Polymer-supported quaternary onium salts catalysts prepared via concentrated emulsion polymerization

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A concentrated emulsion has a very large volume fraction of dispersed phase (0.74–0.95 in this case) and the appearance of a gel. Three procedures based on concentrated emulsion polymerization are suggested for the preparation of polymer-supported quaternary onium salts. (1) Concentrated emulsions of vinylbenzyl chloride (VBC) in water are subjected to polymerization. The polymer resins thus obtained are composed of particles in the micrometre range. A large fraction of the pendant benzyl–chloride groups present in the poly(VBC) particles are converted to onium chloride by a quaternization reaction. (2) A small amount of VBC is added to a partially polymerized concentrated emulsion of styrene (containing a crosslinking agent) in water under vigorous stirring. The system is subsequently subjected to complete polymerization. The obtained polystyrene–poly(VBC) is found to consist of particles having a non-uniform poly(VBC) shell that covers a crosslinked polystyrene core. This polymer is then subjected to a quaternization reaction in order to generate a polymer substrate with bound quaternary onium chloride. (3) A concentrated emulsion of styrene in an aqueous solution of a quaternary onium chloride monomer is prepared. The onium chloride adsorbed on the surface of the dispersed phase polymerizes simultaneously with styrene when the concentrated emulsion is subjected to polymerization. The polymer-supported onium salts thus prepared were used as phase transfer catalysts in the alkylation of isopropylidene malonates. The catalysts containing larger pores had a higher activity than those with a more compact structure. The catalyst prepared by the second approach had a greater catalytic activity than that prepared by the first approach. The catalyst prepared by the third procedure had a low activity because of the small amount of supported onium salt it contains.

(Keywords: polymerization; onium salts; catalysts)

INTRODUCTION

Insoluble polymer-supported phase transfer catalysts have been widely used in organic synthesis[1] because they can avoid the elimination of the catalyst with the product. However, when conventional methods are employed to prepare polymer-supported catalysts, the slow diffusion of reagents into and out of the polymer matrix often limits their utility. In order to avoid this difficulty, colloidal polymer supports[2,3] were prepared by conventional emulsion polymerization because of their high surface area per unit volume. In the present paper, polymer-supported phase transfer catalysts are prepared using the concentrated emulsion polymerization method[4]. In these emulsions, the volume fraction of the dispersed monomer (the internal phase ratio) exceeds the critical value of 0.74 (which represents the volume fraction of the most compact arrangement of spheres of equal radius) and can become as large as 0.99. When its volume fraction is sufficiently small, the continuous phase is present in the form of a network of thin films separating polyhedral droplets of the dispersed phase. In the present paper, the volume fraction of the dispersed phase is in the range of 0.74–0.95. The concentrated emulsions have the appearance of a gel and, as demonstrated in previous papers of this laboratory[5,6], can form at room temperature and remain stable at the polymerization temperature only if one of the phases is sufficiently hydrophobic and the other is sufficiently hydrophilic. The adsorption of an emulsifier, which is dissolved in the continuous phase, on the surface of the droplets ensures the stability of this gel-like emulsion.

In the present investigation, hydrophobic monomers are employed as the dispersed phase and water as the continuous phase. A suitable initiator is included in the dispersed phase and the continuous phase contains an appropriate emulsifier. The concentrated emulsion is prepared at room temperature, and its polymerization occurs by heating at 45°C. A porous polymer composed of a three-dimensional array of small particles with diameters in the micrometre range is thus obtained. The size of the polymer particles can be altered by changing the volume fraction of the dispersed phase and the nature of the dispersant. The main advantage of the concentrated emulsion method is that it allows the preparation of agglomerates of micrometre size particles of polymer-supported catalysts, which, in contrast to the individual particles produced by the conventional emulsion polymerization, can be more easily handled and recovered.

In this paper three procedures have been employed to prepare polymer-supported quaternary onium salts. (1)

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A concentrated emulsion of vinylbenzyl chloride (VBC) (containing a crosslinking agent) in water was prepared at room temperature. This emulsion was subjected to polymerization by heating at 45°C. The porous polymer thus obtained is brittle and can be easily ground to a fine powder. This powder was quaternized with a tertiary phosphine or amine in ethanol at 70–80°C. (2) Because of diffusional limitations, only the region near the surface of the particles is actively involved in the chemical reaction. For this reason the above technique was modified as follows: a concentrated emulsion of styrene (containing a crosslinking agent) in water was prepared at room temperature and was subjected to mild polymerization at 45°C. Then, a small amount of VBC was added under vigorous stirring and the system was subjected to complete polymerization. This was followed by a quaternization reaction by treating the polymer powder with a tertiary phosphine or amine in ethanol at 70–80°C. (3) A quaternary phosphonium or ammonium salt monomer was dissolved in the continuous aqueous phase, from which a part was adsorbed because of its hydrophobic moiety upon the surface of the droplets of styrene (containing a crosslinked agent) of a concentrated emulsion. These adsorbed molecules polymerize with styrene when the concentrated emulsion is subjected through heating to polymerization.

