The effect of polymeric porogen on the properties of macroporous poly(glycidyl methacrylate-*co*-ethylene dimethacrylate)

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Macroporous copolymers of glycidyl methacrylate with ethylene dimethacrylate [poly(GMA-*co*-EDMA)] were prepared using poly(methyl methacrylate) and polystyrene of various molecular weights as a porogen, either pure or in toluene solution. The polymeric porogen remains partly incorporated in the polymer beads. The effect of the polymeric porogen on the shape and size of the particles, porous structure and particle morphology has been studied. The fraction of the oxirane groups accessible to chemical reaction with variously bulky substrates was determined in the particles. Accessibility of the oxirane groups was characterized by the e.p.r. spin-label technique. Quaternary ammonium derivatives of poly(GMA-*co*-EDMA) exhibited high catalytic activity in nucleophilic substitution.

(Keywords: macroporous copolymer; glycidyl methacrylate; ethylene dimethacrylate; polymeric porogen; spin-label; catalytic activity; quaternary ammonium derivative)

INTRODUCTION

Macroporous polymers are used as ion exchangers, catalysts, reagents or separation media, both on a laboratory and on an industrial scale[1]. However, this wide range of applications also requires a wide variety of macroporous materials with 'tailor-made' properties for the given purpose. For example, packings are required for s.e.c. of oligomers and small molecules, which have small pores with a narrow pore size distribution[2]. On the other hand, protein separation, catalysts or polymeric reagents require materials with large-diameter pores, which ensure unrestricted diffusion of the dissolved substances into the polymer and back into the surrounding solution[3].

The present state of the art can offer two procedures for the preparation of macroporous polymers with large pores, differing in the porogenic agent employed[4]. In the first case, polymerization is carried out in the presence of a larger amount of non-solvating solvent, while in the second case the presence of a polymeric porogen or its solution is essential. While the use of low molecular weight porogens is common and has frequently been described in the literature[5–7], only a few studies have been devoted to polymeric porogens[8–10]. Even the mechanism of the formation of porous structure using a polymeric porogen has not yet been convincingly elucidated[11]. In addition, all the papers available in this field describe copolymers of styrene with divinylbenzene[8–11].

This paper reports on the effect of polymeric porogens on the properties of methacrylate-based polymers.

EXPERIMENTAL

Materials

The materials used included glycidyl methacrylate (GMA; Fluka), ethylene dimethacrylate (EDMA; Ugilor) and poly(*N*-vinyl-2-pyrrolidone) K 90 (PVP; $M_w = 360\,000$; Fluka). The poly(methyl methacrylate) used is referred to as PMMA-I (PCHZ Žilina, Czechoslovakia) and PMMA-II (prepared by group transfer polymerization[12]). The polystyrene is referred to as PS-I (prepared by block polymerization at 120°C for 17 h and 150°C for a further 6 h) and PS-II (prepared by block polymerization in the presence of 0.04 wt% t-dodecylmercaptan at 120°C for 17 h, 150°C for 1 h and 170°C for 67 h).

Table 1 lists the characteristics of the polymeric porogens employed. Sodium phenoxide was prepared from equivalent amounts of phenol and sodium ethoxide in ethanol and recrystallized from ethanol. The monomers and solvents were freed of stabilizers and impurities by distillation *in vacuo* and their purity was >98% (g.c.).

Instruments and methods

The polydispersities of PS and PMMA were determined by h.p.l.c. (Laboratorní přístroje, Czechoslovakia) in tetrahydrofuran using GP 109 and GP 103 (Hewlett Packard, USA) columns in tandem for PMMA

Table 1 Characterization of polymeric porogens

Porogen	$\bar{M}_n$ ($\times 10^{-4}$)	$\bar{M}_w$ ($\times 10^{-4}$)	Polydispersity
PMMA-I	36.4	135.0	3.72
PMMA-II	1.99	2.27	1.14
PS-I	8.75	17.5	2.0
PS-II	1.086	4.995	4.6

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and the PL gel 5 μm Mixed-C column (Polymer Laboratories, UK) for PS. The content of oxirane groups was determined from the i.r. spectra recorded using KBr pellets and a PE 577 spectrometer (Perkin-Elmer, USA) on the basis of the peak area at 910 cm^{-1} corrected for the non-specific contribution of EDMA. Simultaneously, the content of oxirane groups was determined by direct titration with perchloric acid of the particles suspended in an aqueous tetraethylammonium bromide solution[13].

The pore volume was determined from the cyclohexane regain[14] (V_{CR}) and from the mercury porosimetry results (V_{Hg}) obtained on a Carlo Erba Strumentazione porosimeter series 200 (Italy) apparatus. The mean pore size ($\bar{d}_{Hg}$) and pore size distribution were also determined by mercury porosimetry. The specific surface areas (S_{BET}) were determined by measuring the adsorption and desorption isotherms of nitrogen on a Quantasorb apparatus (Quantachrome, USA) and evaluated using the BET equation. Microphotographs of the internal structure of the particles were obtained using a JEOL JSM 35 (Japan) scanning electron microscope after coating the surface of broken particles with a vacuum-deposited gold film. The 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 60°C. The spin-label concentration in the copolymers was determined by comparing the second integral of the spectrum of the copolymer with the second integral of the spectrum of the standard. The total concentrations of the modified oxirane groups in the copolymers were calculated on the basis of the spin-label concentration for the particular sample, 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 used. The relative experimental error in these concentrations in various samples determined by e.p.r. was estimated to be 5%. The percentage of spin-labels undergoing rapid rotational diffusion was determined by numerically subtracting the very slow motion spectrum from the spectrum of the sample in question, both measured at the same temperature, and comparing the second integrals of the two components. Because of the complexity of this procedure, the estimated error in the determination of this percentage increased to 10%.

