Mechanism of phase-transfer catalysis using glycidyl methacrylate–ethylene dimethacrylate copolymers modified with tributylammonium groups in nucleophilic displacement reactions

Jiri Hradil and Frantisek Svec
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 16206 Prague 6, Czechoslovakia

and Jean M. J. Fréchet*
Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4
(Received 6 November 1986; revised 28 January 1987; accepted 1 February 1987)

The kinetics of phase-transfer catalysis using glycidyl methacrylate–ethylene dimethacrylate resins modified with pendant quaternary butylammonium groups have been studied. In contrast to expectations based on currently proposed mechanisms, the activity of polymeric catalysts is not improved through modifications that balance the hydrophilic and hydrophobic properties of the material. It is believed that much of the activity of the polymeric catalysts derives from the swelling of the polymer in both aqueous and organic phases. This enhances not only the rate of diffusion of both reagents to the vicinity of the catalytically active groups but also the ability of reactive groups to oscillate between the two phases. Both swelling and diffusion are restricted severely as the percentage of crosslinking is increased. This restriction is of particular importance with macroporous resins. Comparison of kinetic data obtained with various polymers suggests that gel polymers with very small bead sizes and therefore high external surface areas provide much higher reactivities than their macroporous counterparts.

(**Keywords:** phase-transfer catalysis; glycidyl methacrylate; ethylene dimethacrylate; nucleophilic displacement)

INTRODUCTION

Polymer-supported phase-transfer catalysis, also known as triphase catalysis, is a technique that has received considerable attention in recent years. Its main advantage is usually that associated with solid-phase reactions[1], namely the ease with which the catalyst can be separated from the reaction mixture after completion and also its potential for repeated use.

Numerous polymer-supported phase-transfer catalysts have been described in the literature; they include polymers with quaternary alkylammonium[2–6] or phosphonium salts[2,4–16], or with pendant crown ethers[2,10,17,18] or cryptands attached directly to the matrix or to a spacer arm. The mechanism of action of polymer-supported phase-transfer catalysts (PTC) has been the object of numerous studies; of particular interest is a discussion of the kinetics of the process by Tomoi and Ford[4,19]. Their study examined the problem of mass transfer in the medium surrounding the catalyst particles, the diffusion of the reactants through the particles and the rate of the reaction itself. Other studies have focused on the importance of variables such as rate of stirring, concentration and order of addition of the reactants, particle size, and other characteristics of the catalyst.

In almost all cases the phase-transfer catalysts that have been tested were derived from gel-type styrene–divinylbenzene copolymer beads containing only 1–2% of the crosslinking agent. A few notable exceptions involved the use of macroporous styrene–divinylbenzene copolymers[9,14,16] or, in one instance, a crosslinked quaternized polyvinylpyridine resin[20].

Since macroporous resins have structural features well distinguished from their gel-type counterparts, it appeared worth while to study them more extensively. In an earlier study[21,22], we described phase-transfer catalysis involving poly(ethylene glycol) moieties pendant from a macroporous glycidyl methacrylate–ethylene dimethacrylate resin (GMA–EDMA); this resin is potentially of great interest for a mechanistic study as it provides an environment that is much more polar than that afforded by the more usual styrene–divinylbenzene resins.

This study deals with the kinetics of phase-transfer catalysis using GMA–EDMA resins modified with pendant quaternary butylammonium groups and proposes a new mechanism of the triphase catalysis process.

EXPERIMENTAL

Preparation of GMA–EDMA based resins

Copolymers of GMA–EDMA are prepared[23] and modified[24] as described earlier. Macroporous polymers containing 60% and 70% of the glycidyl methacrylate are designated as G-60 and G-70 respectively, while a gel

