An e.p.r. study of the effect of suspension polymerization conditions on the properties of glycidyl methacrylate–ethylene dimethacrylate particles

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Glycidyl methacrylate–ethylene dimethacrylate (GMA–EDMA) copolymer particles were synthesized by both conventional suspension polymerization and a two-step swelling technique. Oxirane groups in the products were modified by reaction with a mixture of 2,2,6,6-tetramethyl-4-aminopiperidine and its 1-oxyl paramagnetic derivative. The characteristics of the synthesized copolymer particles and the modified oxirane groups were studied with respect to the type of synthesis and the type and content of diluent.

(Keywords: glycidyl methacrylate–ethylene dimethacrylate copolymer; electron paramagnetic resonance; spin-labelled oxirane groups; uniform size particles)

INTRODUCTION

Homogeneous and macroporous GMA–EDMA copolymers are reactive polymers that are used as chromatographic sorbents, polymeric reagents and carriers of catalytically active species bound to them via oxirane groups. Concentration, accessibility and localization of these groups in the copolymer particles are important parameters in the characterization of such carriers. Amino derivatives of stable nitroxides may be reacted easily with the oxirane groups in these copolymers. The percentage of oxirane groups modified (spin-labelled) in this way (proportional to the ability of oxirane groups to react with a suitable low molecular weight compound), and the rotational mobility of the spin label, which may reflect the character and localization of a particular type of reactive groups, may be determined by means of e.p.r.

The occurrence of two types of spin label, mobile and immobilized, and hence the existence of two types of modified oxirane groups has been shown previously in studies of GMA–EDMA copolymers prepared by conventional suspension polymerization[1]. We have assumed that the mobile modified oxirane groups that prevail in homogeneous copolymer particles, occur in their lightly crosslinked domains, which are highly swollen and consequently characterized by a T_g lower than the measurement temperature. The immobilized groups in the homogeneous copolymer particles, which are assumed to be situated in their more crosslinked regions, were less swollen and consequently characterized by a higher T_g. The mobile and immobilized modified oxirane groups in the macroporous copolymer particles were supposed to occur inside highly crosslinked microspheres, which make up their inner structure, and in poly(glycidyl methacrylate) chains on the surface of these microspheres, respectively[2–4]. The concentration of the modified oxirane groups in the copolymers studied and their partitioning between these two types were found to depend on: the content of the crosslinking agent in the copolymer; the swelling capacity of the solvent used; and the temperature[1].

A new two-step swelling technique for synthesizing monodisperse copolymer particles has been described by Ugelstad *et al.*[5] This technique uses the latex (usually non-crosslinked) particles prepared in the first step, which are subsequently swollen in a monomer mixture and polymerized in the second step. The equilibrium swelling degree of these latex seeds, which is limited by the interfacial tension at the water–particle interface, may be increased considerably by adding a swelling agent. A low molecular weight ($MW = 200 - 500$) organic compound insoluble in water, e.g. 1-chlorododecane, is used as the swelling agent. Both homogeneous and macroporous copolymer particles of uniform diameter ranging from 2 μm to 100 μm may be prepared by this technique. The monodisperse character of the particles represents a great advantage of the two-step swelling technique, because it eliminates the elaborate fractionation necessary for obtaining a defined size fraction of particles prepared by the conventional suspension polymerization.

The properties of the copolymer particles synthesized by either of the techniques mentioned above may be changed or improved by adding a water-insoluble compound, the so-called diluent, to the monomer mixture which is inert but soluble in the monomer mixture. Macroporous copolymers may be obtained if the polymerization is carried out in the presence of both the diluent and sufficient content of crosslinking agent. Phase

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separation occurs during the polymerization, and permanent pores of various size are formed after extraction of the diluent and drying. The pore volume, pore size and its distribution, and the specific surface area of macroporous copolymers depend strongly on the type, thermodynamic quality and content of the diluent in the reaction mixture. In the case of homogeneous particles prepared by polymerization in the presence of a low concentration of crosslinking agent, the addition of a diluent stabilizes their spherical shape and prevents coalescence at low conversions (10–20%).