Gas chromatography was carried out on a 250 × 0.3 cm i.d. column packed with 5% SP 2100 on Inerton AW-DMCS, with nitrogen as carrier gas, using the CHROM 5 apparatus (Laboratorní přístroje, Czechoslovakia), with a flame-ionization detector.

*Preparation of macroporous poly(GMA-*co*-EDMA)*

A mixture of 8 ml GMA, 12 ml EDMA, 0.2 g (1% w/v) azobisisobutyronitrile (AIBN) and 30 ml of a toluene solution of polymeric porogen of various concentrations, together with a 2 wt% aqueous solution of PVP in a ratio of 1:3 were purged with nitrogen in the reactor for 10 min. The reaction mixture was stirred at 400 rev min^{-1}, first for 10 min at laboratory temperature, and then heated to 70°C for 8 h. The particles formed were washed by multiple decanting with water and methanol. The polymeric porogen was removed from the particles by extraction in a Soxhlet apparatus for 50 h, PS with benzene and PMMA with chloroform. The particles were then vacuum dried to constant weight and their size classified by sieving.

*Preparation of quaternary ammonium derivatives of poly(GMA-*co*-EDMA)*

A mixture of 1 g porous poly(GMA-*co*-EDMA) (particle size 400–600 μm) and 5 ml dibutylamine was heated under stirring to 80°C for 5 h and then left at room temperature for a further 24 h. The particles were separated, washed successively with methanol, water and methanol and were vacuum dried. The nitrogen content was 0.53–0.84 mmol g^{-1}.

The dried product was left to swell for 12 h in 2.5 ml nitromethane and then heated with 2.5 ml 1-bromobutane (a 25 molar excess) in a sealed glass ampoule at 120°C for 48 h. The particles were washed with 200 ml each of methanol, water, 0.1 M NaOH, and water and methanol and were then dried. The content of quaternary ammonium groups in the product was determined from its exchange capacity.

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

Beads of poly(GMA-*co*-EDMA) were swollen in benzene for 24 h. A mixture of 2,2,6,6-tetramethyl-4-aminopiperidine-1-oxyl and 2,2,6,6-tetramethyl-4-aminopiperidine was then added to obtain a two-fold molar excess of amino groups with respect to the concentration of oxirane groups in the copolymer determined by i.r. The optimum concentration of the nitroxide in the aminopiperidine was used to obtain a sufficient concentration of the spin-label for e.p.r. measurements and to prevent line broadening in the e.p.r. spectrum due to spin-spin interaction[15,16]. The reaction mixture was shaken at 50°C for 8 h. The beads were then separated on sintered glass, washed with benzene for 50 h to remove unreacted aminopiperidines, vacuum dried, quantitatively transferred into sample tubes and swollen in benzene at ambient temperature for 24 h.

*Catalytic activity of quaternary ammonium derivatives of poly(GMA-*co*-EDMA)*

A mixture of 1 mmol 1-bromooctane in 0.5 ml dioxane and 25 mg functionalized polymer beads was stirred with a magnetic stirrer at 75°C for 30 min. Then, 0.5 ml 0.5 M sodium phenoxide in dioxane was added under continuous stirring and samples of the liquid phase were analysed by g.l.c. every 10 min. The concentration of phenyl octyl ether was calculated using dodecane as an internal standard. The specific rate constants (k_s) were calculated from the second-order reaction rate constants (k_o):

$$k_s = k_o / c$$

where c is the content of active groups (mol l^{-1}) in the catalyst used.

RESULTS AND DISCUSSION

The aim of this paper was to evaluate the effect of the polymeric porogen, consisting of variously concentrated solutions of PMMA or PS in toluene, on the shape and size of the particles, their porosity and morphology, the accessibility of the oxirane groups and the catalytic activity of the quaternary ammonium derivatives. In addition to the concentration, molecular weight and polydispersity of the polymeric porogen were varied as well (*Table 1*).

Particle size and shape

Suspension polymerization usually yields particles characterized by a spherical shape (beads). Their size is given in a first approximation by the ratio of the amount of energy supplied to the liquid two-phase mixture used for dispersion of the organic phase to form as small droplets as possible and the interfacial tension that prevents dispersion. Simultaneously, the interfacial tension ensures a spherical shape of the droplets, i.e. a shape such that the given volume has the smallest possible surface area. This should also be true of the system containing the polymeric porogen added to the monomers. However, the dissolved polymer affects not only the interfacial tension, but also the viscosity of the droplets of the polymerization mixture prior to the polymerization, which is proportional to the molecular weight of the polymeric porogen. An increase in the viscosity makes it more difficult for the droplet to be broken down as a consequence of the shear tension produced by stirring. The droplet shape is elongated, but it is not divided into two smaller species. Simultaneously, the rate of shape changes in the droplets produced by the interfacial tension, i.e. the rate of assuming the optimal spherical shape, also decreases. Consequently, the polymerization does not result in beads, but rather, e.g., ellipsoids, as occurs in the use of PMMA-I (with a molecular weight over 10^6). When using different polymeric porogens, whose molecular weight is one to two orders of magnitude smaller, the viscosity of the liquid phase was not sufficiently great even at the highest concentrations to have a negative effect on the bead shape.

