Poly(ethylene dimethacrylate) particles with poly(glycidyl methacrylate) functionalities

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Macroporous particles, prepared by the suspension polymerization of ethylene dimethacrylate (EDMA), possessing high specific surface areas (558 $m^2 g^{-1}$) and pore volumes (6.9 $ml g^{-1}$), contain unreacted double bonds which are accessible for free radical polymerization. The amount of unreacted double bonds was determined by ^{13}C CP/MAS n.m.r. These bonds were used for the functionalization of poly(EDMA) particles by the solution grafting copolymerization of glycidyl methacrylate (GMA) into the pore structure of the particles. The poly(GMA) formed in this way is permanently attached to the particles. By this method composite particles, containing up to 77 wt% of oxirane groups (determined by i.r. spectroscopy), were obtained. However, the presence of grafted polymer in the pores leads to a decrease in both the pore volume and the specific surface area. The oxirane groups can be chemically modified, as evidenced by their reactions with hydrogen chloride and 2,2,6,6-tetramethyl-4-aminopiperidine.

(Keywords: macroporous polymer; ethylene dimethacrylate; graft copolymer)

INTRODUCTION

Functional polymer particles are widely used in preparative and analytical chemistry as ion exchange resins for water treatment and chromatography[1], and also as stationary phases in chiral separations[2]. In organic synthesis, they are used as reagents, catalysts or catalytic supports[3]. Recently, interest in the solution of many environmental problems has focused on the sorption of toxic pollutants. These applications require materials that possess high specific surface areas.

If porous polymeric particles of high specific surface area ($> 500 m^2 g^{-1}$) are to be obtained, a 'neat' crosslinking agent must be polymerized on its own, i.e. without the addition of a monovinylic monomer. A shortcoming of such particles is their low reactivity, which makes their chemical modification very difficult. Several techniques can be used to introduce functional groups into the porous, mechanically rigid polymer particles[4,5]. The anchoring of functional polymers to easily accessible double bonds in the particles, e.g. as obtained by the suspension polymerization of trimethylolpropane trimethacrylate[6] or 2-hydroxyethyl methacrylate with ethylene dimethacrylate (EDMA)[7], or styrene with divinylbenzene[8], represents such an approach.

This work reports on the synthesis of porous and mechanically rigid poly(EDMA) particles, prepared using various types and amounts of diluent in the polymerization feed. It also presents a grafting technique for introducing glycidyl methacrylate (GMA) functional groups into these particles. Subsequently, the reactive oxirane groups in the grafted GMA polymer may be substituted by various required functional groups in a similar way to that previously reported for styrene–divinylbenzene[9,10] or trimethylolpropane trimethacrylate[2] porous particles.

EXPERIMENTAL

Materials

The following materials were obtained from commercial sources: ethylene dimethacrylate (Ugilor), glycidyl methacrylate (Fluka), poly(*N*-vinyl-2-pyrrolidone) K 90 ($M_w = 360 000$; Fluka), 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (Aldrich), and 4-amino-2,2,6,6-tetramethylpiperidine (Janssen Chimica).

The monomers and solvents were freed from stabilizers and impurities by distillation, their purity was higher than 98% (g.c.). Azobisisobutyronitrile (AIBN, Ferak) was recrystallized from ethanol.

Instruments and methods

The pore volume was determined using the centrifuge cyclohexane regain method[11]. The specific surface area was determined from nitrogen adsorption/desorption isotherms obtained on a Quantasorb apparatus (Quantachrome, USA) and evaluated by using the BET equation. The texture of cross-sections of the particles was observed by using a scanning electron microscope (JEOL JSM 6400) after fixation on a supporting disc and sputter-coating with a gold layer of ~10 nm thickness. The amount of unreacted double bonds present in the

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particles was determined from high-resolution solid-state ^{13}C n.m.r. spectra, which were recorded on a Bruker MSL-200 spectrometer by using the cross-polarization/magic angle spinning (CP/MAS) technique[12] (contact time = 1.5 ms, pulse repetition time = 3 s, spinning frequency = 4 kHz, decoupling field in frequency units ~65 kHz, number of transients = 2400). Spectra were analysed by reference to the signal of the carbonyl carbon of glycine ($\delta = 176.0$ ppm) by using the method of sample replacement. Raman spectra were measured on a RA spectrometer (Coderg 200), equipped with an argon laser and connected on-line with a Tracor 400 spectral analyser. The content of the oxirane groups was determined from the 910 cm^{-1} peak area of the i.r. spectra, which were recorded on a Perkin–Elmer 577 spectrometer using KBr pellets[13], and also by the titration of unreacted hydrogen chloride, after an excess of the latter had been allowed to react with the oxirane groups. The values reported (see *Table 2*, below) represent an average of at least two i.r. or titrimetric determinations.