This paper presents a comparative study of the concentration and character of the oxirane groups in both homogeneous and macroporous GMA–EDMA copolymers, synthesized by either conventional suspension polymerization or the new two-step swelling technique. The effect of the diluent type and its concentration on the characteristics of oxirane groups is also studied.

EXPERIMENTAL

Synthesis of copolymers by conventional suspension polymerization

Monomer feed (200 ml) composed of: GMA; crosslinking agent (EDMA); initiator azobisisobutyronitrile (AIBN) (crystallized from ethanol, 1 wt% of monomers); inert diluent if required; and a 2% aqueous solution of poly(vinyl alcohol) (PVA, 600 ml), was purged with nitrogen and stirred (at 1000 rpm) in a 1 l SFS reactor at 343 K for 8 h. The resulting polymer particles were separated, purified by consecutive decantation in water (10 times), methanol (10 times), acetone (10 times) and ether (3 times), dried and fractionated according to their size using a Multiplex Zickzacksichter.

Synthesis of copolymers by two-step swelling technique

Latex seeds were prepared by emulsifier-free emulsion polymerization. A solution of NaCl (0.65 g) in redistilled water (700 ml) and styrene (85 g), purged with nitrogen (15 min), and a solution of potassium persulphate (0.5 g) in redistilled water (65 ml) added after heating the reaction mixture to 348 K, were stirred in a 1 l reactor with an anchor-type stirrer (300 rpm) for 24 h. The resulting monodisperse latex particles (1.4 μm in diameter) were purified by repeated centrifugation and redispersion in water. The particles (1 ml of particles in 10 ml of water) were preswollen in a microemulsion of 1-chlorododecane (3 ml) in a 0.25% aqueous sodium dodecyl sulphate solution (20 ml) at room temperature for 48 h, and subsequently allowed to swell in a microemulsion of monomer feed composed of: GMA; EDMA; diluent (if required); and dibenzoylperoxide initiator (0.5 wt% of monomers) in 0.25% aqueous solution of sodium dodecyl sulphate (90 ml) for 10 h. After adding a 4% aqueous solution of PVA (60 ml) and a 4% aqueous solution of poly(vinyl pyrrolidone) K 90 (30 ml) and purging the reaction mixture with nitrogen (20 min), suspension polymerization was allowed to proceed with stirring (100 rpm) at 343 K for 15 h. The monodisperse particles (6 μm in diameter) thus obtained were washed and dried in the same way as in the case of particles prepared by conventional suspension polymerization.

Modification of copolymers

Copolymers were swollen in sufficient volume of benzene with a solution of paramagnetic 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl (4-amino-TEMPO) in 2,2,6,6-tetramethyl-4-aminopiperidine (4-amino-TEMP), added in an amount which ensured a two-fold molar excess of amine groups with respect to the concentration of oxirane groups c_A in the particular copolymer. The optimum concentrations of 4-amino-TEMPO in 4-amino-TEMP were used to obtain sufficient concentrations of paramagnetic modified groups in the copolymers, and to prevent line broadening in the e.p.r. spectra due to spin–spin interaction. The reaction mixture was shaken in a water bath at 323 K for 8 h (or for 10, 20 or 60 min when the kinetics of the modification reaction was studied). Modified copolymers were separated on sintered glass, rinsed in benzene for 50 h to remove the non-reacted 4-amino-TEMPO, vacuum dried and transferred quantitatively to e.p.r. sample tubes. A sufficient amount of benzene was then added to the sample tubes, and the copolymers were allowed to swell at room temperature for at least 24 h. Details of this modification reaction were described earlier[1].