The viscosity of the dispersed polymerization mixture is also reflected in the size of the beads formed[17]. A higher content of polymeric porogen in this mixture at a constant stirring rate leads to the formation of larger particles, as documented in *Table 2*.

Polymeric porogen recovery

An important part of the process of preparation of porous beads using a polymeric porogen is the extraction of this polymer from the final product. Extraction is most effective with a Soxhlet apparatus, but is still tedious. For practical reasons, an extraction time of 50 h was used, but was found to be sufficient only for removal of PMMA-II, which has low polydispersity and low molecular weight. The amount of this porogen recovered was practically identical with the amount added to the polymerization mixture. PMMA-I, similarly to PS-I and PS-II, is not removed quantitatively, especially when present in larger amounts in the polymerization mixture (*Table 2*). This may be a consequence of both kinetic and chemical factors. The extraction rate will certainly be retarded if the chains of the polymeric porogen are entangled in the network chains. Similarly, the linear polymers may remain buried inside the microspheres constituting the basic morphological species in the macroporous beads. The recovery of the polymeric porogen will then be especially complicated for chains with higher molecular weight, which are certainly present in polymers with high polydispersity. If the porogen is held in the porous particles by only physical forces, it can be completely extracted, although this process can take a very long time.

Table 2 Synthesis[a] and properties of macroporous poly(GMA-*co*-EDMA)

	Polymeric porogen							
Code[b]	Type	Amount (g)	Particle size (μm)	Porogen recovery (%)	S_{BET} ($m^2\ g^{-1}$)	V_{CR} (ml g^{-1})	V_{Hg} (ml g^{-1})	$\bar{d}_{Hg}$ (nm)
T(0)[c]	–	–	360	–	102.0	1.00	0.89	13
M-I(1)	PMMA-I	0.26	450	100	40.9	1.28	1.18	570
M-I(2.5)	PMMA-I	0.65	570	83	15.6	1.47	1.31	580
MI-(5)	PMMA-I	1.3	630	77	2.5	0.99	1.03	540
M-I(10)	PMMA-I	2.6	670[d]	94	5.7	1.44	1.42	750
M-I(15)	PMMA-I	3.9	570[d]	93	6.9	1.12	–	–
M-I(100)	PMMA-I	2[e]	1030	71	1.6	0.05	0.12	–[f]
M-II(2)	PMMA-II	0.56	390	100	88.8	1.14	1.15	98
M-II(5)	PMMA-II	1.3	450	100	85.2	1.02	1.00	48
M-II(10)	PMMA-II	2.6	460	100	44.5	1.12	1.48	97
M-II(100)	PMMA-II	2[e]	420	100	15.6	0.18	0.23	–[f]
S-I(5)	PS-I	1.3	380	98	0.1	1.14	1.66	390
S-I(10)	PS-I	2.6	430	61	0.2	1.16	0.84	450
S-I(100)	PS-I	1.8[e]	970	63	1.7	0.19	0.34	–[f]
S-II(5)	PS-II	1.3	390	88	2.9	1.10	1.15	900
S-II(10)	PS-II	2.6	440	95	1.0	0.95	0.93	7500
S-II(15)	PS-II	3.9	480	62	0.2	1.08	1.36	7500
S-II(100)	PS-II	2[e]	1020	85	4.0	0.38	0.23	140

[a] Polymerization mixture: 8 ml GMA, 12 ml EDMA, 0.2 g AIBN, solution of polymeric porogen in 30 ml of toluene; aqueous phase: 150 ml 2% solution of PVP

[b] The numbers in parentheses refer to the per cent concentration of the polymeric porogen in toluene

[c] Toluene alone used as porogen

[d] Non-spherical particles

[e] No toluene used

[f] The distribution curve does not have a maximum

Unfortunately, the polymerization reaction can also involve the transfer of radicals to the polymeric porogen, so that it becomes part of the matrix of the final porous product. Grafting in principle excludes extraction of all the polymeric porogen. The probability of incorporation into the network again increases with increasing molecular weight and concentration in the batch and is also partly dependent on the type of polymer employed. By analogy with the transfer constants for methyl methacrylate to PMMA ($C_p = 1.5 \times 10^4$) and to PS ($C_p = 2.2 \times 10^4$) at 60°C[18], it can be concluded that the transfer constants of both the methacrylates used in this work will be similarly close and the degree of grafting of PMMA and PS, used as porogens, will also be similar.

Because of their very different chemical nature compared to the GMA–EDMA copolymer, the polystyrenes PS-I and PS-II can readily be detected in the i.r. spectrum on the basis of the characteristic aromatic band at 700 cm^{-1}.

Porous structure

The porous properties in the dry state can be described quantitatively on the basis of the specific surface area data obtained from the sorption of nitrogen, which covers particularly the micropores (<2 nm) and the mesopores (2–50 nm), and also on the basis of pore volume and pore size distribution, calculated from mercury porosimetry, describing particularly the meso- and macropores (>50 nm).