The e.p.r. spectra of the (2,2,6,6-tetramethylpiperidinyl)amino derivatives of poly(GMA-*g*-EDMA) that had been swollen in benzene were recorded with a JEOL-PE-3X spectrometer in quartz sample tubes (o.d. = 5 mm) at 60°C. The spin-label concentration in the copolymers was determined by comparing the second integral of the spectrum of the copolymer with that of the standard. The total concentrations of modified oxirane groups in the copolymers were calculated on the basis of the spin-label concentration for the particular sample, by taking into account the concentration of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl in the 4-amino-2,2,6,6-tetramethylpiperidine solution that were used. The relative experimental error in the e.p.r. determination of the spin labels was estimated to be 5%. The percentage of spin labels undergoing rapid rotational diffusion was determined by subtracting, numerically, the very-slow-motion spectrum from the spectrum of the sample in question, with both being measured at the same temperature, and then comparing the second integrals of the two components. Because of the complexity of this procedure, the estimated error in the determination of this spin-label percentage increased to 10%.

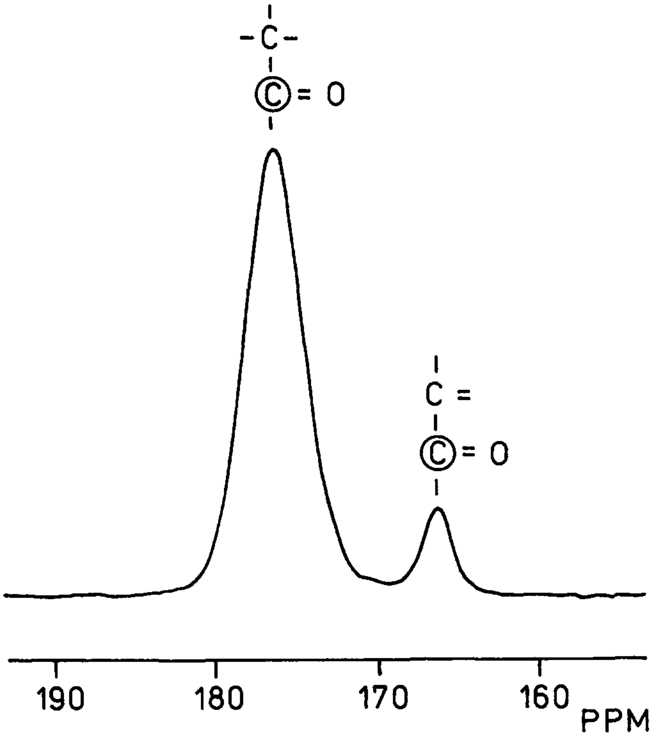


Figure 1 Part of the ^{13}C CP/MAS n.m.r. spectra of poly(EDMA) (sample 2 in *Table 1*) showing the peaks used for the determination of the double bond content

Preparation of poly(EDMA) particles

Spherical macroporous particles were prepared by the suspension polymerization of EDMA, in an aqueous dispersion in the presence of diluent (toluene, butyl acetate, 4-heptanone, dichlorethane or a mixture of cyclohexanol and 1-dodecanol) by using various ratios of EDMA/diluent. A 250 ml Büchi reactor vessel was charged with 25 ml of an organic phase consisting of EDMA, diluent, initiator (AIBN—1 wt% relative to the monomer) and 75 ml of a 1% aqueous solution of poly(*N*-vinyl-2-pyrrolidone) (PVP), which was used as a suspension stabilizer. The reaction mixture was purged with nitrogen and polymerized at 70°C for 8 h with stirring (400 rev min^{-1}). This process produced particles with diameters ranging from 30 to 700 μm. The polymerization product was filtered off, washed successively with water, methanol and acetone, and finally vacuum-dried.

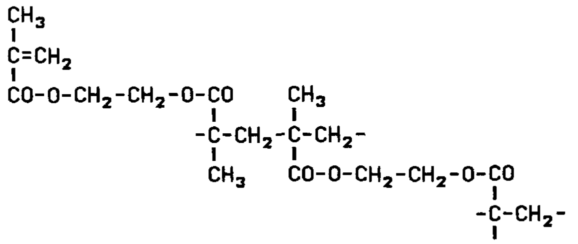
Some of the particles obtained were subjected to a post-polymerization treatment. This involved heating of the toluene-swollen particles in a sealed glass tube at 70°C for a period of 12 h.

Functionalization

Dry poly(EDMA) particles (1.45 g) were added to a mixture of toluene (4 ml), AIBN (83 mg) and GMA (6 ml) in a 100 ml glass vessel. The reaction mixture was degassed, purged with nitrogen and the vessel was then sealed. The particles were allowed to swell for 10 h and then polymerization was conducted at 70°C for 12 h. The polymerization was then stopped, the viscous slurry was extracted with acetone in a Soxhlet extractor for 25 h and the particles were finally vacuum-dried. The graft content was determined by weighing the sample before and after this treatment and is expressed as a percentage of the total graft copolymer weight. This grafting yield represents the weight percentage of GMA relative to the initial EDMA.

