the nitroxide in aminopiperidine (0.15 wt% for GX-2.5, GX-7.5 and GM-40, 1.5 wt% for GM-85, GM-95 and for all ST–DVB copolymers and 15 wt% for GX-25) were used in the spin-labelling of particular copolymers to obtain a sufficient concentration of paramagnetic modified groups Ia or IIa and to prevent line broadening in the e.p.r. spectrum due to spin–spin interaction (modified groups Ib or IIb formed in the reaction with aminopiperidine are not paramagnetic). The reaction mixture was shaken in a water bath at 323 K for up to 150 h in the case of long-term spin-labelling. Spin-labelled copolymers were separated on sintered glass, rinsed in benzene for 50 h to remove the non-reacted spin label and amine, vacuum dried and quantitatively transferred into the sample tubes. A sufficient amount of solvent was then added to the sample tubes and the copolymers were allowed to swell at room temperature for at least 24 h.

E.p.r. measurements

E.p.r. spectra were recorded with a Jeol PE-3X spectrometer provided with an EC-100 computer. The measurements were performed at a microwave output of 2 mW and with a 100 kHz magnetic modulation. The cavity temperature was stabilized with a Jes-VT-3A temperature controller to ±0.5 K and measured with a platinum resistance thermometer. The samples were measured in quartz sample tubes of 5 mm o.d. The spin label concentrations in the polymers were determined by comparing the second integral of the spectra of the polymer with the second integral of the spectrum of the standard (benzene solution of diphenylpicrylhydrazyl). As no free nitroxide was identified in the samples, the concentrations of modified groups Ia + Ib or IIa + IIb in the copolymers (c_{SL}) were determined using the spin label concentration in the copolymers (which is identical with the concentration of paramagnetic modified groups Ia or IIa) and the concentrations of the nitroxide in aminopiperidine used in the spin labelling of a given copolymer. Relative concentrations of the spin labels subjected to the very slow or rapid rotational diffusion (r^{s}_{SL} and r^{r}_{SL}) were determined by numerical subtraction of the very slow motional spectra from the spectra of the samples in question, both measured at the same temperature and in the same solvent, and comparing the second integrals of both components.

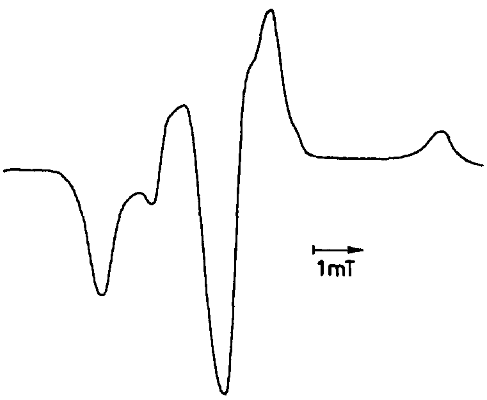

Figure 1 E.p.r. spectrum of the GMA–EDMA copolymer GX-2.5, spin-labelled and swollen in benzene, measured at 288 K

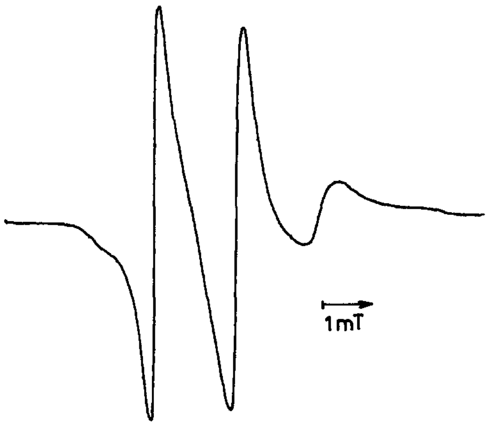

Figure 2 E.p.r. spectrum of the GMA–EDMA copolymer GX-2.5, spin-labelled and swollen in benzene, measured at 333 K