The polymer-supported quaternary onium salts thus prepared were employed as phase transfer catalysts in an alkylation reaction. The emphasis in this paper is on the relations among the preparation method, the morphology of the prepared polymers and the phase transfer catalytic activities.

EXPERIMENTAL

Reagents

Styrene (Aldrich), divinylbenzene (DVB) (45% 3- and 4-ethylvinylbenzene) (Aldrich) and VBC (Kodak) were used after distillation under reduced pressure. The dispersant, sodium dodecylsulphate (SDS) (Aldrich) was used as received. The initiator, azobis(isobutyronitrile) (AIBN) (Alfa) was recrystallized from methanol. Tributylphosphine (TBP) (99%, Aldrich), triethylphosphine (TEP) (99%, Aldrich), tributylamine (TBA) (99%, Aldrich), triethylamine (TEA) (99%, Aldrich), trimethylamine (TMA) (99%, Aldrich), ethyl bromoacetate (98%, Aldrich), 2,2-dimethyl-1,3-dioxane-4,6-dione (98%, Aldrich), potassium chromate (98%, A.C.S. Aldrich), silver nitrate (>99%, A.C.S. Aldrich) and various solvents were used without further purification.

Synthesis of the quaternary phosphonium and ammonium salts

Tributylvinylbenzyl phosphonium chloride (VBPC) was synthesized using the method reported by Nishikubo *et al.*[7], and tributylvinylbenzyl ammonium chloride (VBAC) was synthesized as suggested by Brandstrom and Ldamm[8]. Triethylvinylbenzyl phosphonium chloride (VEPC) was prepared from a mixture of VBC (6.7 g, 44 mmol) and TEP (5 g, 42 mmol) dissolved in 10 ml absolute ethyl alcohol. After the solution was heated at 40°C under a nitrogen atmosphere for 6 days, the ethyl alcohol was evaporated using an aspirator. The white solid that remained in the flask was recrystallized twice by dissolving it in chloroform and precipitating subsequently with ethyl ether. A final drying in vacuum yielded 5.5 g of pure product. Triethylvinylbenzyl ammonium chloride (VEAC) was synthesized using the method indicated by Fieser[9]. Trimethylvinylbenzyl ammonium chloride (VMAC) was prepared as follows: TMA (4.0 g, 68.3 mmol) was introduced at −5°C into 10 ml acetonitrile containing 11.04 g (70 mmol) of VBC. The white solid that precipitated after 5 min was recrystallized by dissolving in acetone, and precipitating with ethyl ether. A final drying in vacuum yielded 9.5 g (66 mol%) of VMAC.

Preparation of poly(VBC)

The poly(VBC) crosslinked with 1.3 mol% DVB was prepared by the polymerization of a concentrated emulsion of VBC (containing DVB) in water. Various volume fractions of dispersed phase were employed. A typical procedure for the preparation of the concentrated emulsion is as follows. A small amount of aqueous solution of SDS was placed in a single-necked flask (100 ml capacity) equipped with a mechanical stirrer. A mixture of VBC and DVB containing the initiator AIBN was added dropwise with a syringe, under stirring, at room temperature. The obtained gel-like emulsion was packed in a tube, and subjected to polymerization in a water bath at 45°C for 48 h.

Preparation of poly(VBC)-supported onium chloride

A typical procedure for the preparation of poly(VBC)-supported onium chloride is as follows. A powder of poly(VBC) polymer (3 g, 0.02 mol of chlorine) and 5.56 g (0.027 mol) of TBA were introduced into 30 ml ethyl alcohol and subjected to heating at 80°C for 48 h under stirring. After reaction, 20 ml acetone were poured into the flask and the obtained system was stirred and subsequently filtered. The quaternized polymer powder was then introduced in acetone and subjected to heating under reflux for 0.5 h in order to eliminate the unreacted reactants. Finally, the solid was dried under vacuum at 50°C.