Double bond determination

The content of unreacted double bonds was determined[14] from the integral intensities of the 166.3 ppm band (assigned to the carbonyl carbon in the vicinity of a double bond, see *Scheme 1*) and of the 176.3 ppm band (assigned to other carbonyl carbons) in the ^{13}C CP/MAS n.m.r. spectra (*Figure 1*). For both the original poly(EDMA) samples and in the samples after grafting, the double bond content *DB* was determined as the molar ratio of the EDMA units containing unreacted double bonds to the total amount



Scheme 1

of EDMA units:

$$DB(\%) = 100(2+k)I_B/(I_A+I_B) \quad (1)$$

where I_A and I_B are the integral intensities of the 176.3 ppm and the 166.3 ppm bands, respectively, and k is the molar ratio of GMA units to EDMA units. Because of the large overlap of the GMA and EDMA bands in the ^{13}C CP/MAS n.m.r. spectra, the content of GMA in modified samples was determined independently i.e. from i.r. spectra.

The problem of quantitative analysis by ^{13}C CP/MAS n.m.r. spectra should be discussed briefly. In the case of model GMA–EDMA copolymers it was found[14,15] that the relaxation parameters involved in the cross-polarization dynamics of the 176.3 ppm band differ from those of the 166.3 ppm band. In such systems the relative band intensities $I(\tau)$, measured at particular contact times should be recalculated[16] to obtain directly comparable intensities I_0 by using equation (2):

$$I(\tau) = I_0(1 - T_{CH}/T_{1\rho}^{H})^{-1}[\exp(-\tau/T_{1\rho}^{H}) - \exp(-\tau/T_{CH})] \quad (2)$$

where T_{CH} is the relaxation time characterizing the effectivity of cross-polarization and $T_{1\rho}^{H}$ is the proton-rotating-frame relaxation time. Within experimental error, the same values for the T_{CH} and $T_{1\rho}^{H}$ parameters were observed with the previously studied GMA–EDMA copolymers[15] and with sample 2 in this study (see *Table 1* below). Therefore, the values $T_{CH} = 575\,\mu s$ and $T_{1\rho}^{H} = 8.7$ ms (176.3 ppm band), and $T_{CH} = 1150\,\mu s$ and $T_{1\rho}^{H} = 11.3$ ms (166.3 ppm band), determined as an average from the previously studied model GMA–EDMA copolymers[15] and from sample 2 in this work, were used for the intensity recalculations. This also involves a reasonable assumption that these parameters do not differ significantly in the studied samples. The values of the T_{CH} and $T_{1\rho}^{H}$ parameters were not determined individually for each sample because of the mainly low intensity of the 166.3 ppm band and the rather time-consuming procedures that are involved.

In CP/MAS spectra the band intensities are partially distributed in spinning side bands (SSB), particularly for chemical groups with a large chemical shift anisotropy (typically, carbonyl carbons), due to the modulation of the chemical shift interaction by rotation. In the case of the GMA–EDMA systems the integral intensity of the SSB at a spinning speed of 4 kHz amounts to ~23% for the 176.3 ppm band and to ~13% for the 166.3 ppm band, again as determined from the model compounds[15] and checked with sample 2 (as above). Therefore, the integral intensities of these two bands, directly determined from the spectra, were corrected for the SSB intensity and then recalculated with respect to the cross-polarization dynamics. These final values were used for the double bond content determination when using equation (1).

Table 1 Synthesis[a] and properties of poly(EDMA) particles

Sample	Diluent[b]		Double bonds[c]	S_{BET}	V_{CR}[d]
	Type	Vol%	(mol%)	($m^2\,g^{-1}$)	($ml\,g^{-1}$)
1	COL/DOL	80	15	375	3.93
2	DCHE	60	23	20	0.65
3	DCHE	80	15	379	2.23
4	HON	60	19	415	1.31
5	HON	80	14	509	3.40
6	BuOAc	60	18	435	1.73
7	BuOAc	80	11	530	2.72
8	BuOAc	85	9	415	3.94
9	T	60	21 (21[e])	394	1.23
10	T	80	16	558	2.22
11	T	85	17	394	4.19
12	T	95	16	258	6.91

[a] Polymerization feed, 25 ml of a mixture of EDMA and diluent, plus 1 wt% AIBN relative to EDMA; aqueous phase, 75 ml of 1% solution of PVP

[b] Diluents and contents in mixtures with EDMA: COL/DOL, cyclohexanol/1-dodecanol = 9/1 (vol/vol); DCHE, 1,2-dichlorethane; HON, 4-heptanone; BuOAc, butyl acetate and; T, toluene