RESULTS

GMA–EDMA copolymers

Lineshapes of e.p.r. spectra of spin-labelled GMA–EDMA copolymers depend on the type of the copolymer, on the crosslinking agent concentration, on the solvent, and on temperature. Homogeneous copolymers, spin-labelled and swollen in benzene (which is a thermodynamically good solvent) at 288 K gave typical very slow motional e.p.r. spectra (*Figure 1*). Such e.p.r. spectra are characteristic of the nitroxide spin labels subjected to very slow rotational diffusion characterized by a correlation time approaching 1×10^{-7} s. The spectrum of the highly crosslinked homogeneous copolymer GX-25 has a similar lineshape, even at 333 K. The spectra of homogeneous copolymers containing lower concentration of the crosslinking agent (GX-2.5 and GX-7.5) measured at 333 K (*Figure 2*) represent a superposition of the very slow motional spectrum and of the predominant share of the simple three-line motionally narrowed spectrum which is characteristic of the nitroxide spin label subjected to rapid rotational diffusion. The concentrations of the modified oxirane groups and the relative concentrations of the spin labels subjected to very slow and rapid rotational diffusion determined in the analysis of the e.p.r. spectra of GMA–EDMA copolymers are summarized in *Table 2*. We did not attempt to determine parameters characterizing the rotational diffusion of the spin labels (orientation and components of their rotational diffusion tensors) because the lineshapes of their e.p.r. spectra had not been determined accurately enough by the subtraction method; moreover, the motionally narrowed spectra cannot be analysed unambiguously[13] and the sensitivity of the very slow motional spectra to these parameters is limited[3].

The macroporous copolymer containing the lowest concentration of the crosslinking agent (GM-40), spin-labelled and swollen in benzene, showed at 288 K only the very slow motional spectrum. The e.p.r. spectrum of this copolymer at 333 K and the spectra of highly crosslinked macroporous copolymers GM-85 and GM-95, spin-labelled and swollen in benzene and measured at both temperatures, again present a superposition of the very slow motional and motionally narrowed spectra (*Figure 3*). The relative concentrations of the spin labels subjected to rapid rotational diffusion (r^{r}_{SL}) in these copolymers increase with both the temperature and the crosslinking agent concentration (*Table 2*), but are substantially lower in all macroporous copolymers than those determined in less highly crosslinked homogeneous copolymers GX-2.5 and GX-7.5 at 333 K. The relative concentrations of modified oxirane groups (p_{SL}) determined in these two homogeneous copolymers are higher than those determined in macroporous copolymers. The relative concentrations, lower by three orders of magnitude, were determined in highly crosslinked glassy homogeneous copolymer GX-25 (*Table 2*).

Lineshapes of some of the e.p.r. spectra (*Figure 3*) were analysed in terms of superposition of the spectra of two types of spin label which differ in the nature of their rotational diffusion (i.e. in terms of the two-site model).

Table 2 Data obtained in the analysis of e.p.r. spectra of GMA–EDMA copolymers measured in benzene

				Relative concentration of spin label[d] (%)			
				at 288 K		at 333 K	
Sample	Medium[a]	c_{SL}[b] (mmol g^{-1})	p_{SL}[c] (%)	r^{r}_{SL}	r^{s}_{SL}	r^{r}_{SL}	r^{s}_{SL}
GX-2.5	Benzene Hexane	2.91	56	0	100	80	20
GX-7.5	Benzene	3.26	57	0	100	70	30
GX-25	Benzene	0.004	0.08	0	100	0	100
GM-40	Benzene	1.17	28	0	100	20	80
	Hexane	1.79	42	0	100	20	80
GM-85	Benzene	0.21	20	10	90	30	70
GM-95	Benzene	0.027	5.5	25	75	45	55
	Hexane	0.11	22	15	85	45	55

[a] Solvent in which spin-labelling of the GMA–EDMA copolymers was performed

[b] Concentration of modified oxirane groups after 150 h reaction time determined by e.p.r.

[c] Relative concentration of modified oxirane groups $p_{SL} = 100\, c_{SL}/c_A$, c_A see *Table 1*

[d] Relative concentrations of spin labels subjected to the rapid (r^{r}_{SL}) and to the very slow (r^{s}_{SL}) rotational diffusion determined by analysis of e.p.r. spectra