Characterization of copolymers

The specific surface area of the copolymers S_0 was determined by the nitrogen dynamic desorption method with a Quantasorb apparatus[6]. The benzene regain of copolymer particles, *BR*, was determined by centrifugation[7]. Infrared spectra of the copolymers were measured quantitatively on KBr pellets with a PE 577 spectrometer. The concentrations of the oxirane groups in these copolymers c_A^{IR} were determined using the 910 cm^{-1} band, corrected for non-specific contributions of EDMA (ref. 8). The concentrations of oxirane groups in the copolymers c_A^{Ti} were determined by direct titration with perchloric acid of a particular copolymer suspended in a solution of tetraethylammonium bromide in acetic acid[9].

E.p.r. measurements

E.p.r. spectra of the modified copolymers swollen in benzene were recorded with a JEOL-PE-3X spectrometer in quartz sample tubes (5 mm o.d.) at 333 K. The spin label concentration in the copolymers was determind by comparing the second integral of the copolymer spectrum with the second integral of the spectrum of the standard (benzene solution of diphenylpicrylhydrazyl). The concentrations of the modified oxirane groups in the copolymers c_M were calculated using the concentration of the spin label determined in the particular sample, taking into account the concentration of 4-amino-TEMPO in the 4-amino-TEMP solution used. The relative experimental error of these concentrations in various samples determined by e.p.r. was estimated to be 5%. The percentage of spin labels undergoing the rapid rotational diffusion r_{SL}^r was determined by subtracting the very slow motional spectrum from the spectrum of the sample in question, both measured at the same temperature, and comparing the second integrals of both components. Due to the complexity of this procedure, the estimated error in the determination of this percentage was found to increase to 10%. Additional particulars concerning the e.p.r. measurements and the analysis of e.p.r. spectra were given earlier[1].

RESULTS

Uniform spherical GMA-EDMA copolymer particles 6 μm in diameter (*Figure 1*) were prepared by the two-step swelling technique (Ugelstad's method). Conventional suspension polymerization supplied regular spherical particles with polydispersity in size depending on polymerization conditions. A size fraction 3-11 μm in diameter (comparable to the size of monodisperse particles) was used in most experiments. Within all four copolymer types (homogeneous conventional, HC; homogeneous uniform, HU; macroporous conventional, MC; and macroporous uniform, MU) samples were synthesized (*Table 1*), differing in the crosslinking agent content and in the type and content of the diluent used.

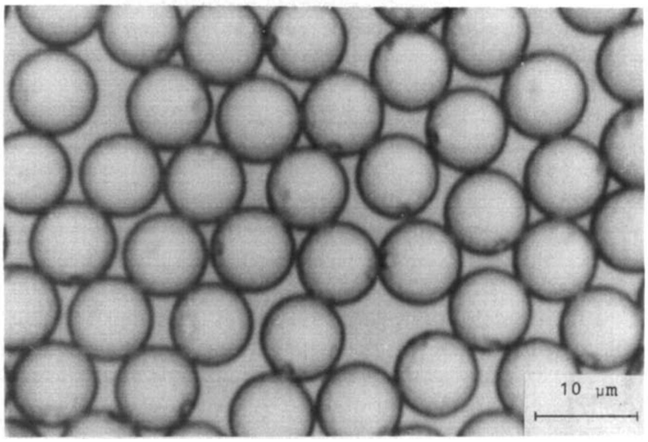

Figure 1 Uniform GMA-EDMA MU-4 copolymer particles prepared by the two-step swelling technique. The surface deformation of the particles is due to the incompatibility of the GMA-EDMA copolymer with latex seeds. Particulars concerning the morphology of the particles are discussed elsewhere[10]

Homogeneous copolymers are characterized by very small values of the specific surface area S_0 in the dry state, which increases slightly when diluents are added to the reaction mixture (*Table 1*). The benzene regain, *BR*, of the homogeneous copolymers varies only slightly. The macroporous copolymers exhibited a markedly higher specific surface area and benzene regain in comparison with the homogeneous ones. Moreover, for MU-2, MU-3 and MU-4 copolymers, both these parameters were found to depend strongly on the type of diluent (*Table 1*). Macroporous copolymers cannot be prepared without diluent.