[c] Determined by ^{13}C CP/MAS n.m.r. spectroscopy

[d] Pore volume determined by the cyclohexane regain method

[e] Determined by Raman spectroscopy

Because of the rather complicated procedures used for determination of the double bond content an independent check was considered to be necessary. Therefore, Raman spectra of some of the samples were recorded. The double bond content can be determined from the bands at 1730 and 1640 cm^{-1}, corresponding to the vibration of the C=O and C=C groups, respectively. The vibrations of the EDMA carbonyls in the vicinity of the unreacted double bonds, other EDMA carbonyl groups and, also in the grafted samples, GMA carbonyls, all contribute to the band at 1730 cm^{-1}. The extinction coefficient for the vibrations of the EDMA carbonyls in the vicinity of the unreacted double bonds must be generally considered to be different from those of the other carbonyls. Therefore, the Raman spectra were analysed quantitatively using three different extinction coefficients, i.e. for the vibrations of the C=O bonds in the vicinity of the C=C bonds (k_1), other C=O bonds (k_2) and C=C bonds (k_3). Therefore, we can write for the band intensities in the Raman spectra of the non-grafted samples:

$$I_{1640}/I_{1730} = k_3 y/(2k_2 x + k_2 y + k_1 y) \quad (3)$$

and for the samples after grafting

$$I_{1640}/I_{1730} = k_3 y/(2k_2 x + k_2 y + k_1 y + k_2 z) \quad (4)$$

where x, y and z are the molar concentrations of the 'built-in' EDMA units, the EDMA units with pendent double bonds, and the GMA units, respectively. The ratio of the third and first extinction coefficients was determined from the EDMA monomer measurement. The ratio of the second and first extinction coefficients was determined by using the n.m.r.-derived quantity for the non-grafted sample 2 and equation (3). The ratios of the extinction coefficients determined in this way were used in the double bond content determination by Raman spectroscopy.

Preparation of (2,2,6,6-tetramethylpiperidinyl)amino derivatives of poly(GMA-g-EDMA)

The method used has been described elsewhere[17].

RESULTS AND DISCUSSION

Characterization of particles

From the screening of various solvents used as diluents in the suspension polymerization of EDMA only those were chosen which could lead to the formation of products with high values of the specific surface area. The choice of diluents is also restricted by the necessary condition of complete miscibility with the monomers being used. Moreover, they must not be water-soluble, in order to prevent their extraction from the organic phase

Table 2 Properties of poly(GMA-*g*-EDMA) particles

Sample	Double bonds[a] (mol%)	S_{BET} ($m^2 g^{-1}$)	V_{CR}[b] ($ml\,g^{-1}$)	Grafting yield[c] (rel%)	Oxirane group concentration (wt%)					
					Graft content[d]	I.r.	Titration[e]		E.p.r.[f]	
							25 h	125 h	Total	Mobile
1	11	9	1.11	80	44	55	40	45	38	12
2	14(11[g])	0	0.01	–	–	42	7	21	1	0.2
3	<10	0	0.01	219	69	77	6	20	18	0.5
4	14	0	0.04	106	51	55	10	27	14	0
5	<10	8	0.65	111	53	56	45	53	39	13
6	14	1	0.05	140	58	65	9	22	12	0.2
7	<10	6	0.27	163	62	66	46	53	49	15
8	<10	11	0.87	133	57	68	50	53	46	18
9	16(16[g])	4	0.03	96	49	61	11	26	6	0.4
10	<10(8[g])	11	0.39	122	55	70	47	53	35	14
11	0	11	0.75	112	53	64	48	51	32	11
12	0	10	1.93	103	53	68	48	55	–	–

[a] Determined by ^{13}C CP/MAS n.m.r. spectroscopy

[b] Pore volume determined by the cyclohexane regain method

[c] Weight increase, after the reaction with GMA, related to the weight of the original poly(EDMA)

[d] Weight increase, related to the weight of poly(GMA-*g*-EDMA)

[e] Titration of unreacted HCl after an excess had been allowed to react with poly(GMA-*g*-EDMA) for periods of 25 and 125 h

[f] Based on the reaction with the mixture of 2,2,6,6-tetramethyl-4-aminopiperidine and its l-oxyl derivative

[g] Determined by Raman spectroscopy

in the course of the polymerization process. Boiling points represent another limiting factor, because the polymerizations usually proceed at 70°C. The various diluents used, as well as the properties of the poly(EDMA) spherical particles that are formed, are listed in *Table 1*; particle sizes ranged from 50 to 500 μm.

The amount of unreacted double bonds present in the particles varied between ~10 and ~20 mol% (see *Table 1*), values which were independent of the diluent used. The samples prepared in the presence of larger amounts of diluent usually contained smaller amounts of unreacted double bonds.