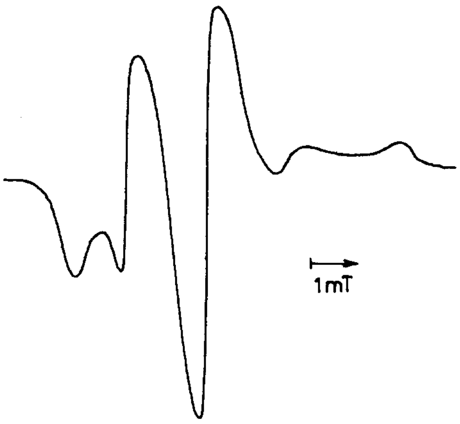

Figure 3 E.p.r. spectrum of the GMA–EDMA copolymer GM-40, spin-labelled and swollen in benzene, measured at 333 K

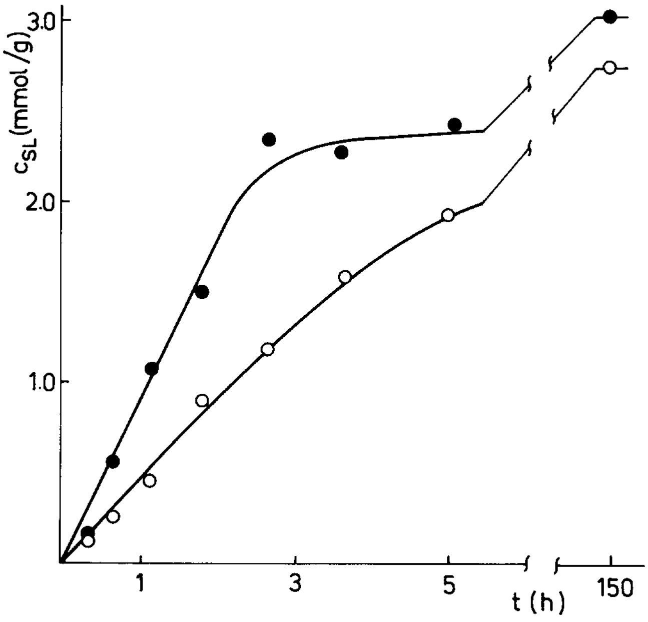

Figure 4 Kinetics of the modification reaction of the GMA–EDMA copolymer GX-2.5 in: ○, benzene; ●, hexane

They seem to be similar to the recently published[14] lineshapes of the e.p.r. spectra of spin-labelled poly(methyl methacrylate) (PMMA) which were analysed in terms of the single-site model. There exists a number of differences between these two classes of e.p.r. spectra, the most important of which concerns the outer extrema separation. In all the e.p.r. spectra analysed in this work in terms of two-site model this separation agrees with the outer extrema separation in the very slow motional spectrum. The outer extrema separation in the e.p.r. spectra analysed in terms of the single-site model depends on the character of spin-label rotational diffusion, and in general decreases with increasing rotational mobility of the spin label[14].

To gain a more detailed insight into the problem, some further experiments were performed. E.p.r. spectra of GMA–EDMA copolymers, spin-labelled in benzene but swollen in dioxane (which is also a good solvent for this copolymer, and the regain is even higher than in benzene), and in thermodynamically bad solvents (cyclohexane and dibutyl ether), were measured. Lineshapes of the e.p.r. spectra of copolymers GX-2.5, GX-25 and GM-95 swollen either in benzene or in dioxane were identical. Spin-labelled homogeneous copolymers GX-2.5 and GX-7.5, swollen in cyclohexane and in dibutyl ether, even at 333 K showed only the very slow motional spectra. The relative concentrations of the spin labels subjected to rapid rotational diffusion in the macroporous copolymers GM-40 and GM-95 swollen in cyclohexane and in dibutyl ether are lower by approximately 10–20 % in comparison with the values determined in benzene. In a further series of experiments the GMA–EDMA copolymers were spin-labelled in the thermodynamically bad solvent hexane and swollen in benzene. The results obtained from the analysis of e.p.r. spectra of homogeneous copolymers, spin-labelled in hexane and in benzene, are the same, within the limits of experimental error. The macroporous copolymers GM-40 and GM-95, spin-labelled in hexane, show a significant increase in the relative concentration of modified oxirane groups (p_{SL}) with respect to the values determined in these copolymers, spin-labelled in benzene (*Table 2*). In the last series of experiments the time-course of modification reaction was studied. The time dependences of the concentration of modified oxirane groups c_{SL} found in GX-2.5 and GM-95 copolymers, spin-labelled in benzene and in hexane, swollen in benzene and measured at 333 K are given in *Figures 4* and *5*, respectively. There is no significant change in the lineshapes of e.p.r. spectra of the GM-95 copolymer spin-labelled in both reaction media during a 5 h reaction. In comparison with the values determined after the 5 h reaction, the relative concentrations of the spin labels subjected to rapid rotational diffusion in the early stage of the modification reaction are somewhat higher in the copolymer GX-2.5 spin-labelled in benzene and somewhat lower in the same copolymer spin-labelled in hexane. It was further found that long-term spin-labelling (150 h) increases the yield of the modification reaction by 30–50 % in comparison with the 5 h reaction, but does not further change the lineshapes of the e.p.r. spectra.