The dramatic consequences of the presence of a toluene solution of polystyrene porogen are evident from *Table 2*, documenting the decrease in the specific surface area by two orders of magnitude compared to toluene alone. The effect of a toluene solution of PMMA, especially of a monodisperse PMMA-II, with lower molecular weight, is less marked; however, the importance of the amount of polymer present in the batch is more evident. For example, the addition of a 1% solution of PMMA-I in toluene leads to a decrease in the specific surface area of the particles from 102 to 41 $m^2 g^{-1}$, addition of a 2.5% solution leads to a decrease to 16 $m^2 g^{-1}$ and a 5% solution produces a decrease to 3 $m^2 g^{-1}$; on the other hand, the addition of a 5% toluene solution of PS-I leads to a decrease in the specific surface area to <1 $m^2 g^{-1}$, i.e. well below the experimental error.

Similarly to the effect on the specific surface area, the presence of a toluene solution of polymeric porogen in the polymerization mixture leads to a shift in the pore size distribution curve to higher values. Where the mean pore size in poly(GMA-*co*-EDMA) prepared in the presence of toluene as porogen was equal to 13 nm, the addition of a 10% solution of PMMA-II in toluene leads to an increase to 100 nm, PMMA-I to 750 nm and PS-II to almost 8000 nm. *Figure 1* depicts the overlay of the typical distribution curves of porous particles prepared using various polymeric porogens.

These results clearly document the great effect of the type of polymeric porogen. The greater the difference in the chemical composition of the polymeric porogen and the polymeric product prepared, the larger are the pores formed. The effect of incompatibility appears here, leading to rapid separation of the two polymeric phases in the polymerization mixture. Crosslinking polymerization does not occur in the separated polymeric porogen phase and the original pool of separated polymeric porogen in the particles appears as a large pore. The sooner the separation occurs, determined not only by the chemical nature of the porogenic polymer, but also by its molecular weight and distribution, the larger are the pores formed. On the other hand, the addition of the polymer alone, dissolved directly in the polymerization mixture, does not have the required effect, the pore size distribution curves are rather anomalous and have no clear maximum.

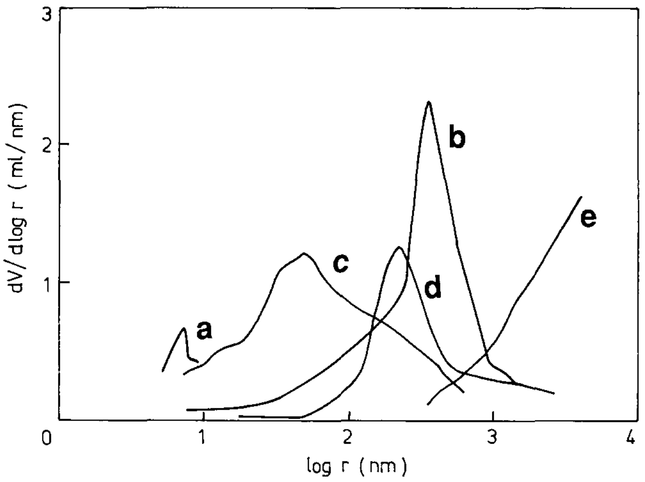

Figure 1 Pore size distribution of poly(GMA-*co*-EDMA) as determined by mercury porosimetry: (a) T(0), (b) M-I(10), (c) M-II(10), (d) S-I(10), (e) S-II(15)

Important information is also provided by measurement of the overall pore volume, either as the cyclohexane regain or by mercury porosimetry. The agreement of the results of these two measurements, which correspond to rather different intervals of measured values, is satisfactory within experimental error. Primarily, as expected, the pore volume is not very dependent on the type of polymeric porogen. The volume of the pores of the particles prepared is practically identical with the volume of porogens in the polymerization mixture and volume of any porogen does not change during the polymerization, assuming that it does not react with the polymer being formed, e.g. through grafting. Thus, the pore volume after removal of the porogen must represent the volume of the original porogen, as confirmed by the results. Porous polymers, prepared in the presence of 30 ml of toluene or toluene solution of polymer, thus corresponding to 60% of the volume of the polymerization mixture, have similar pore volumes of ~1 ml g^{-1}. The polymer itself, present in amounts of <10% of the polymerization mixture, leads to the formation of pores with a volume of ~0.2 ml g^{-1}.

Morphology of the porous particles

The best developed microspherical structure with regularly ordered microspheres with dimensions of ~200 nm can be observed for polymer particles prepared in the presence of toluene alone (*Figure 2a*). Poly(GMA-*co*-EDMA) prepared in the presence of a toluene solution of low molecular weight, monodisperse PMMA-II has a similar morphology, although the microspheres are less perfectly ordered in the particles. There are apparently greater spaces between the agglomerates, appearing as a shift in the mean pore size to values of ~100 nm (*Figure 2b*). The morphology of polymer particles prepared in the presence of a toluene solution of PMMA-I (*Figures 3a–c*) is completely different. The microspheres are less