Pore volume and specific surface area

The pore volume of the material was determined using the cyclohexane regain method. Cyclohexane has the advantage that it is an inert, non-swelling solvent with regard to poly(EDMA). The pore volume and specific surface area of the poly(EDMA) particles were found to depend on the amount and composition of the diluent. Polymerization of EDMA in the presence of a good solvent for methacrylate polymers, such as toluene, butyl acetate or 4-heptanone, yielded particles with total pore volumes ranging from 1.3 to 6.9 $ml\,g^{-1}$ and with average specific surface areas over the range 260–558 $m^2 g^{-1}$. Such values for the specific surface area exceed the values obtained for the best commercially available methacrylate-based sorbents, such as Amberlite XAD 7 (450 $m^2 g^{-1}$) or XAD 8 (140 $m^2 g^{-1}$)[18]. As the solvent power of the diluent towards EDMA was reduced, the specific surface area of the dry particles decreased, e.g. with the dichlorethane/EDMA (3/2) diluent it was only 20 $m^2 g^{-1}$ (sample 2, *Table 1*).

The porosity of the dry poly(EDMA) particles corresponds quite well, in most cases, to the percentage of diluent in the polymerization feed. It follows from *Table 1* that the pore volume of the particles increased with an increase in the diluent percentage level. However, the specific surface areas of the particles prepared at the highest diluent levels (85 vol% in samples 8 and 11, and 95 vol% in sample 12) are reduced. In the phase diagram which plots the amount of crosslinking agent *versus* the amount of diluent[19] these particles are in the region of unstable porous structures, which is characteristic of high diluent contents. It follows that the diluent percentage in the polymerization feed which is equal to 80 vol% can be considered optimal for attaining maximum values of the specific surface area. Particles prepared with a higher content of diluent were already too 'open' in structure to sustain the capillary forces during the drying process. In this case, the dried product partly consisted of a fine powder of agglomerated microspheres.

Table 3 The effect of extraction time in acetone on the graft content in poly(EDMA) sample 7 (see *Table 1*) after reaction with GMA

Extraction time (h)	Grafting yield[a] (rel%)	Graft content (wt%)	
		Wt increase[b]	I.r.[c]
7	171	63	70
15	163	62	69
25	167	62	72
50	182	64	71
80	183	64	72

[a] Weight increase, after reaction with GMA, related to the weight of the original poly(EDMA)

[b] Weight increase, related to the weight of poly(GMA-*g*-EDMA)

[c] Concentration of oxirane groups determined by i.r. spectroscopy

Functionalization

The graft contents of GMA in the particles after functionalization and the corresponding grafting yields are presented in *Table 2*. After grafting, the particles were thoroughly extracted with acetone in order to remove any unreacted monomer or homopolymer. Both were already completely removed during the initial stages of the extraction process because the amount of grafted poly(GMA) does not decrease when the extraction time increases from 7 to 80 h (see *Table 3*). From *Table 2* it follows that a substantial amount of poly(GMA) was incorporated into the poly(EDMA) particles and remained there even after extensive extraction with acetone.

After the functionalization of poly(EDMA) particles the content of double bonds decreased in all of the samples that were studied. Almost no signs of pendent double bonds were observed after the functionalization of samples 11 and 12. The experimental error in the determination of the double bond content was estimated to be ~5% for the original poly(EDMA) samples. However, after grafting this error becomes higher due to the low signal-to-noise ratio of the 166.3 ppm band, particularly when compared to the increased intensity of the 176.3 ppm band caused by the grafting of GMA. After functionalization, the experimental error was estimated to be 5–10%, depending on the actual value of the double bond content. Therefore, values below 10% could not be determined with any reasonable accuracy. Although the change in double bond content of some samples was within the experimental error, they can be considered as real values, because they are systematically observed in all of the samples, including those containing higher contents of residual double bonds, determined with a relatively small experimental error (e.g. samples 2 and 9). This is further supported by the results from Raman spectroscopy. In *Tables 1* and *2*, the results of the double bond content determinations by Raman spectroscopy are given. These results are in good agreement with the n.m.r.-based results and confirm the decrease in the double bond content in the samples after functionalization.

In order to prove that double bonds were consumed in the grafting reaction, particles with 21 mol% of unreacted double bonds (sample 9) were subjected to heat treatment in toluene at 70°C, primarily to see if such treatment might reduce the unreacted double bond content. No effects of this treatment were observed within the limits of experimental error. It follows that no additional crosslinking, due to thermal polymerization of the unreacted double bonds, occurred in this case. Unreacted vicinal methacrylic units are probably unable to react for steric reasons. These results, together with the fact that neither poly(GMA) nor GMA could be extracted from the samples, provide strong evidence for the grafting mechanism of GMA polymerized in the poly(EDMA) particles. Therefore, the permanent attachment of poly(GMA) to the particles can be explained by copolymerization which involves the GMA and unreacted double bonds in the poly(EDMA) matrix.