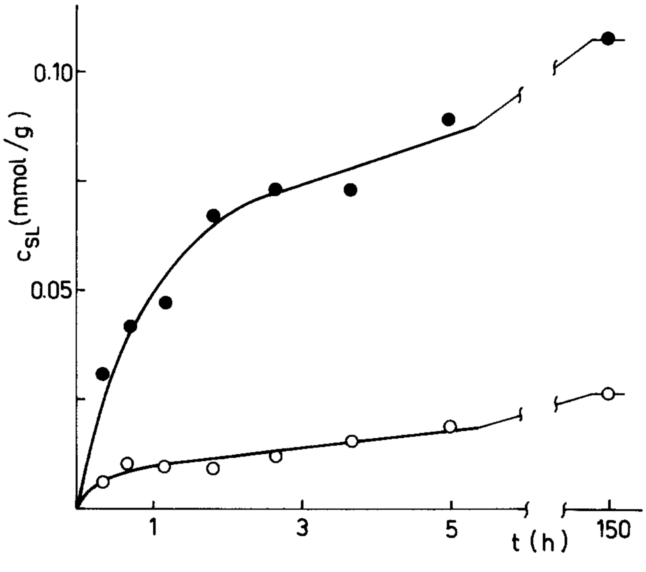

Figure 5 Kinetics of the modification reaction of the GMA–EDMA copolymer GM-95 in: ○, benzene; ●, hexane

Figure 6 E.p.r. spectrum of the ST–DVB copolymer SX-2, spin-labelled and swollen in benzene, measured at 288 K

Table 3 Data determined in the analysis of e.p.r. spectra of ST–DVB copolymers measured in benzene

				Relative concentration of spin label[d] (%)			
				at 288 K		at 333 K	
Sample	Medium[a]	c_{SL}[b] (mmol g^{-1})	p_{SL}[c] (%)	r_{SL}^{ξ}	$r_{SL}^{\S}$	r_{SL}^{ξ}	$r_{SL}^{\S}$
SX-1	Benzene	0.22	9.6	55	45	100	0
	Hexane	1.44	63	25	75	55	45
SX-2	Benzene	0.25	9.3	50	50	100	0
	Hexane	1.75	65	30	70	55	45
SM-10	Benzene	0.66	23	0	100	0	100
	Hexane	0.86	30	0	100	0	100
SM-60	Benzene	0.17	11	20	80	40	60
	Hexane	0.43	27	15	85	40	60

[a] Solvent in which spin-labelling of chloromethylated ST–DVB copolymers was performed
[b] Concentration of modified chloromethylated groups after 150 h reaction time determined by e.p.r.
[c] Relative concentration of modified chloromethylated groups $p_{SL} = 100\ c_{SL}/c_A$, c_A see *Table 1*
[d] See *Table 2*