The concentrations of oxirane groups in the copolymers (determined from infrared spectra and by the titration method, c_A^{IR} and c_A^{Ti}, respectively) and the corresponding respective percentages p_A^{IR} and p_A^{Ti} characterize the ability of oxirane groups to survive polymerization. Both methods provided similar concentrations of the surviving oxirane groups in homogeneous copolymers. On the other hand, the concentrations c_A^{IR} were higher than c_A^{Ti} by about 20% in the macroporous copolymers. This difference (which is almost comparable

Table 1 Characterization of copolymers

Copolymer		EDMA[e]	Diluent[f]		S_0[g]	BR[h]	c_A[i]	c_A^{IR}[j]	c_A^{Ti}[k]	c_M[m]	p_A^{IR}[n]	p_A^{Ti}[p]	p_M^{Ti}[r]	r_{SL}[s]
Type[a]	Sample	(wt%)	Type	Vol%	(m^2 g^{-1})	(ml g^{-1})	(mmol g^{-1})				(%)			
HC	1[c]	2.5	–	–	0	0.72	6.9	5.8	6.4	3.3	84	93	52	55
	2[b]	2.8	COL	20	2	0.79	6.8	6.2	6.1	2.4	91	90	39	58
	3[b]	0.55	–	–	1	0.96	7.0	6.8	6.8	2.2	97	97	32	77
	4[b]	0.55	DBP	49	1	0.83	7.0	6.9	6.5	2.0	99	93	31	75
	5[b]	0.55	COL	49	1	1.00	7.0	6.8	6.7	2.0	97	96	30	77
HU	1[b]	0.55	–	–	1	0.88	7.0	5.8	5.8	2.3	83	83	40	65
	2[b]	2.5	–	–	1	0.98	6.8	5.0	4.5	1.9	74	66	42	60
	3[b]	5.0	–	–	1	0.69	6.7	5.5	5.4	2.1	82	81	39	73
	4[b]	0.55	DBP	25	9	0.88	7.0	5.8	5.5	2.0	83	79	36	55
	5[b]	0.55	DBP	49	2.5	0.95	7.0	5.8	5.7	2.2	83	81	39	65
	6[b]	0.55	COL	49	1	0.87	7.0	5.5	5.7	1.7	79	81	30	60
MC	1[b]	40	COL	60	52	1.89	4.2	3.9	3.2	0.58	93	76	18	15
	2[d]	40	COL	60	82	1.34	4.2	4.2	3.6	0.83	100	86	22	13
MU	1[b]	40	DBP	49	20	1.21	4.2	3.6	2.6	0.42	86	62	16	10
	2[b]	40	DBP	60	31	3.22	4.2	3.6	2.5	0.30	86	60	12	15
	3[b]	40	CON	60	4	2.09	4.2	4.2	3.3	0.77	100	79	23	8
	4[b]	40	COL	60	79	2.16	4.2	3.9	3.2	0.72	93	76	22	13

[a] Types of copolymers specified in the text

[b] Particle diameter 6 μm

[c] Particle diameter 60-120 μm

[d] Particle diameter 200-600 μm

[e] Crosslinking agent, EDMA, content

[f] Diluents and their content in the polymerization feed: COL, cyclohexanol; DBP, dibutyl phthalate; CON, cyclohexanone

[g] Specific surface area

[h] Benzene regain

[i] Concentration of oxirane groups in the polymerization feed

[j] Concentration of oxirane groups in copolymers determined by i.r.

[k] Concentration of oxirane groups in copolymers determined by titration with $HClO_4$

[m] Concentration of modified oxirane groups in copolymer determined by e.p.r. after standard modification reaction for 8 h at 323 K

[n] Oxirane groups (%) surviving in copolymers determined by i.r., $p_A^{IR} = 100c_A^{IR}/c_A$

[p] Oxirane groups (%) surviving in copolymers determined by titration, $p_A^{Ti} = 100c_A^{Ti}/c_A$

[r] Modified oxirane groups (%) determined by e.p.r., $p_M^{Ti} = 100c_M/c_A^{Ti}$