Several factors, such as the structure and swelling capacity of the poly(EDMA) particles, the accessibility of the unreacted double bonds, and the concentration of GMA in the GMA/solvent mixture, may affect the grafting yield. This last factor was kept constant in our experiments. The data which are presented in *Table 4* illustrate that an extension of polymerization time from 1 to 24 h does not have any effect on the graft content. Hence, a polymerization time of 12 h, for all of the samples given in *Table 1*, is quite sufficient.

According to a quantitative analysis of the i.r. spectra, the functionalization procedure yielded reactive poly(EDMA)-based particles containing 42–77 wt% poly(GMA). If the spectrometrically determined content of the oxirane groups is compared with that calculated on the basis of the weight increase, a systematic difference becomes distinct, with the results from the i.r. analysis being higher on average, by ~9 wt%. The grafting yield obtained from the weight increase with respect to the initial poly(EDMA) varied between 80 and 219%, depending on the initial polymer being used. A maximum grafting yield of 219% was found with sample 3 in which up to 77 wt% of poly(GMA) (by i.r.) could be immobilized. On the other hand, the minimum grafting yield was observed with sample 2 (poly(EDMA) prepared with 60 vol% of dichlorethane). When discussing the reasons for the differences between the gravimetric and i.r. data, one should keep in mind that there is a lower accuracy with the spectrometric measurements.

Table 4 The effect on the graft content of the time of reaction of poly(EDMA) sample 7 (see *Table 1*) with GMA

Reaction time (h)	Grafting yield[a] (rel%)	Graft content (wt%)	
		Wt increase[b]	I.r.[c]
1	150	60	66
3	151	60	66
6	154	59	67
12	151	59	66
24	166	62	66

[a] Weight increase, after reaction with GMA, related to the weight of the original poly(EDMA)
[b] Weight increase, related to the weight of poly(GMA-*g*-EDMA)
[c] Concentration of oxirane groups determined by i.r. spectroscopy

Functionalization of the poly(EDMA) particles by the grafting of GMA resulted in a steep decrease in both the pore volume and the specific surface area (as shown in *Table 2*). This indicated that a large fraction of the pores was filled up with the functional polymer. The fact that the pores contained functional polymer is discussed in the following section.

Particle texture

The morphology of the products was studied by scanning electron microscopy (SEM). The particles are built up of rather open agglomerates of microspheres,

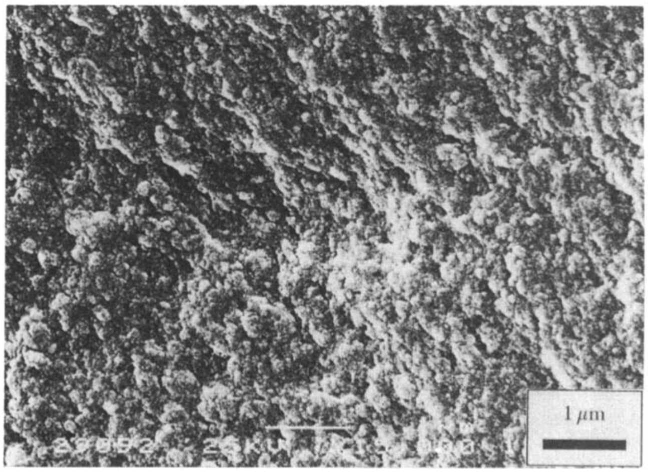


Figure 2 Scanning electron micrograph of the interior of poly(EDMA) (sample 2 in *Table 1*)

which are assumed to be composed of nodules. While the size of these microspheres varies between 30 and 400 nm, the size of their aggregates is approximately 10 times larger than this. The size and the separated structure of these aggregates and nodules is obviously closely related to the specific surface area, while the gaps between the aggregates correspond to the porosity, which evidently depends on the amount of diluent in the polymerization mixture. The size of the microspheres of the original poly(EDMA) seems to depend both on the type of diluent used and on its concentration (see *Figures 2* and *3*). The smallest microspheres (~30 nm in size) are observed in sample 2 (see *Table 1*), prepared with dichlorethane as the diluent (*Figure 2*). No difference in size of the microparticles was observed between samples prepared with butyl acetate and those prepared with toluene or 4-heptanone as diluents, providing that the diluent contents were about the same. The electron micrographs given in *Figures 3a–c* show that the amount of diluent in the polymerization mixture had a substantial effect on the particle structure, i.e. the size of the microspheres increases with the increasing percentage content of the diluent in the polymerization mixture. The largest microspheres (~400 nm in size) are formed in sample 12