ST–DVB copolymers

The e.p.r. spectra of homogeneous, lightly crosslinked ST–DVB copolymers SX-1 and SX-2, spin-labelled in benzene, which is a good solvent also for this copolymer, swollen in the same solvent and measured at 288 K (*Figure 6*), are a superposition of the very slow motional spectra and motionally narrowed spectra, in contrast to the corresponding homogeneous GMA–EDMA copolymers. It was found that the relative concentrations of the spin labels subjected to the rapid rotational diffusion in these copolymers is about 50% (*Table 3*). No spin labels subjected to the very slow rotational diffusion were identified in the e.p.r. spectra of SX-1 and SX-2 copolymers measured at 333 K. Lineshapes of the motionally narrowed spectra clearly indicate that the rotational diffusion of this type of spin label in these copolymers is more rapid than in the corresponding GMA–EDMA copolymers under the same conditions (compare *Figures 7* and *2*). It should be stressed that the motionally narrowed e.p.r. spectrum of the nitroxide spin label consists of three narrow lines, whereas the very slow motional spectrum is much broader. Hence, in the e.p.r. spectrum of a polymer containing the same relative concentrations of the spin labels subjected to rapid and to very slow rotational diffusion the amplitude of the motionally narrowed spectrum is much higher than that of the very slow motional spectrum (*Figure 6*). The more rapid the rotational diffusion of the former type of spin label, the narrower the lines in the motionally narrowed spectrum and the more complicated is the identification of small concentrations of the spin labels subjected to very slow rotational diffusion.

The moderately crosslinked macroporous ST–DVB copolymer SM-10, spin-labelled in benzene and swollen in the same solvent, gave a very slow motional spectrum at both temperatures, 288 and 333 K. The e.p.r. spectra of the macroporous copolymer SM-60, swollen and measured under the same conditions, represent a superposition of both types of e.p.r. spectra, again with the relative concentration of the spin labels subjected to rapid rotational diffusion increasing with increasing temperature (*Table 3*).

From the data obtained in the analysis of e.p.r. spectra of homogeneous copolymers SX-1 and SX-2, spin-labelled in hexane and swollen and measured in benzene (*Table 3*), we can see that these copolymers differ from those spin-labelled in benzene in that the relative concentrations of the spin labels subjected to rapid rotational diffusion are lower and the yield of the modification reaction is significantly higher. In the case of the macroporous copolymers SM-10 and SM-60, spin-labelled in hexane and swollen and measured in benzene, only a slight increase of the relative concentration of modified chloromethylated groups is observed in comparison with the same copolymers modified in benzene.

Comparison of the results after 10 and 150 h reaction shows that long-term spin-labelling increases the yield of the modification reaction of chloromethylated groups in both reaction media (benzene and hexane) five to ten times in homogeneous (SX-1 and SX-2) copolymers and two to three times in macroporous (SM-10 and SM-60) copolymers. These differences are much higher than those observed in the case of the corresponding GMA–EDMA copolymers. In addition, the lineshapes of the motionally narrowed component of the e.p.r. spectra of homogeneous ST–DVB copolymers prepared by long-

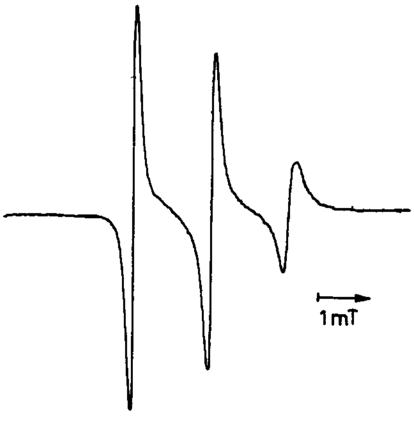

Figure 7 E.p.r. spectrum of the ST–DVB copolymer SX-2, spin-labelled and swollen in benzene, measured at 333 K

term spin-labelling seem to indicate a slower rotational diffusion of the spin labels in comparison with the copolymers spin-labelled for 10 h.

DISCUSSION

Internal rotation of the spin label around the bonds through which it is bound to the polymer chain segment and local motions of this segment contribute to the rotational diffusion of the spin label bound to the high molecular weight polymer. Both these motions are drastically hindered at temperatures in the vicinity of and below the T_g of a given polymer system. Spin-labelled polymers then supply only very slow motional e.p.r. spectra at such temperatures. On the other hand, the rotational mobility of the spin labels is relatively high at temperatures sufficiently above the T_g of the particular polymer system, when the thermal motion is able to overcome the barriers to rotational diffusion, and spin-labelled polymers supply motionally narrowed e.p.r. spectra under such conditions. The T_g value of swollen crosslinked copolymers generally increases with their density of crosslinking and decreases with increasing content of the low molecular weight solvent.