Preparation of the polystyrene core-poly(VBC) shell-bound benzyltributyl phosphonium or ammonium chloride

A mixture of styrene (12.49 g, 120 mmol) and DVB (2.73 g, 11.6 mmol) containing AIBN (0.030 g) was added dropwise at room temperature to an aqueous solution of SDS (0.34 g of SDS dissolved in 2 ml water) under stirring. The flask containing the gel-like emulsion was immersed in a water bath (40–45°C) for 6 h for mild polymerization. VBC (1.85 g, 12.1 mmol) was subsequently added, under vigorous mechanical stirring (about 700 rev min^{-1}), to this partially polymerized concentrated emulsion. Vigorous stirring was necessary because of the relatively high viscosity of the partially polymerized concentrated emulsion. The polymerization was then continued for another 40 h at 40–50°C. The polymer thus obtained was washed twice with ethyl alcohol and subsequently heated in methanol under reflux for 2 h to remove the unpolymerized VBC. After drying in vacuum at 50°C overnight, a polymer containing polystyrene particles (crosslinked with 9.7 mol% DVB) covered with a non-uniform shell of poly(VBC) was obtained. The material thus obtained was ground to a fine powder.

Further, 2.48 g (1.88 mmol chlorine) of the polymer

powder were introduced together with 2.85 g (14 mmol) of TBP or 2.40 g (14 mmol) of TBA in 20 ml of ethyl alcohol and allowed to react at 80°C for 24 h under magnetic stirring. The polymer powder containing pendant benzyltributyl phosphonium chloride or benzyltributyl ammonium chloride was filtered, washed twice (first in refluxing methanol and subsequently in refluxing acetone) and finally dried under vacuum at 50°C.

Preparation of polystyrene porous media with surface-bound quaternary onium salts

A concentrated emulsion was prepared at ambient temperature by dropwise addition under stirring of a mixture of styrene and DVB to an aqueous solution containing SDS and a quaternary onium monomer such as VBPC. The obtained gel-like emulsion was packed into a tube by gentle tapping and subjected to polymerization by heating the tube in a water bath at 40°C for 72 h. After polymerization, the polymer was ground and the powder was introduced several times (for a total of 2–3 h) in warm water, under stirring, and filtered, and finally was dried in vacuum.

Determination of the quaternary ammonium chloride content in the poly(VBC)-supported PTC catalysts

The Mohr method[10] was employed to determine quantitatively the chloride anion, which is the counterion of the onium cation. To a flask (100 ml) containing 10 ml of aqueous solution of K_2CrO_4 (about 0.4 M), 0.1 g poly(VBC)-supported onium salt powder was added. The system was subjected to ultrasonic cleaning for 15 min to ensure ion exchange between Cl^- and CrO_4^{2-} ions. Then, the system containing the fully swollen polymer was titrated with a 0.020 N solution of silver nitrate.

Electronic spectroscopy for chemical analysis

Polystyrene powder (50 mg) containing bound onium salts was dissolved in 2–3 ml chloroform. The sticky solution was poured into an aluminium pan (2 cm in diameter), the solvent (chloroform) was evaporated and the obtained disc was employed for the e.s.c.a. analysis.

Monoalkylation reaction in the triphase reaction system

The alkylation reaction of propylidene malonate (the Meldrum acid[11]) was carried out under triphase (polymer-supported phase transfer catalyst/inorganic base/reagent and solvent) conditions. In a typical run, propylidene malonate (0.77 g, 5 mmol), a powder of potassium carbonate (0.69 g, 5 mmol) and a powder of poly(VBC)-supported benzyltributyl ammonium chloride catalyst (0.42 g, 1.0 mmol) were introduced into a flask (25 ml). Chloroform (10 ml) followed, under magnetic stirring, by a solution of ethyl bromoacetate (1.18 g, 7.0 mmol) in 4 ml chloroform were added to the flask. The heterogeneous system was heated at 60–65°C under stirring for 4 h. After reaction, the catalyst and the inorganic salt were filtered and the filtrate was subjected to evaporation under a water aspiratory pump. Acetonitrile (5 ml) was added to the residual liquid and the crude product, which precipitated when 40 ml of distilled water were poured into the acetonitrile solution, was purified by recrystallization from benzene with petroleum ether. The isolated yield of the adduct was 0.64 g (molar yield 55.6%). ^{1}H n.m.r. ($CDCl_3$) 1.30 (t, 3H), 1.91 (s, 3H), 1.89 (s, 3H), 2.40 (d, 2H), 4.01 (t, 1H), 4.20 (q, 2H).

Instruments

Infra-red spectra were obtained with a Mattson Alpha Centauri *FT*i.r. instrument, and the ^{1}H n.m.r. analyses were performed with a GEM-300 spectrometer. The morphologies of the polymer samples were investigated with a scanning electron microscope (Amray 100A). The elemental analysis of Cl, N and P was carried out by Quantitative Technologies, Inc. (Bound Brook, New Jersey). Angular dependent e.s.c.a. (Physical Electronics PHI 5100) and energy dispersive spectroscopy (e.d.s.) (PGT/IMIX) were employed to identify the surface-bound phosphonium salt and chloromethyl groups.