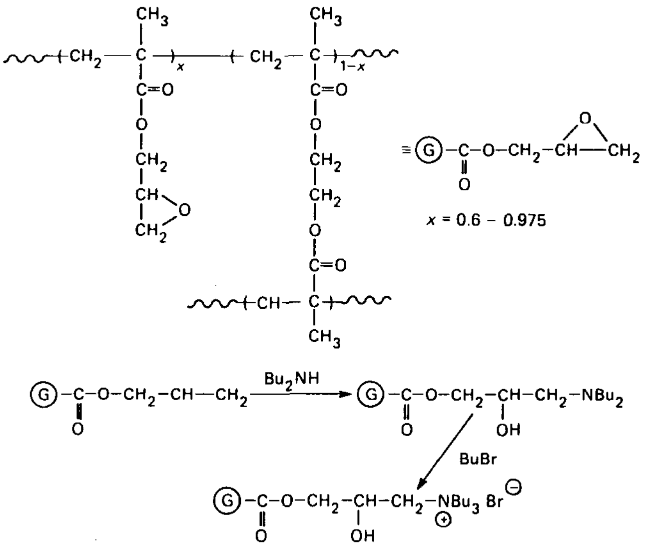
---

*Current address: Department of Chemistry, Cornell University, Ithaca, NY 14853, USA

0032–3861/87/091593–06$03.00

polymer with 97.5% GMA is designated as G-97.5; in all cases the remaining monomer is the crosslinking agent, ethylene dimethacrylate. The various polymers are modified in two successive steps (*Scheme 1*), amination and quaternization, to yield catalysts with various degrees of substitution (*Table 1*). A dispersion of 50 ml of the GMA–EDMA copolymer in 50 ml dibutylamine is stirred mechanically while heated to 80°C in a 250 ml flask for 5 h. The mixture is then left at room temperature for 24 h before being transferred to a column where the solid polymer is washed successively with methanol (500 ml), water (1 l) and methanol (500 ml) before being dried. The chemical modification of a typical G-60 resin leads to an aminated product that contains approximately 1.9 mmol of amino group per gram (*Table 1*, catalyst 2).

The quaternization reaction is carried out on a small scale using 2 g of the aminated resin 2 in a sealed glass ampoule containing 5 ml 1-bromobutane and 5 ml nitromethane. The ampoule is then heated to 120°C for four to 168 hours in the case of resin G-60 (40% crosslinking) to afford varying degrees of quaternization. Copolymers G-70 and G-97.5 are quaternized at 120°C under the same conditions using a 48 h reaction time.



Scheme 1

After opening the ampoule, the resin is washed with methanol (50 ml) and water (100 ml), then transformed into its hydroxide form using 0.1 M NaOH (30 ml). An aliquot of the resin is then taken for titration while the rest of the resin is washed with 0.1 M HCl (30 ml) to transform it into its chloride form or with 0.1 M KBr to transform it into the bromide form. In general, the bromide resin could be dried for storage without deleterious effect on its use in further experiments.

Preparation of styrene–divinylbenzene based resins

Monodisperse small particles of styrene (ST), divinylbenzene (DVB) and vinylbenzyl chloride (VBC) in 81:3:16 ratio are prepared by dispersion polymerization[25]. The particles are then quaternized using tributylamine as described earlier[3]. Nitrogen analysis indicates 2.32% N (1.65 mmol g^{-1}) while potentiometric analysis with an automatic Mettler titrator shows 1.6 mmol g^{-1} quaternary ammonium groups.

Experiments in phase-transfer catalysis

Reactions using the quaternized resins as PTC are carried out under rigorously controlled conditions using a thermostatted glass reactor with an overhead mechanical stirrer.

The catalyst (0.05–0.15 g) is suspended in a mixture of 0.8 ml toluene, 0.14 ml (0.8 mmol) 1-bromooctane and 0.03 ml 1,2-dichlorobenzene used as an internal g.l.c. standard[4]. After 5 min stirring at 560 rpm, 0.392 g NaCN (8 mmol) in 1.2 ml water is added. The addition of the aqueous phase marks the initial time for the kinetic measurements. As the various catalysts have a very high hydrophilicity, the reaction starts immediately and no induction period is seen in the kinetic curves (*Figure 1*). Aliquots of the organic phase are withdrawn at regular time intervals (10–30 min) for g.l.c. analysis; in all cases sampling was done after stopping the stirrer and letting the phases separate. The apparent rate constants k_{obs} are calculated for the loss of 1-bromooctane assuming pseudo-first-order kinetics:

$$k_{obs} = \frac{1}{t}(\ln c_0 - \ln c)$$

In this equation t is the time at which the concentration of 1-bromooctane is c and c_0 is the initial concentration