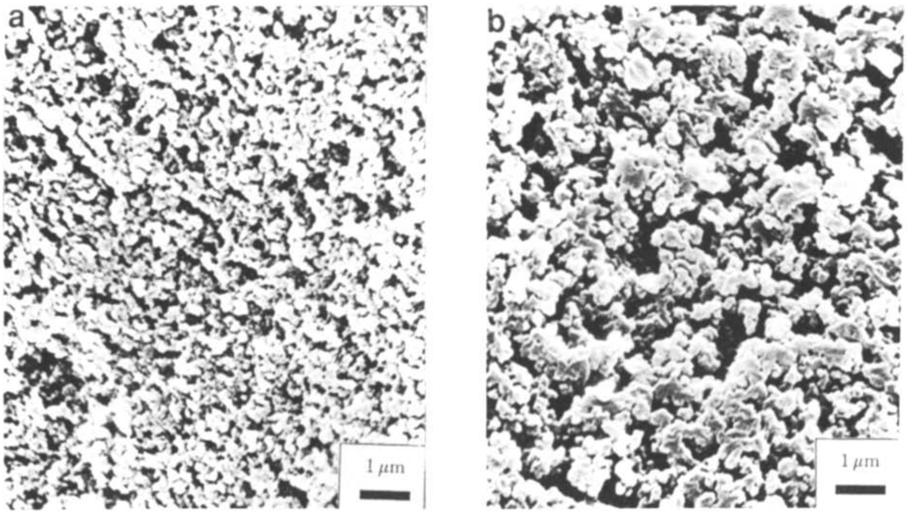

Figure 2 Scanning electron micrographs of poly(GMA-*co*-EDMA): (a) T(0); (b) M-II(10)

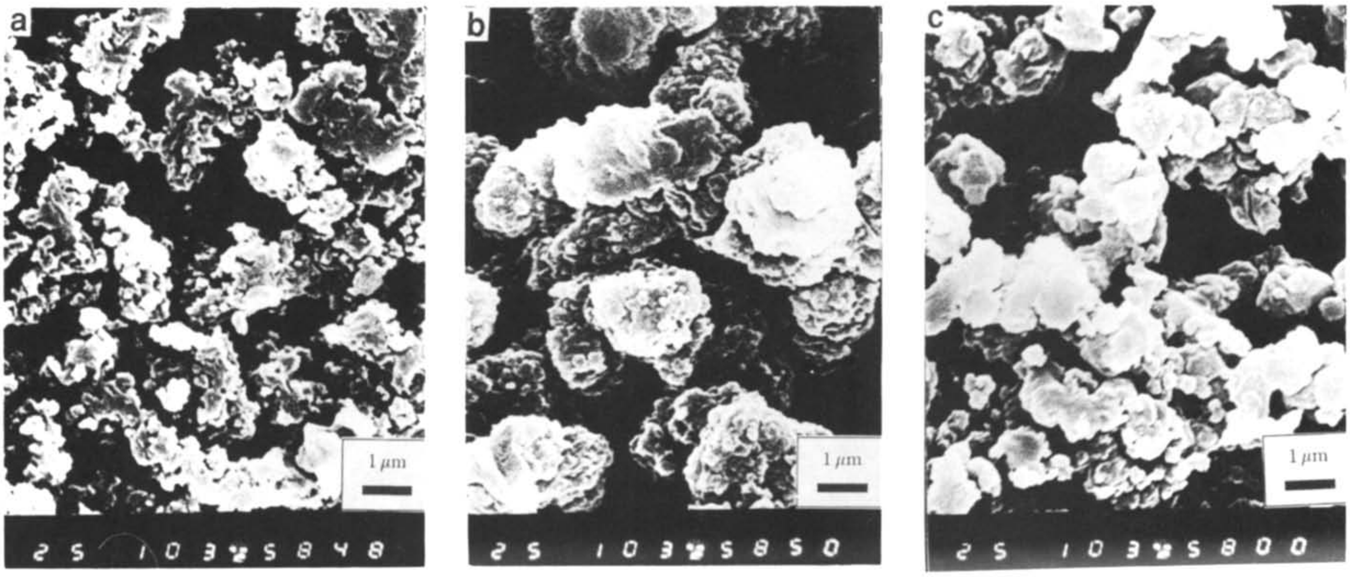

Figure 3 Scanning electron micrographs of poly(GMA-*co*-EDMA): (a) M-I(1); (b) M-I(2.5); (c) M-I(10)

readily observable and form poorly defined agglomerates with dimensions of >1 μm, which can hardly be termed microspheres. As the content of polymeric porogen increases, the morphology changes from a structure in which poorly defined microspheres are still apparent (1% solution of polymeric porogen in toluene, *Figure 3a*) to one consisting of large unstructured agglomerates (10% solution, *Figure 3c*). The morphological changes are even more marked when a toluene solution of PS, which differs in chemical structure from poly(GMA-*co*-EDMA) much more than PMMA, is used as a porogen (*Figures 4a–d*). The internal morphology of such porous beads consists of agglomerates with dimensions of up to several micrometres and includes holes of the same dimensions. The microspherical structure is not discernible. No significant dependence of morphology on the molecular weight of PS was observed in this case.

Poly(GMA-*co*-EDMA) prepared in the presence of the neat polymer as porogen has a completely different morphology. High molecular weight PMMA-I occupies a special position. Its dissolution in monomers never yielded a clear solution and the mixture was transferred to the reactor in heterogeneous form. A very heterogeneous product is then formed during the polymerization. Irregular opaque particles with a large size distribution can be clearly discerned under an optical microscope. Their morphology is shown in *Figure 5a*. These particles are easily spread out and have low mechanical strength. Some of these agglomerated beads have not only an opaque, porous part but also a glassy, transparent part. They can be recognized as large lens-shaped particles with glassy character, forming ~70% of the product, along with broken pieces of these larger species. Unusual inclusions of porous polymer can be discerned on the fracture surfaces of these particles (*Figure 5b*); magnification of these inclusions reveals a morphology exhibiting all the characteristics typical of porous poly(GMA-*co*-EDMA) prepared in the presence of low molecular weight PMMA-II with a narrow molecular weight distribution. The study of a large number of these large particles leads to the conclusion that they consist of porous particles formed by the