[s] Mobile modified oxirane groups (%) determined by the numerical analysis of e.p.r. spectra of the copolymer particles taken in benzene solvent at 333 K

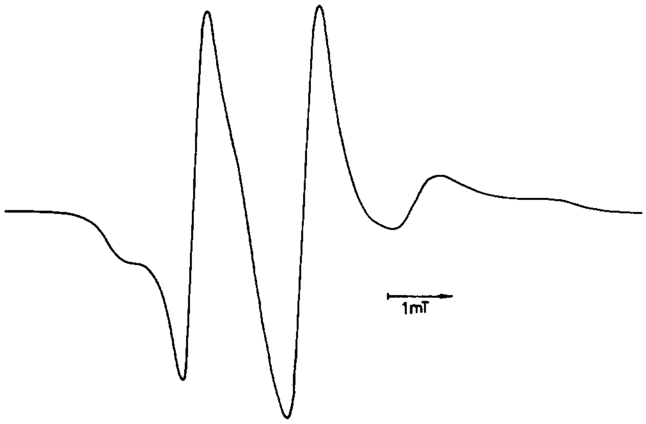

Figure 2 E.p.r. spectrum, measured at 333 K, of HU-1 copolymer particles swollen in benzene after standard modification reaction lasting 8 h at 323 K

to experimental error) may be explained by assuming that some of the oxirane groups in macroporous copolymers are inaccessible to reagents as small as HBr. The concentrations of modified oxirane groups c_M found by e.p.r. in the copolymers modified in a standard way (for 8 h) are substantially lower than c_A^{Ti}. This finding may be explained by either steric hindrance to diffusion of the bulky 4-amino-TEMPO molecules to the oxirane groups in the copolymer particles, or a repulsion effect of reacted amino groups preventing further penetration of 4-amino-TEMPO molecules into the microspheres. The percentage p_M^{Ti} characterizes the fraction of the oxirane groups accessible to 4-amino-TEMPO from the oxirane groups accessible to HBr, and may be considered to a certain approximation as a parameter characterizing the accessibility of catalytically active sites, which may be attached to the oxirane groups, to bulky molecules.

E.p.r. spectra of all copolymers measured at 333 K represent a superposition of a very slow motional spectrum and of the simple three-line motionally narrowed spectrum, which is characteristic of spin labels subjected to rapid rotational diffusion, as was described in our previous paper[1] (e.g. *Figure 2*). The character of the e.p.r. spectra excludes the existence of a continuous distribution of the spin label rotational mobilites. Consequently, the modified oxirane groups may be classified as mobile or immobilized according to the rotational mobilities of the attached spin labels, which we expect to be determined by localization of these groups in copolymer particles. The numerical analysis of the experimental e.p.r. spectra reported above does not supply reliable lineshapes, thus preventing us from studying possible variations between rotational dynamics of the spin labels carried by both the mobile and immobilized modified oxirane groups in various samples. The percentage r_{SL}^r (*Table 1*) characterizes the fraction of mobile modified oxirane groups in the copolymer particles swollen in benzene at 333 K. A temperature of 333 K has been shown to be suitable for distinguishing the two different rotational mobilities of the spin labels bound to the particles swollen in benzene.

Most homogeneous copolymers contained 0.55 wt% of crosslinking agent. The percentage of oxirane groups that had survived polymerization in the HC copolymer prepared without any diluent (HC-3) exceeded 95%; more than one-third of them were modified, and approximately 75% of modified oxirane groups were mobile (*Table 1*). A higher crosslinking agent concentration and the presence of diluents do not seem to affect markedly the characteristics of copolymers HC-2, HC-4 and HC-5 as compared to those of copolymer HC-3. A significantly higher particle diameter may be responsible for a slight change of copolymer HC-1 characteristics, compared to those of copolymer HC-3. The more complicated and lengthy preparation of HU copolymers may be responsible for the observed somewhat lower concentrations of surviving oxirane groups found in them, in comparison with the HC copolymers. Partial solvolysis of the oxirane groups may take place during polymerization as indicated by the lower intensity of the characteristic bands of oxirane groups at 910 cm^{-1} and 850 cm^{-1}, the appearance of bands of OH groups at 3450 cm^{-1}, and changes in the bands of aliphatic (2940 cm^{-1}) and carbonyl (1760 cm^{-1}) groups in the infrared spectra of these copolymers recorded after modification. As in the case of HC copolymers, the higher crosslinking agent concentration and the presence of diluents do not change significantly the characteristics of the HU copolymers, compared to those of copolymer HU-1, except for the above-mentioned increase of S_0 in copolymers HU-4 and HU-5 prepared using dibutyl phthalate as diluent.