Table 1 Properties of phase-transfer catalysts based on glycidyl methacrylate–ethylene dimethacrylate copolymers bearing tributylammonium groups

Catalyst no.	Crosslinking (%)	Particle size (μm)	Active groups (mmol g^{-1})	Elemental analysis (%N)	Porosity (%)
1	40[a]	25–32	0.19	0.98	65
2[c]	40[a]	150–250	–[c]	2.66	68
3	40[a]	150–250	0.21	2.40	65
4	40[a]	150–250	0.30	2.26	64
5	40[a]	150–250	0.61	2.07	64
6	40[a]	150–250	0.79	2.97	63
7	40[a]	150–250	0.97	2.40	65
8	30[b]	150–250	0.74	2.27	43
9	2.5	150–300	1.52	4.99	68[d]
10	2.5	300–500	1.63	4.96	74[d]

[a] Specific surface area 60 $m^2 g^{-1}$, most frequent pore diameter 25 mm
[b] Specific surface area 28 $m^2 g^{-1}$, most frequent pore diameter 109 mm
[c] 1.90 mmol of dibutylamino groups per gram of polymer; this resin was used to prepare polymers 3–7
[d] Extent of swelling in water

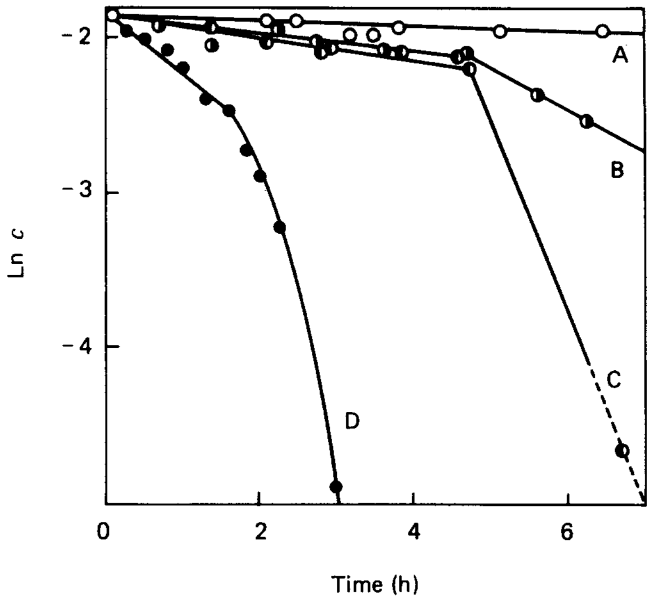


Figure 1 Decrease of octyl bromide concentration by nucleophilic displacement by cyanide anion at various temperatures in presence of polymer-supported phase-transfer catalysts: curve A, cat. 7, 60°C; curve B, cat. 7, 80°C; curve C, cat. 7, 90°C; curve D, cat. 9, 90°C. (Experimental conditions: 0.1 g catalyst; 0.14 ml bromooctane (0.8 mmol) in 0.8 ml toluene and 0.03 ml 1,2-dichlorobenzene; 0.392 g (8 mmol) NaCN in 1.2 ml H_2O; stirred at 560 rpm)

(mol l^{-1}). The following equation is used to normalize the results and express a rate constant k' for a uniform 1 mol of active groups in the catalyst:

$$k' = \frac{k_{obs}}{wa/V}$$

In this equation, w is the weight (g) of polymer used, a is the capacity of the polymer (mmol g^{-1}) and V is the volume of the liquid phase.

It should be noted that experimental evidence indicates that any unquaternized dibutylamino groups that may remain on the resin are not catalytically active but only contribute to the hydrophilicity of the catalyst (see *Table 2*, catalyst 2).

Solvent regain and distribution coefficients

Water and toluene regain in the polymeric catalysts are determined using the centrifugation technique[26]. A simultaneous regain of both solvents, which corresponds best to the conditions that prevail during the phase-transfer experiments, can be accomplished by the method of Regen[8]. The distribution coefficient of n-bromooctane between toluene and the polymer is determined for four different concentrations from the g.l.c. measurements of changes in its concentration in bulk solution after shaking the mixture for 24 h in the absence of reactant.