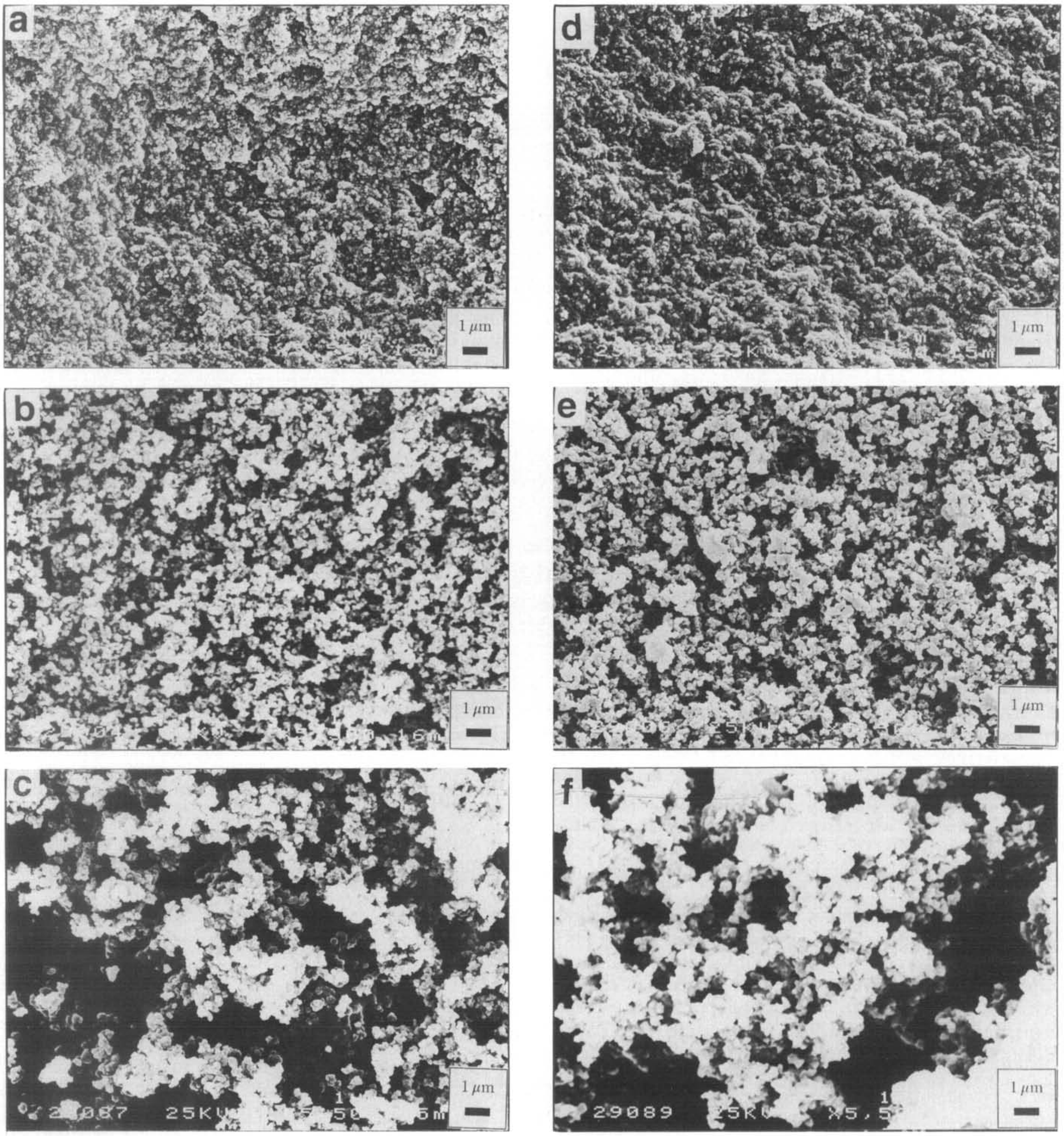


Figure 3 Scanning electron micrographs of the interior of various poly(EDMA) specimens: (a) sample 9, (b) sample 11 and (c) sample 12, before functionalization; (d) sample 9, (e) sample 11 and (f) sample 12, after functionalization. Sample details are given in *Table 1*

(*Table 1*), which was prepared with 95 wt% of toluene in the polymerization mixture (*Figure 3c*).

The comparison of *Figures 3b* and *3e* illustrates distinct differences in the morphology of the original sample prepared with 85 vol% of toluene or butyl acetate, and that of the same sample after functionalization. The microspherical structure of the sample after functionalization seems to be more compact. The same holds true for sample 12 (see *Table 1*), prepared with the highest amount of diluent (95 vol% of toluene) in the polymerization mixture (compare *Figures 3c* and *3f*). Moreover, the mechanical properties of the samples after functionalization seem to be improved when compared with those of the original specimens. Differences in the morphology of the original samples and the samples after functionalization are not quite so pronounced with poly(EDMA) particles prepared in the presence of lower levels of diluent (e.g. 60 vol% of either toluene, butyl acetate, dichlorethane, or 4-heptanone) in the polymerization mixture (compare *Figures 3a* and *3d*).