All macroporous copolymers contain 40 wt% of crosslinking agent. They differ from homogeneous copolymers in a lower percentage of modified oxirane groups (which does not exceed 25%) and a lower percentage of mobile modified oxirane groups (which does not exceed 15%) (*Table 1*). No relevant effect of particle size was found when comparing the data characterizing copolymers MC-1 and MC-2. Somewhat higher concentrations of the surviving oxirane groups were found in the MU copolymers prepared using cyclohexanol and cyclohexanone as diluents than in the copolymers prepared using dibutyl phthalate.

The results of studies that characterize the kinetics of the modification reaction are shown in *Table 2*. The data indicate that the modification reaction of the HC-type copolymers is the slowest one. Only at most 8% of mobile and 30–65% of immobilized oxirane groups undergo modification during the first 60 min. The somewhat more rapid modification of HU-type copolymers yields about 20% of mobile and more than 70% of immobilized modified oxirane groups during the first 60 min. A completely reversed concentration ratio of mobile and immobilized oxirane groups modified during the first 60 min was found in macroporous copolymers. In particular, the majority of mobile and about 30% of immobilized oxirane groups in the MC- and MU-type copolymers were modified during this period.

DISCUSSION

The data presented in this paper show the principal differences between the characteristics of homogeneous and macroporous GMA–EDMA copolymer particles, and some additional minor dependences of these characteristics on the type of synthesis, diluent, and on particle size. As reported earlier[1], a much higher percentage of both the modified oxirane groups, p_M^{Ti}, and the mobile ones, r_{SL}^r, was found in the homogeneous copolymer particles after standard modification than in the macroporous particles. In accordance with a concept

Table 2 Dependence of the concentrations[a] and percentages[b] of mobile (c^m_M, p^m_M) and immobilized (c^i_M, p^i_M) modified oxirane groups determined in copolymers by e.p.r. on the duration of the modification reaction

Copolymer		Duration of reaction (min)													
		10				20				60				480	
Type[c]	Sample	c^m_M	p^m_M	c^i_M	p^i_M	c^m_M	p^m_M	c^i_M	p^i_M	c^m_M	p^m_M	c^i_M	p^i_M	c^m_M	c^i_M
HC	3	0.07	4	0.00	0	0.11	6	0.00	1	0.13	8	0.17	35	1.66	0.50
	4	0.03	2	0.04	8	0.06	4	0.06	13	0.06	4	0.33	65	1.54	0.51
	5	0.01	1	0.04	7	0.02	1	0.08	16	0.08	5	0.14	31	1.58	0.47
HU	1	0.03	2	0.08	10	0.06	4	0.17	20	0.42	27	0.57	71	1.50	0.81
	2	0.06	5	0.28	36	0.06	5	0.39	51	0.22	19	0.61	80	1.16	0.77
	3	0.04	3	0.15	26	0.07	5	0.21	37	0.28	18	0.44	78	1.54	0.57
	5	0.03	2	0.16	21	0.06	4	0.22	29	0.29	21	0.60	79	1.40	0.76
	6	0.01	1	0.18	27	0.04	4	0.33	50	0.25	25	0.58	88	1.00	0.66
MC	1	0.03	30	0.06	13	0.06	64	0.11	23	0.08	91	0.19	38	0.09	0.49
	2	0.04	34	0.05	7	0.04	40	0.07	9	0.08	78	0.19	26	0.11	0.72
MU	1	0.02	55	0.08	20	0.04	86	0.10	27	0.03	69	0.12	32	0.04	0.38
	2	0.01	31	0.05	18	0.02	36	0.05	21	0.02	51	0.10	38	0.05	0.26
	3	0.03	42	0.05	8	0.03	55	0.09	12	0.06	95	0.15	22	0.06	0.71
	4	0.05	51	0.09	15	0.05	53	0.13	21	0.08	82	0.23	37	0.09	0.63