RESULTS AND DISCUSSION

An early view of the mechanism of triphase catalysis was proposed by Regen and coworkers[8] in 1980. According to this proposed mechanism, the ions that are pendant on the polymer backbone aggregate with the formation of ordered areas resembling inverse micelles within the polymer beads. The aqueous phase is located within these micelles and the reaction occurs at the phase boundary where the organic as well as the aqueous phases undergo microhomogenization. While this mechanism affords a good preliminary view of polymer-supported phase-transfer catalysis, it suffers from some significant shortcomings. For example, it would be expected that an increase in polymer capacity, and therefore in concentration of active groups on the catalyst, should raise the number of micelles and therefore also result in an increase in reaction rate; in practice this is not always the case[12,16]. Conversely, a decrease in polymer capacity should lead to a state where the reactive groups are so isolated from one another that formation of micelles becomes impossible; again this is not observed experimentally and the catalytic activity persists even at very low concentrations of catalytic sites. Perhaps more importantly, another weakness of the reverse-micelle theory is that it does not explain how the isolated micelles remain supplied with fresh salt; consideration of such mass transfer is important as the initial 'filling' of the micelles would not be sufficient to allow the reaction to proceed to high conversions.

An alternative mechanism, which does not require the formation of micelles and is much more similar to that believed to be operative for classical phase-transfer catalysis, has been proposed by Montanari and coworkers[27]. In classical two-phase systems, a true phase boundary exists through which anion transport is achieved. In a triphase system, the insoluble polymer is a third phase and therefore the normal planar phase boundary is transformed into a very small three-dimensional volume which incorporates the catalytic ends as well as the two liquid phases. The reaction only proceeds if the polymer-bound cation possesses a balance in hydrophobicity and hydrophilicity which allows it to interact equally well with organic and aqueous phases depending on the counterion. The first step of the process is one in which the polymer-bound cation exchanges its counterion for the anion that is to be involved in the reaction; this exchange takes place in the aqueous phase which provides the pool of reactive anions. In the next step of the process, the reaction itself occurs in non-aqueous medium and is slowed down considerably if the anion is hydrated; therefore the reaction will only proceed satisfactorily if the medium surrounding the initial ion pair is changed after the initial ion-exchange step. Even though some motions of the aqueous and organic phases about the polymer matrix can probably occur[28], it is also probable that motions of the solvated polymer chains themselves contribute to the change in hydrophobic character of the domain surrounding a reactive site. Such changes in polymer conformations should occur easily

Table 2 Amount of imbibed solvent in phase-transfer catalysts under biphase and triphase conditions at 20°C

Catalyst no.	Water ($g\ g^{-1}$)	Water + Toluene (1:1) ($g\ g^{-1}$)	Toluene ($g\ g^{-1}$)
G-60[a]	1.62	1.41 + 0.26	1.64
4	1.37	1.29 + 0.08	1.14
7	1.40	1.24 + 0.12	1.03
G-97.5[a]	0.80	0.68 + 0.17	0.07
9	1.60	1.14 + 0.10	0.46

[a] Non-modified glycidyl methacrylate–ethylene dimethacrylate resin (40% and 2.5% crosslinked, respectively)

Table 3 Preferential sorption of octyl bromide on polymer beads

Catalyst no.	Crosslinking (%)	Octyl bromide in resin (g g^{-1})	
		Calc.	Found[b]
7	40	0.18	0.39
9	2.5	0.07	0.22

[a] Calculated from amount of imbibed toluene (*Table 2*) assuming no preferential sorption. Initial concentration of octyl bromide in toluene is 0.188 g ml^{-1}

[b] Measured by g.l.c.

and amount essentially to oscillations of the reactive ionic groups getween the aqueous and organic phases.

In the case of polymeric phase-transfer catalysts that possess additional spacer chains between the polymer backbone and the reactive ionic groups, oscillations of this type are expected to be facilitated. The presence of such spacers has previously been shown to result in increased reaction rates[5,11,12,14,16,18]; yet the spacer should not be too long as it may hinder the exchange process and the passage from water into organic solvent or vice versa.