The occurrence of two types of spin label in the less highly crosslinked spin-labelled homogeneous GMA–EDMA copolymers, GX-2.5 and GX-7.5, swollen in benzene at 333 K may only be explained by the existence of inhomogeneities in the copolymer forming the beads. The spin labels subjected to rapid rotational diffusion clearly belong to the modified groups localized in the less crosslinked, and consequently more swollen, domains of these copolymers, the T_g of which is substantially lower than 333 K. The spin labels subjected to very slow rotational diffusion then belong to the modified groups localized in the more crosslinked, and consequently less swollen, domains that form the nuclei of beads and are characterized by a substantially higher T_g value. The finding that even the spin labels belonging to the modified groups localized in the less crosslinked domains of these copolymers are subjected to very slow rotational diffusion at 288 K indicates that the T_g in these domains is simultaneously approximately equal to, or higher than, 288 K. Only the spin labels subjected to very slow rotational diffusion were identified in the highly crosslinked spin-labelled homogeneous GMA–EDMA copolymer GX-25, swollen in benzene, and in the less highly crosslinked GX-2.5 and GX-7.5 copolymers swollen in thermodynamically poor solvents (cyclohexane or dibutyl ether). This observation may be explained by an increase in T_g of these copolymers under mentioned conditions above 333 K, caused by the high crosslinking density and negligible swelling in benzene of the former copolymer and by negligible swelling of both lightly crosslinked copolymers in thermodynamically poor solvents in the latter case. In addition, the low accessibility of oxirane groups in the glassy copolymer GX-25 is responsible for the pronounced decrease in the concentration of modified groups c_{SL} in this copolymer with respect to the values of this concentration determined in the two less highly crosslinked homogeneous copolymers.

In contrast to the homogeneous copolymers, which possess only the swelling porosity and have no measurable specific surface area in the dry state, the macroporous copolymers possess dry porosity and a large specific surface area in the dry state, which increases with increasing concentration of the crosslinking agent in the polymerization feed[15] (*Table 1*). According to the globular model, the inner structure of both GMA–EDMA and ST–DVB macroporous copolymers is thought to be formed by small globules composed of a highly crosslinked copolymer. These globules are bound together by poly(glycidyl methacrylate) or polystyrene chains containing much fewer units capable of crosslinking attached to their surface which forms the inner surface of the macroporous copolymers[16]. We have found that the rotational diffusion of the spin labels belonging to the modified groups localized in the swollen homogeneous GMA–EDMA copolymer containing 25% of the crosslinking agent is very slow even at 333 K, and that the accessibility of oxirane groups in such a copolymer during the modification reaction is low due to its high crosslinking and negligible swelling; we infer the same behaviour also for more highly crosslinked GMA–EDMA copolymers. On the other hand, the attached polymer chains contain a large number of readily accessible reactive groups, and therefore a significant part of modified groups may be localized on them. Hence, the spin labels subjected to the rapid rotational diffusion found in the highly crosslinked macroporous copolymers may belong only to the modified groups localized on the polymer chains attached to the inner surface of these copolymers, where steric hindrance to the spin label rotational diffusion is substantially reduced. Spin labels subjected to very slow rotational diffusion found in these copolymers belong to the modified groups localized inside the highly crosslinked globules. The observed decrease in the concentration of modified groups with the crosslinking agent concentration is due to the decreasing amount of the reactive groups in the copolymers. The simultaneously observed rise of the relative concentration of spin labels subjected to rapid rotational diffusion may be explained by an increase in the specific surface area, and consequently an increase in the number of polymer chains attached. The slight temperature dependence of relative concentrations of the spin labels subjected to both rapid and very slow rotational diffusion reveals the existence of inhomogeneity in the values of local T_g and in the efficiencies of steric barriers hindering the spin label rotational diffusion. The lower yields of the modification reaction in the case of macroporous copolymers may be explained by the low accessibility of reactive groups localized inside the highly crosslinked copolymer globules during their reaction with the spin label.