RESULTS AND DISCUSSION

Morphology and phase transfer catalytic reactivity of poly(VBC)-supported quaternary benzyltributyl ammonium chloride

Because VBC has a reactive chloromethyl group, it has frequently been used as a precursor for functionalization[12]. In the present concentrated emulsion method various volume fractions of VBC were employed to prepare poly(VBC) resins (*Table 1*). The SEM micrographs of the quaternized resins show that their morphology changes from macropores (samples 1a and 1b, *Figures 1a* and *1b*) to a more compact structure (sample 1d, *Figure 1d*) with increasing volume fraction of VBC. The morphology of sample 1c is intermediary (*Figure 1c*). A comparison between *Figures 1a* and *1a'* indicates that the quaternization reaction (*Scheme 1*) does not change the morphology.

In *Scheme 1* y and z represent the content of VBC and onium salt units, respectively, in mol%: for $Z = N$, $y:z$

Table 1 Compositions of various concentrated emulsions of VBC in water used for the preparation of the substrates of the catalysts 1a, 1b, 1c and 1d

	1a	1b	1c	1d
Dispersed phase $\left[\text{VBC} + \text{DVB}\left(13.2 \times 10^{-3} \frac{\text{mol DVB}}{\text{mol VBC}}\right)\right]$ (ml)	17.0	16.0	15.0	18.0
AIBN g/ml (VBC + DVB)		2.6×10^{-3}		
Continuous phase				
Water (ml)	6	4	2	1
SDS g/ml (VBC + DVB)		0.02		
Volume fraction of VBC, ϕ	0.74	0.80	0.88	0.95

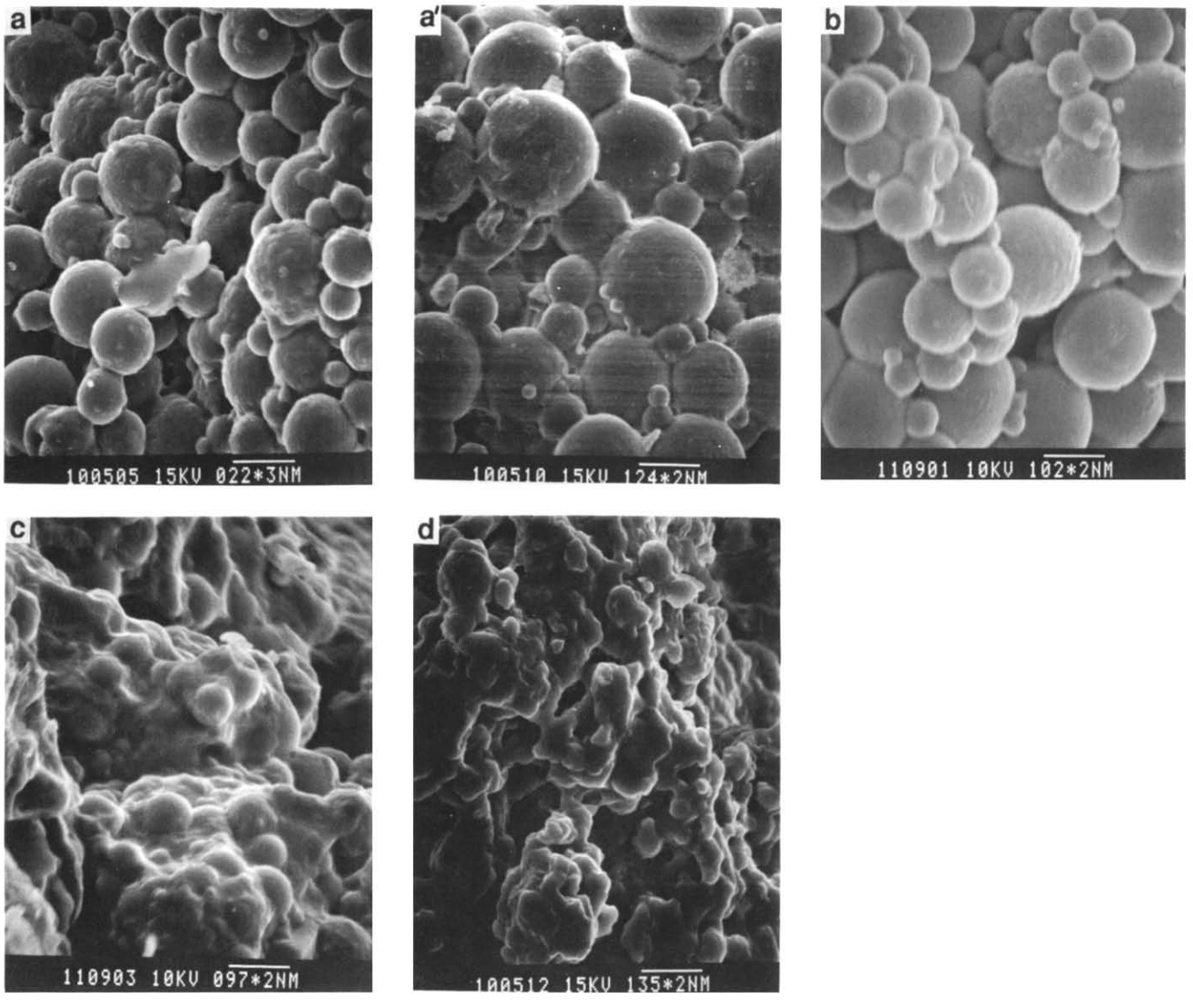
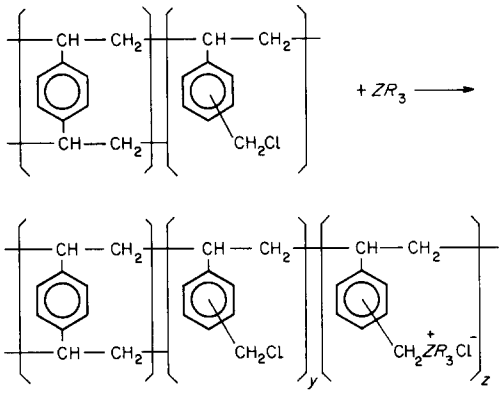