The inverse relationship between particle size and reaction rates has generally been observed for polymeric phase-transfer catalysts. This phenomenon may be due to diffusion effects or to improved transfer to substrate from bulk solution into the catalyst particles. However, it is difficult to prepare, by suspension polymerization, bead copolymers based on styrene–divinylbenzene with average particle size smaller than 3–5 μm. Much smaller particles[13] can be prepared by emulsion polymerization but these are difficult to use in triphase systems due to aggregation problems. An alternative to the use of independent submicrometre particles takes advantage of the special morphology of some macroporous polymers which are composed of a three-dimensional array of very small 'globules' with individual diameters of approximately 0.1 μm (ref. 29) separated from one another by large void spaces or 'macropores'. When compared to gel polymers, the macropores may actually contribute to facilitate diffusion of the liquid phases to the individual globules where the reactive centres are located. Diffusion through the bulk of an individual globule is somewhat similar to diffusion through a gel polymer bead with the same degree of crosslinking[9], though the distance to be covered within the individual particle is much shorter in the case of an individual globule located within a macroporous bead. In effect, the major part of the transport takes place in the macropores and might therefore be facilitated. In fact, it is this property of enhanced diffusion which provided much of the drive for the development of macroporous resins[9,15,16]. Yet actual rate measurements for model reactions have consistently shown that, in the case of macroporous resins, reactions proceed slower[30] than with gel polymers containing the same percentage of crosslinking, up to approximately 10% divinylbenzene (DVB) in the case of styrene–DVB copolymers. Further increases in the percentages of crosslinking are accompanied by steep decreases in reaction rates with essentially no reaction observed for highly crosslinked materials[9].

A possible explanation for this phenomenon which is observed for styrene–DVB resins is that the lipophilic character of the pores favours their penetration and filling by the organic phase with concomitant exclusion of the aqueous phase[9]; if this were indeed the case, then a solution to this problem would be to design and use more hydrophilic polymer matrices.

Copolymers of GMA–EDMA modified to incorporate quaternary ammonium groups can safely be considered to be more hydrophilic than similarly crosslinked styrene–DVB resins. This assumption is in fact confirmed by the simple water regain experiment summarized in *Table 2*. Although water regain data are useful when comparing the relative hydrophobicities of several polymers, they do not provide any information about the state that prevails within the polymer during its actual operation as a phase-transfer catalyst. This contrasts with swelling data for single-solvent reactions[2,4,5,8,11]. More accurate information can be obtained from measurements in water–organic solvent mixtures as shown in *Table 2*. A similar approach was followed by Regen[8] and Chau[31] for styrene–divinylbenzene based materials but the results obtained with the GMA–EDMA beads are very different from those of Regen. The GMA–EDMA resins are characterized by their very high hydrophilicity, which results in a water content within the beads far exceeding that of the organic solvent (toluene); nevertheless both phases are present inside the polymer (*Table 2*) and the fact that the aqueous phase often accounts for more than 90% of the total liquid within the beads should not be rate-limiting if the distribution coefficients are such that preferential sorption by the polymer occurs. Measurements of the distribution coefficients for octyl bromide between the catalysts 7 and 9 and the liquid organic phase ($D_g = 2.07$ and 1.19 ml g^{-1} respectively) show that preferential sorption of octyl bromide in the catalyst does indeed take place (*Table 3*). Catalyst 7, which has a capacity three times that of catalyst 4, retains 50% more organic phase (*Table 2*), yet both catalysts afford essentially the same reaction rate. This strongly suggests that diffusion of octyl bromide is not the rate-controling step, but that the reaction proceeds differently.