The results obtained in the study of spin-labelled ST–DVB copolymers agree qualitatively with those of studies of the GMA–EDMA copolymers discussed above. In the discussion of quantitative differences found for these two copolymers it is difficult to distinguish between the effects given by their different chemical structures, the effects caused by different crosslinking densities of particular copolymers and the effects of their different swelling ratios. The behaviour of GMA–EDMA and ST–DVB copolymers cannot be correlated according to the crosslinking agent concentration in the polymerization feed, because the reactivities of the double bonds of the crosslinking agents used (EDMA or DVB) are different and there is no proportionality between their concentration and the crosslinking density of the copolymer. Moreover, the crosslinking densities of the GMA–EDMA copolymers may be increased by reactions between the oxirane groups, whereas the probability of a reaction between chloromethylated groups of the ST–DVB copolymers is negligible at the low degree of chloromethylation used. The lower concentration of the crosslinking agent in the ST–DVB copolymers than in the GMA–EDMA homogeneous copolymers studied and the possibility of additional crosslinking by reactions between the oxirane groups in the GMA–EDMA copolymers seem to indicate lower crosslinking densities in the homogeneous ST–DVB copolymers, in agreement with the higher rotational mobility of the spin labels responsible for the motionally narrowed component of the e.p.r. spectra of these copolymers when compared with the rotational mobility of the spin labels responsible for the same component of the spectra of homogeneous GMA–EDMA copolymers.

Long-term spin-labelling of both GMA–EDMA and ST–DVB macroporous copolymers results in higher yields of the modified groups in the thermodynamically poor solvent (hexane) compared to the good solvent (benzene). This may have a kinetic reason. Permeation of the spin label into the macroporous copolymers swollen in the thermodynamically poor solvent is easier. The higher swelling ratio of these copolymers in benzene may result in the narrowing or stopping of pores, and consequently in a lower accessibility of reactive groups. The reason for the slower course of the modification reaction of homogeneous less highly crosslinked ST–DVB copolymers and its lower yields in benzene compared with homogeneous less highly crosslinked GMA–EDMA copolymers, is not quite clear. At the beginning of the modification reaction, the reactive groups localized in the less crosslinked outer domains of the beads take part in the reaction. Gradual modification of the reactive groups localized in the more crosslinked domains deeper under the surface of the beads is probably responsible for the observed change of the lineshape of the motionally narrowed component of the e.p.r. spectra of the homogeneous lightly crosslinked ST–DVB copolymers in the course of the modification reaction.

Regen studied homogeneous low-crosslinked ST-DVB copolymers which had been spin-labelled using the reaction between their chloromethylated derivatives and 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl[4]. This reaction was performed in dimethylformamide (DMF) in the presence of sodium hydride at room temperature for 24 h. DMF is a good solvent for this copolymer and the swelling ratio is similar to that in benzene[4]. Regen measured at room temperature the e.p.r. spectra of these spin-labelled copolymers swollen in tetrachloromethane (CCl_4), which is another good solvent for this copolymer. He did not identify any very slow motional component in the experimental e.p.r. spectra. The relatively short-term spin-labelling (24 h in comparison with 150 h in the case of our long-term spin-labelling), which was moreover performed at a lower temperature, could be responsible for the variance between those results and our experiments. Both the low concentration of the modified groups and the narrow lines in the motionally narrowed e.p.r. spectra complicate the identification of spin labels subjected to very slow rotational diffusion in the early stage of the modification reaction.

CONCLUSIONS

We have found two types of spin label in swollen spin-labelled GMA–EDMA and ST–DVB copolymers. According to our interpretation, the spin labels subjected to rapid rotational diffusion belong to the modified groups localized in the polymer chains attached to the inner surface of the macroporous copolymers, whereas the spin labels subjected to very slow rotational diffusion belong to the modified groups localized inside the highly crosslinked globules. In the less highly crosslinked homogeneous copolymers, both types of spin label belong to the modified groups localized inside the beads, but the latter belongs to the modified groups localized in the more crosslinked domains forming the nuclei of the beads. Both the amount of modified groups and the relative concentrations of the spin labels subjected to rapid rotational diffusion are higher in the less highly crosslinked homogeneous copolymers than in the highly crosslinked macroporous GMA–EDMA copolymers. The same conclusion is valid for ST–DVB copolymers spin-labelled in hexane. The relative concentration of the modified groups localized in the polymer chains attached to the inner surface of both types of highly crosslinked macroporous copolymers increases with the specific surface area of these copolymers. Use of the e.p.r. method together with spin-labelling proved to be useful and efficient in the study of the reactivity, accessibility and type of reactive groups in polymer carriers, i.e. groups with which the molecules carrying catalytic or other functions are to be reacted.

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