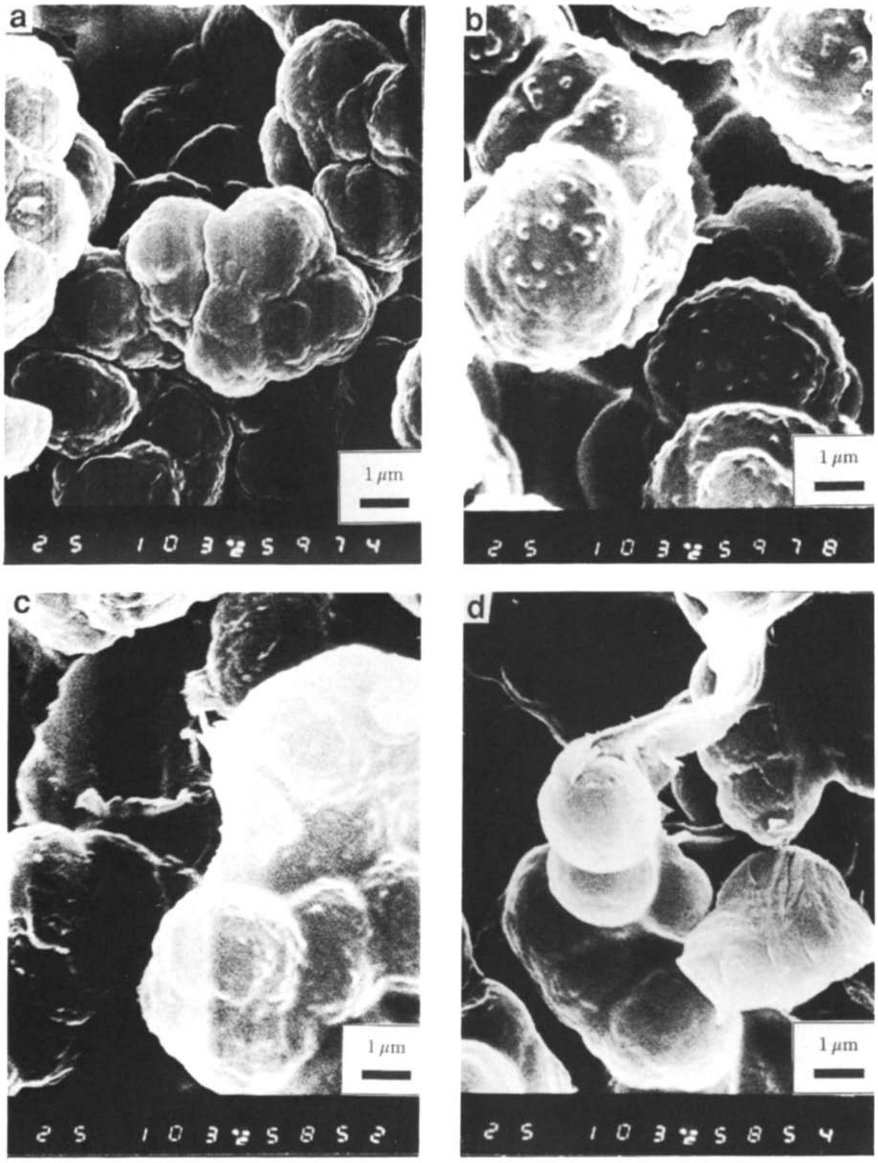

Figure 4 Scanning electron micrographs of poly(GMA-*co*-EDMA): (a) S-II(5); (b) S-II(15); (c) S-I(5); (d) S-I(10)