Figure 2 shows the effect of the capacity of the macroporous resin (millimoles of quaternary groups per gram of resin) on the rate constants *k* and *k'*. Curve A, which plots the change in *k* with capacity, is of particular

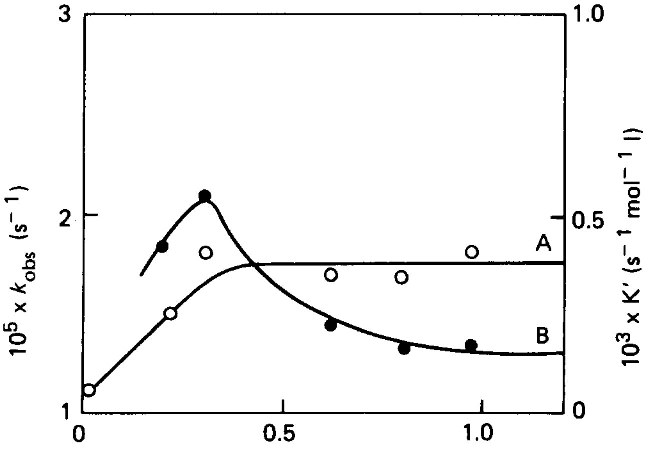


Figure 2 Effect of functionalization of macroporous polymer catalysts on the observed, *k* (curve A), and normalized, *k'* (curve B), reaction rate constants using the same weight of resin

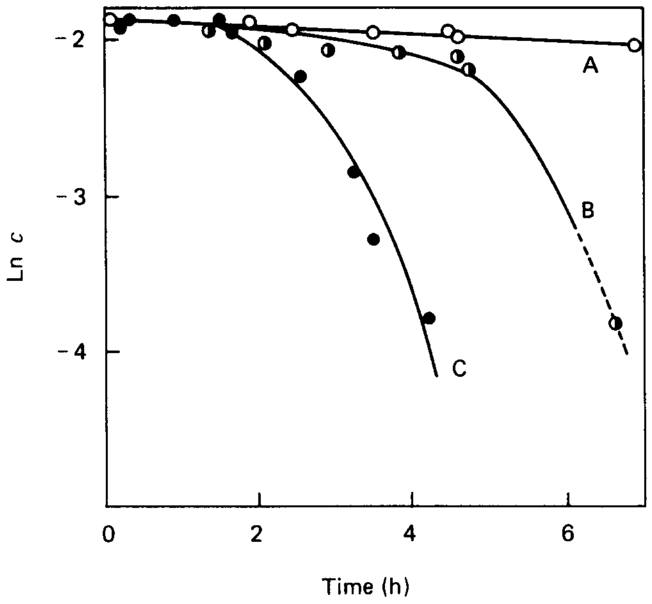


Figure 3 Effect of stirring rate on decrease of octyl bromide concentration: curve A, 220 rpm; curve B, 560 rpm; curve C, 690 rpm

interest as it shows an initial rate increase until a maximum is reached when the concentration of active groups reaches approximately 0.3 mmol g^{-1}. A further increase in capacity does not result in further acceleration of the reaction; in fact, the recalculated rate constant k' is seen to decrease. Such behaviour clearly suggests that not all functionalized sites possess equal reactivity and it can safely be speculated that the most active sites are those exposed on the surface of the globules. In contrast, the groups located within the globules are essentially unreactive owing to restricted diffusion within the highly crosslinked polymer mass. This assumption is in fact supported experimentally as a significant decrease in reaction rate is observed when a catalyst with a lower surface area is used. A comparative study between catalyst 6, which is crosslinked with 40% EDMA, and catalyst 8, which is crosslinked with only 30% EDMA and has both much larger pores (109 vs. 25 nm) and much lower surface area than 6 (28 vs. 60 m^2 g^{-1}), can be made. This study shows that both rate constants for resin 8 ($k_{obs} = 0.75 \times 10^{-5}$ s^{-1} and $k' = 0.082 \times 10^{-3}$ s^{-1}) have values only about half those obtained for 6 though both catalysts have essentially the same capacity and 8 has much larger pores. These observations appear to suggest that, in the case of macroreticular resins, the reaction is a surface reaction and therefore that surface area and not diffusion is the consideration of prime importance. This finding should not, however, be extrapolated to systems of widely differing polarities. A comparison of the rate constants k' obtained using the modified GMA–EDMA copolymers (recalculated to 1 mol l^{-1} of catalyst functional group) with the results obtained by others for tributylphosphonium derivatives of styrene–divinylbenzene gel[4,11,13,15] as well as macroporous[9,14,16] beads can easily be carried out. This shows that the styrene–divinylbenzene gels afford the highest reaction rates while our macroporous resins with increased hydrophilicity may be marginally better than their more hydrophobic styrene–divinylbenzene based counterparts. The activation energies calculated from standard measurements for catalysts based on G-60 and G-97.5 beads are 57 J mol^{-1} and 46 J mol^{-1} respectively, in a range which compares favourably to that for styrene–divinylbenzene based phosphonium salt phase-transfer catalysts[4,5].