Reactivity of grafted oxirane groups

For catalytic or chromatographic applications oxirane groups must be reactive enough to be able to bind functional compounds of interest. The interesting question in this context is whether the oxirane groups in poly(GMA-*g*-EDMA) particles (determined by i.r. spectroscopy) are accessible to reactants. Their accessibility has been investigated using HCl (titration method) and 2,2,6,6-tetramethyl-4-aminopiperidines (modification reaction), representing reactants which differ considerably in size. The different yields observed in the reaction of the oxirane group with HCl and 2,2,6,6-tetramethyl-4-aminopiperidines should reflect the steric constraints imposed by the structure of the poly(EDMA) particles and/or the reactants.

I.r. spectrometry reveals all of the oxirane groups present in the particles, irrespective of their accessibility. Typically, the content of oxirane groups determined by i.r. is within the range 55–70 wt% (see *Table 2*). Only in a sample with low specific surface area (sample 2), was a somewhat lower value found; on the other hand, a somewhat higher value was found in sample 3, which also had a low specific surface area.

In contrast to i.r. spectrometry, titration determines only those groups that are accessible to the reactant. The time of reaction between the oxirane groups and HCl plays an important role in this determination; this holds true especially for GMA-grafted samples with pore volumes smaller than 0.3 ml g^{-1}. The oxirane group content found by the treatment of sample 3 with a dioxane solution of HCl for 25 h was as low as 6 wt% (see *Table 2*). A possible reason for this low conversion may be that the swelling equilibrium was not reached. However, if the same reaction was allowed to proceed for 125 h, a substantially higher content of oxirane groups was found. In samples prepared with $\geqslant$80 vol% of diluent (with the exception of sample 3), the groups detectable by reaction with HCl after 125 h correspond to $\sim$80% of those found by i.r. spectroscopy. This difference (which almost lies within the range of experimental error) may be explained by the inaccessibility of some of the oxirane groups, even to the small HCl molecules. In the remaining poly(GMA-*g*-EDMA) samples (2–4, 6 and 9), which possess pore volume values lower than 0.3 ml g^{-1}, the difference between the i.r. and the titrimetrically determined groups is larger (oxirane groups determined by titration constitute 30–50% of those found by i.r.). The low accessibility of the oxirane groups to HCl in these samples is probably due to their reduced porosity.

Even lower concentrations of oxirane groups were found by e.p.r. spectroscopy after modification reactions with the bulky 2,2,6,6-tetramethyl-4-aminopiperidine reagents (see *Table 2*). This finding may be explained by the steric hindrance to diffusion of the bulky aminopiperidine molecules towards the oxirane groups in the copolymer particles. A ratio of the oxirane groups accessible to aminopiperidines compared to those accessible to HCl may be considered, to a certain approximation, as representing a parameter characterizing the accessibility of catalytically active sites (which may be attached to the oxirane groups) to bulky molecules. These values are higher than 50% (with the exception of samples 2 and 4), which is substantially more than in the macroporous copolymers of glycidyl methacrylate and ethylene dimethacrylate that have been reported elsewhere[17,20,21]. This indicates a suprisingly high accessibility of the oxirane groups in these poly(GMA-*g*-EDMA) copolymers to 2,2,6,6-tetramethyl-4-aminopiperidine molecules, with no direct dependence on the type of the diluent used.

The oxirane groups accessible to aminopiperidines can be divided into two classes on the basis of the rotational mobility of the nitroxide spin-labels in the modified product[20]. The reason for the low percentage of mobile nitroxide groups may be explained by the fact that their rotational mobility is strongly restricted due to the steric hindrance imposed by both the pores containing the poly(GMA) grafts and the high crosslinking densities of the polymers which form the particles.

CONCLUSIONS

Highly crosslinked poly(EDMA) particles, differing in porosity and specific surface area, were prepared by the suspension polymerization of EDMA in the presence of various amounts of diluents (toluene, butyl acetate, 4-heptanone, dichlorethane, and cyclohexanol/1-dodecanol). The maximum specific surface area value that was obtained was 558 m^2 g^{-1}. The amount of unreacted double bonds in the particles was determined by ^{13}C CP/MAS n.m.r. spectroscopy. A reactive polymer was anchored to the particles by grafting GMA from a toluene solution which was imbibed in the pores of the particles. The grafting process significantly reduced both the pore volume and the specific surface area. Various functional groups may be introduced by the reaction of the oxirane groups in the graft copolymer with a suitable reactant, a procedure which can be used for the preparation of functional polymer particles. Such particles would be particularly useful for the preparation of solid catalysts, while other applications might also be found in chromatography.

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