[a] Concentrations c^m_M and c^i_M given in mmol g^{-1} were calculated using c_M and r^r_{SL} determined in the samples subjected to the modification reaction for the time period stated

[b] Percentages p^m_M and p^i_M characterize fractions of both mobile and immobilized modified oxirane groups reacted during the time period stated from the respective concentrations of oxirane groups modified during the reaction lasting 8 h

[c] Types of copolymers specified in the text and characterized in *Table 1*

concerning the structure of macroporous particles[2–4] we assume that in the GMA–EDMA macroporous copolymer particles, the immobilized modified oxirane groups are localized in microspheres composed of highly crosslinked copolymer which form their inner structure, and the mobile modified oxirane groups are localized in the polyGMA chains situated on the surface of these microspheres. This interpretation is supported by the following: first, the preferential modification of the rapidly accessible mobile oxirane groups during the first 60 min; and second, their low percentage after standard modification lasting 8 h. The concentration of the immobilized modified oxirane groups, which may be present in the bulk of highly crosslinked microspheres, should be higher than the concentration of the mobile groups in the macroporous copolymer particles after standard modification. Moreover, we believe that the mobile groups that represent a majority of modified oxirane groups in the homogeneous GMA–EDMA copolymer particles are localized in the lightly crosslinked highly swollen regions inside these particles, and that the immobilized groups are localized in the more crosslinked regions. The preferential modification of the immobilized oxirane groups in the homogeneous particles cannot be explained in a straightforward manner, and is subject to further research.

The data in *Table 1*, characterizing copolymers MC-1 and MC-2, indicate that both the percentage of modified oxirane groups and the fraction of mobile ones are independent of the size of the macroporous copolymer particles. This is, however, no longer true for the homogeneous copolymer particles, because the volume ratios of their less and more crosslinked domains may depend on the particle diameter, as suggested by a comparison between the data on copolymers HC-1 and HC-3 in *Table 1*. The data characterizing copolymers MU-2, MU-3 and MU-4 synthesized at the same content of the crosslinking agent confirm that neither the percentage of modified oxirane groups nor the fraction of mobile ones depends directly on the specific surface area. Both quantities are practically constant even when the specific surface area of these samples changes by a factor of 20 with varying type of diluent.

CONCLUSIONS

Homogeneous copolymers were found to contain a higher percentage of both modified and mobile oxirane groups than macroporous copolymers, indicating a higher accessibility of oxirane groups to 4-amino-TEMPO molecules. The percentage of modified oxirane groups depends on the content of crosslinking agent in both types of copolymers[1], but no direct dependence on the specific surface area was found in the macroporous copolymers. The percentage of mobile modified oxirane groups, which depends on the crosslinking agent content in the copolymers may, in addition, be influenced by the size of homogeneous copolymer particles. No such effect of particle size was found in the case of macroporous copolymers. The presence of diluents in the reaction mixture affects the specific surface area of both the HU and MU copolymer particles, and influences slightly the concentration of the surviving oxirane groups in MU copolymers. Practically no difference was found between the characteristics of copolymer particles prepared by conventional suspension polymerization and by the two-step swelling technique, respectively, except for a higher rate of the modification reaction in the HU copolymers and a somewhat lower concentration of surviving oxirane groups in comparison with the HC copolymers. The dependence of the concentration of mobile and immobilized modified oxirane groups on reaction time was found to agree with the assumed localization of these groups in the two types of copolymer particles.

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