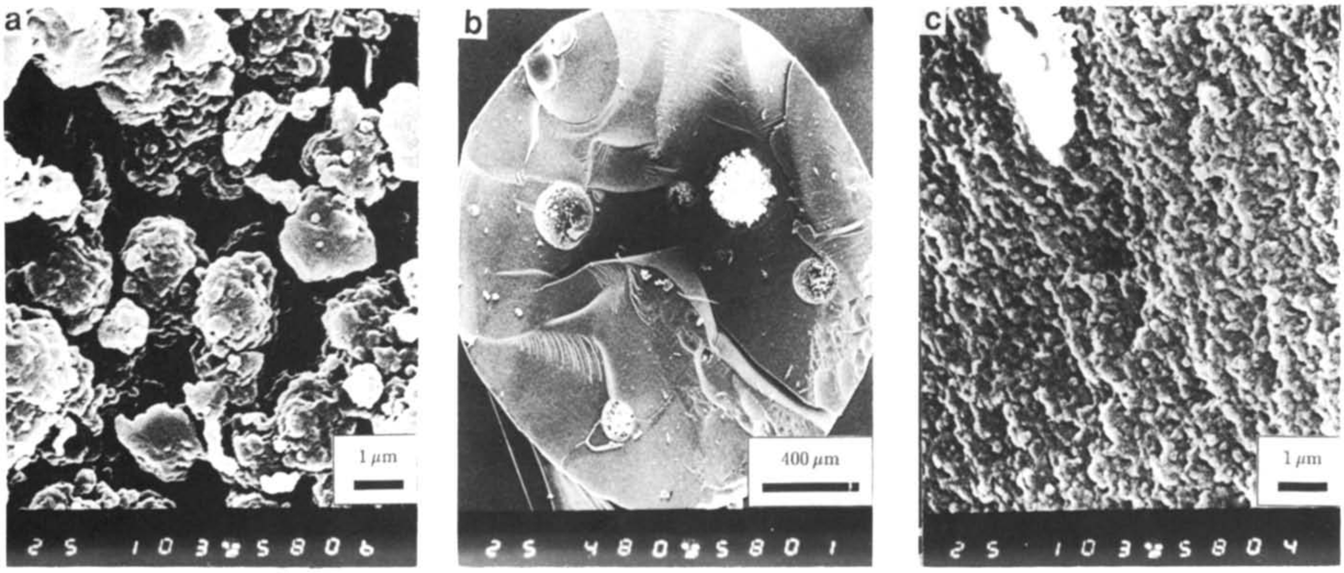

Figure 5 Scanning electron micrographs of poly(GMA-*co*-EDMA) M-I(100): (a) irregular particles; (b), (c) ellipsoidal particles

coalescence of fine porous particles and droplets in which polymerization has not yet occurred. It remains to explain why some particles or their agglomerates are porous while others are not, and why all the droplets do not polymerize at the same rate. The explanation probably lies in the distribution of the polymeric porogen among the individual particles as a consequence of the fact that complete dissolution was not possible.

In the presence of the polystyrene porogens PS-I and PS-II, dissolved in the monomers, the texture of the final polymer particles is similar to that formed in the presence of a toluene solution of the given polymer. As no solvent is present in the droplets of the organic phase, the crosslinked polymeric phase that separates during the polymerization is solvated only by the rapidly disappearing monomers and exhibits no tendency to agglomeration. Thus, the microspheres are smaller and more readily discernible.

Accessibility of the oxirane groups

All the polymerization experiments were carried out using an identical batch containing 40 vol% GMA and 60 vol% EDMA. If all the oxirane groups survive the polymerization, the resulting poly(GMA-*co*-EDMA) should contain 2.8 mmol oxirane groups per gram of sorbent regardless of the type of porogen used. I.r. spectroscopy reveals all the oxirane groups present in the particles, irrespective of their accessibility. Thus, the number of oxirane groups in beads prepared in the presence of a solution of polymeric porogen is close to the theoretical value (*Table 3*). Consequently, the oxirane groups do not undergo practically any reaction during the suspension polymerization. If toluene is not added to the polymerization mixture, but only neat polymeric porogen, then the contents of oxirane groups are much lower, probably as a consequence of the low porosity of the beads formed. The local GMA concentrations are then higher and the system is reminiscent of block polymerization, known to yield polyGMA crosslinked by interaction of oxirane groups[19]. In contrast to i.r. spectroscopy, titration determination of the oxirane groups in the beads reveals only those groups that are accessible for chemical reaction, i.e. those located on the immediate surface of the microspheres or in sufficiently swollen domains. The fraction of chemically detectable groups always corresponds to >50% of the theoretical amount (*Table 3*). An even lower fraction of the oxirane groups undergoes reaction with bulky 2,2,6,6-tetramethyl-4-aminopiperidines (*Table 3*). The effect of the accessibility of the oxirane groups is once again apparent.

Table 3 Oxirane group concentration in macroporous poly(GMA-*co*-EDMA) as found by various methods

Code	I.r. (mmol g^{-1})	Titration[a] (mmol g^{-1})	E.p.r.[b] Total (%)[c]	E.p.r.[b] Mobile (%)[c]
T(0)	2.81	1.62	23	6.5
M-I(1)	2.80	1.63	18	3.6
M-I(2.5)	2.81	1.47	19	2.9
M-I(5)	2.80	1.80	18	2.7
M-I(10)	2.81	1.70	12	1.6
M-I(100)	1.81	0.05	–	–
M-II(2)	2.69	1.75	23	5.0
M-II(5)	2.68	1.33	25	6.2
M-II(10)	2.62	1.68	27	6.7
M-II(100)	2.51	1.84	15	4.5
S-I(5)	2.73	2.16	11	3.0
S-I(10)	2.71	1.74	15	4.6
S-I(100)	1.99	1.47	13	2.3
S-II(5)	2.81	1.82	13	2.7
S-II(10)	2.80	1.37	15	2.5
S-II(15)	2.57	1.54	12	3.6
S-II(100)	2.21	1.79	12	2.0

[a] With $HClO_4$
[b] Based on the reaction with the mixture of 2,2,6,6-tetramethyl-4-aminopiperidine and its 1-oxyl derivative
[c] Based on titration figures

Table 4 Effect of reaction time on the percentage of mobile (p^m) and immobile (p^i) nitroxide groups in poly(GMA-*co*-EDMA)[a]

	Reaction time (min)					
	10		20		60	
Code	p^m	p^i	p^m	p^i	p^m	p^i
T(0)	7	5	14	8	40	22
M-I(5)	15	5	19	8	30	24
M-II(5)	14	7	11	10	29	22
S-I(5)	6	3	8	6	17	17
S-II(15)	13	5	14	9	28	24

[a] p^m and p^i are the fractions of the polymer nitroxide groups produced in the reaction with the mixture of 2,2,6,6-tetramethyl-4-aminopiperidine and its oxyl derivative (after 8 h reaction, $p^m = p^i = 100$)

The data given in *Table 3* indicate that both the porosity and specific surface area are important, but less so than could have been expected. While the specific surface area differs by more than two orders of magnitude for various beads, the differences in the contents of chemically determined oxirane groups are small and the values for titration-detected groups mostly vary in the range 1.6–1.8 mmol g^{-1}, while the content of groups determined by e.p.r. varies from 0.2 to 0.4 mmol g^{-1}. It should be noted that the content of oxirane groups reacting with 2,2,6,6-tetramethyl-4-aminopiperidines in poly(GMA-*co*-EDMA) prepared using PMMA-II as porogen is almost double that in beads prepared in the presence of PS. It would seem that the similar chemical composition of the methacrylate matrix and the porogen or the higher polarity of PMMA could be important here.