As was previously emphasized, a major disadvantage of macroporous polymers is their low mechanical stability. The beads lack flexibility and are easily broken into fine particles when stirred; the fine particles are then difficult to handle and to filter[30]. *Figure 3* shows the change in concentration of octyl bromide with time at different stirring speeds using an overhead mechanical stirrer. As can be seen in this figure, even overhead stirring, if carried out at high speed, can lead to mechanical breakdown. In practice, this is observed as a sharp discontinuity in the conversion curve due to the formation of fine particles which contribute to a rate acceleration; *Table 4* confirms that resins with smaller particle sizes have a higher reactivity. With overhead stirring the stirring rate is important as little bead breakdown is observed at 220 rpm while extensive formation of fine particles is observed after a certain time at 690 rpm. In contrast, gel polymers have a very good mechanical stability and can easily withstand mechanical and even magnetic stirring without apparent degradation.

In view of the previously mentioned negligible swelling of globules inside the macroporous beads which results in serious diffusion and motion restrictions, it appeared desirable to test similar polymers with low degrees of crosslinking and therefore enhanced swelling ability. As can be seen in *Table 4* catalysts having a low degree of crosslinking have a significantly higher reactivity than highly crosslinked macroporous resins. This higher reactivity is best seen through a comparison of the values of the normalized reaction rate constant k for polymers that possess similar concentrations of reactive groups (see for example catalysts 7 and 9 in *Table 4*). As *Table 4* only reports *normalized* rate constants (observed rate constant divided by capacity) direct comparisons of polymers with different capacities are to be avoided (also note the variation of normalized data with capacity seen in *Figure 2*). However, even with low degrees of crosslinking, the activities of polymeric catalysts are still vastly inferior to those of soluble phase-transfer catalysts such as tetrabutylammonium bromide. *Table 4* also shows that further improvements in polymeric catalyst efficiency can be obtained through a combination of low crosslinking and low particle size (high *external* surface area). This is demonstrated by catalyst 11, which is composed of

Table 4 Effect of crosslinking and particle size on catalytic activity

Catalyst no.	Crosslinking (%)	Particle size (μm)	Active groups (mmol g^{-1})	k' (10^{-3} s^{-1} mol^{-1} l)
7	40	150–250	0.97	0.37
3	40	150–250	0.21	0.91
1	40	25–32	0.19	1.42
10	2.5	300–500	1.63	0.93
9	2.5	150–300	1.52	1.14
11[a]	3	2.7	1.60	10.61
TBAB[b]	–	–	3.11	18.06

[a] Based on copolymer styrene–vinylbenzyl chloride–divinylbenzene (81:16:3 mol%)

[b] Tetrabutylammonium bromide

particles with an average size of 2.7 μm, a figure that approaches the lower limit for most practical use. With catalyst 11 a 10-fold increase in activity can be directly tied to the presence of more reactive groups on the external surface of the beads.

CONCLUSIONS

The future of macroporous polymeric phase-transfer catalysts does not appear to be bright because of inherent limitations that have a deleterious effect on reaction kinetics. A major limitation is that imposed by the highly crosslinked nature of the resins. With highly crosslinked materials, the lack of swelling results in severe restrictions in the placement of aqueous and organic phases within the beads. This, in turn, affects the ability of catalytic sites to oscillate between the two liquid phases within the polymer matrix. It would appear that the rate-limiting step is not related to the reaction itself or to any diffusion of reagents in and out of the polymers but is related to the frequency of oscillation of reactive sites within the beads.

Better approaches to polymeric phase-transfer catalysts should therefore focus on loosely crosslinked micrometre-sized particles which we have shown to possess relatively high activities.

ACKNOWLEDGEMENTS

The authors acknowledge with thanks support from the Natural Sciences and Engineering Research Council of Canada, and of the Czechoslavak Academy of Sciences which facilitated travel for this collaborative project.