Location of the oxirane groups

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 transformation products. The percentage of mobile nitroxide groups in the particles swollen in benzene characterizes the groups whose rotational diffusion is not decreased by environmental steric effects. These groups are assumed to be localized in the polyGMA chains on the surface of the microspheres. The remainder of the nitroxide groups detected by e.p.r. (and thus also oxirane groups) are localized inside the microspheres composed of highly crosslinked polyGMA chains.

In all the macroporous polymers, the mobile nitroxide groups appear in the initial stages of the reaction with aminopiperidines (*Table 4*), corresponding to the expectation that aminopiperidines react preferentially with oxirane groups localized in chains on the microsphere surface. Only after all these groups have reacted do the less accessible groups in more highly crosslinked zones react.

Table 5 Catalytic activity of quaternary ammonium derivatives[a] of macroporous poly(GMA-*co*-EDMA) in the reaction of sodium phenoxide and 1-bromooctane in dioxane at 75°C

Code	N^+Bu_3 content[b] (mmol g^{-1})	k_s ($\times 10^4$) (l^2 mol^{-2} s^{-1})	Code	N^+Bu_3 content[b] (mmol g^{-1})	k_s ($\times 10^4$) (l^2 mol^{-2} s^{-1})
T(0)	0.75	21.1	M-II(10)	0.74	20.0
M-I(1)	0.76	28.2	M-II(100)	0.51	28.1
M-I(2.5)	0.86	7.5	S-I(5)	0.81	8.4
M-I(5)	0.78	9.0	S-II(5)	0.73	7.4
M-I(10)	0.86	0.9	S-II(10)	0.75	5.9
M-II(2)	0.82	25.6	S-II(15)	0.89	5.5
M-II(5)	0.64	14.0	S-II(100)	0.33	31.0

[a] See Experimental
[b] Determined from the exchange capacity

Catalytic activity

The catalytic activity of the heterogeneous catalyst is dependent on the mass transport and is a function of the catalyst particle size, pore size and specific surface area. The first two quantities are closely connected with the diffusion of the reagents to the active sites on the surface of the porous catalyst. The particle size determines the length of the diffusion flux inside the particles. The pore size can affect the diffusion when it is smaller than approximately five times the dimension of the diffusing substrate[20]. The specific surface area becomes decisive when only the sites on the surface of a solid matrix are catalytically active. As the surface area increases, the catalytic activity per unit catalyst weight also increases. Simultaneously, the specific surface area is known to be inversely proportional to the pore size. In other words, if the pore diameter decreases at constant total pore volume, then the number of pores increases, as does their surface area. As substrate diffusion may be restricted in small pores, the specific surface area cannot be increased without limit and the most active catalysts have an optimal pore diameter and specific surface area.

The catalytic activity of the quaternary ammonium polymer-supported catalysts was tested in the nucleophilic reaction of 1-bromooctane with sodium phenoxide (NaOPh) in dioxane[21]:

$$C_8H_{17}Br + NaOPh \xrightarrow[\text{Dioxane, 75°C}]{\text{Catalyst}} C_8H_{17}OPh + NaBr$$

The uncatalysed reaction is very slow[21]: after 22 h at 75°C, the yield of phenyl octyl ether is only 9%. The addition of the unfunctionalized porous polymer leads to a seven-fold increase in the reaction rate. The observed second-order rate constant is $k_0 = 9 \times 10^{-6}\ l\ mol^{-1}\ s^{-1}$. The positive effect of the polymer matrix can be attributed to the sorption of the reagents on the surface of porous particles, leading to an increase in their local concentration.

Table 5 gives a comparison of the specific rate constant (k_s) related to unit weight of polymer catalyst. As the concentrations of quaternary ammonium groups are similar in most catalysts, differences in the reaction kinetics can be attributed particularly to the accessibility of the catalytically active sites. It can be seen from *Table 5* that there is good correlation between the specific surface area and the specific rate constant. The highest reaction rates were achieved with quaternary ammonium polymers based on poly(GMA-*co*-EDMA) prepared in the presence of toluene solutions of PMMA. Polymers prepared in the presence of toluene solutions of PS have, in general, very low specific surface areas and are catalytically less active after modification. An unexpectedly high reaction rate was achieved in the presence of modified low porosity particles prepared in the presence of a polymeric porogen dissolved in the monomers without addition of toluene. The catalytically active groups are thus most probably localized close to the outer surface of the particles.

The most effective of the tested catalysts have an activity that is completely comparable with the polymer-supported quaternary ammonium catalysts[22]. The catalytic efficiency of the catalysts described in this work is about one-half that of benzyl triethylammonium chloride[23], with $k_s = 4.74 \times 10^{-3}\ l^{-2}\ mol^{-2}\ s^{-1}$.

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