REFERENCES

1 Merrifield, R. B. *J. Am. Chem. Soc.* 1963, **85**, 2149
2 Cinquini, M., Colonna, S., Molinari, H., Montanari, F. and Tundo, P. *J. Chem. Soc., Chem. Commun.* 1976, 393
3 Regen, S. L. *J. Am. Chem. Soc.* 1976, **98**, 6270; *J. Org. Chem.* 1977, **42**, 875
4 Tomoi, M. and Ford, W. T. *J. Am. Chem. Soc.* 1981, **103**, 3821
5 Molinari, H., Montanari, F., Quici, S. and Tundo, P. *J. Am. Chem. Soc.* 1979, **101**, 3920
6 Regen, S. L., Hesh, J. C. K. and McLick, J. *J. Org. Chem.* 1979, **44**, 1961
7 Tundo, P. Synthesis 1978, 315
8 Ohtani, N., Wilkie, C. A., Nigam, A. and Regen, S. L. *Macromolecules* 1980, **14**, 516
9 Ford, W. T., Lee, J. and Tomoi, M. *Macromolecules* 1982, **15**, 1246
10 Blasius, E., Jansen, K. P., Klotz, H. and Toussaint, A. *Makromol. Chem.* 1982, **183**, 1401
11 Tomoi, M., Ogawa, E., Hosokawa, Y. and Kakiuchi, H. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 3015
12 Tomoi, M., Ogawa, E., Hosokawa, Y. and Kakiuchi, H. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 3421
13 Bernard, M., Ford, W. T. and Taylor, T. W. *Polym. Prep.* 1984, **25**, 170
14 Tomoi, M., Hosokawa, Y. and Kakiuchi, H. *Macromol. Chem., Rapid Commun.* 1983, **4**, 227
15 Tomoi, M., Nakamura, E., Hosokawa, Y. and Kakiuchi, H. *Makromol. Chem., Rapid Commun.* 1984, **5**, 281
16 Tomoi, M., Hosokawa, Y. and Kakiuchi, H. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**
17 Fukunishi, K., Czech, B. and Regen, S. L. *J. Org. Chem.* 1981, **46**, 1218
18 Montanari, F. and Tundo, P. *J. Org. Chem.* 1981, **46**, 2125
19 Ford, W. T. and Tomoi, M. *Adv. Polym. Sci.* 1984, 51
20 Serita, H., Ohtani, N. and Kimura, K. *Kobunshi Ronbunshu* 1978, **35**, 203; *Chem. Abstr.* 1979, **91**, 192388
21 Hradil, J. and Svec, F. *Polym. Bull.* 1983, **10**, 14
22 Hradil, J. and Svec, F. *Polym. Bull.* 1984, **11**, 159
23 Svec, F., Hradil, J., Coupek, J. and Kalal, J. *Angew. Makromol. Chem.* 1975, **48**, 135
24 Hradil, J. and Svec, F. *Polym. Bull.* 1985, **12**, 165
25 Almog, Y., Reich, S. and Levy, M. *Br. Polym. J.* 1982, 131
26 Stamberg, J. and Sevik, S. *Collect. Czech. Chem. Commun.* 1966, **31**, 1009
27 Montanari, F., Quici, S. and Tundo, P. *J. Org. Chem.* 1983, **48**, 199
28 Ford, W. T., Periyasamy, M. and Spivey, H. O. *Macromolecules* 1984, **17**, 2881
29 Pelzbauer, Z., Lukas, J., Svec, F. and Kalal, J. *J. Chromatogr.* 1979, **171**, 101
30 Fréchet, J. M. J. *Tetrahedron* 1981, **37**, 663
31 Telford, S., Schlunt, P. and Chau, P. C. *Macromolecules* 1986, **19**, 2435
32 Sherrington, D. C., 'Polymer-Supported Reactions in Organic Chemistry' (Eds. P. Hodge and C. E. Sherrington), Wiley, New York, 1980, p. 169
33 Regen, S. L. and Besse, J. J. *J. Am. Chem. Soc.* 1979, **101**, 4059