Figure 1 SEM micrographs: (a) poly(VBC)-supported benzyltributyl ammonium chloride 1a (*Table 2*) for a volume fraction $\phi = 0.74$ of VBC after quaternization; (a') poly(VBC) of sample 1a before quaternization; (b) poly(VBC)-supported benzyltributyl ammonium chloride 1b (*Table 2*) for a volume fraction $\phi = 0.80$ of VBC after quaternization; (c) poly(VBC)-supported benzyltributyl ammonium chloride 1c (*Table 2*) for a volume fraction $\phi = 0.88$ of VBC after quaternization; (d) poly(VBC)-supported benzyltributyl ammonium chloride 1d (*Table 2*) for a volume fraction $\phi = 0.95$ of VBC after quaternization



Z = N, P; R = n-C_4H_9

Scheme 1

is about 33:65 (samples 1a, 1b, 1c and 1d); for Z = P, $y:z$ is 41:57 (sample 1e).

The content of pendant benzyltributyl ammonium chloride in this poly(VBC)-supported catalyst was determined both by the titration of Cl^- and by the elemental analysis of N and P as described in the Experimental section; the results of these independent analyses are listed in *Table 2*. Since the yield of quaternization is in the range of 65–68%, the bound-benzyltributyl ammonium chloride is present in a large portion of the poly(VBC) particles. The *FT*i.r. spectrum of sample 1c shows the characteristic absorption bands of bound benzyltributyl ammonium chloride (1636 cm^{-1}, 1379 cm^{-1} and 1099 cm^{-1}) and of bound benzyl chloride (707 cm^{-1}) (*Figure 2*).

The relation between the phase transfer catalytic activity and the morphology of the poly(VBC)-supported quaternary benzyltributyl ammonium chloride was investigated for the alkylation reaction of isopropylidene malonate *1* (*Scheme 2*).

The yields of monoalkyl-isopropylidene malonate *3* are used to compare the catalytic activities of the poly(VBC)-supported quaternary benzyltributyl ammonium chloride catalysts with their unsupported counterpart VBAC (*Table 3*). *Table 3* demonstrates that the catalysts 1a and

Table 2 Titration for Cl^- and elemental analysis for N and P in the poly(VBC)-supported quaternary onium salts and the diameters of their particles

	1a	1b	1c	1d	1e[a]
Volume fraction, ϕ	0.74	0.80	0.88	0.95	0.88
Cl^- (mmol/g polymer)	2.41	2.37	2.43	2.43	2.10
N (mmol/g polymer)			2.44		
P (mmol/g polymer)					2.13
Range of diameters in *Figure 1* (μm)					
Before quaternization	2.5–25				
After quaternization	12–29	3.4–17	0.97–1.1		

[a]1e has the same substrate as 1c but has a phosphonium salt instead of an ammonium salt

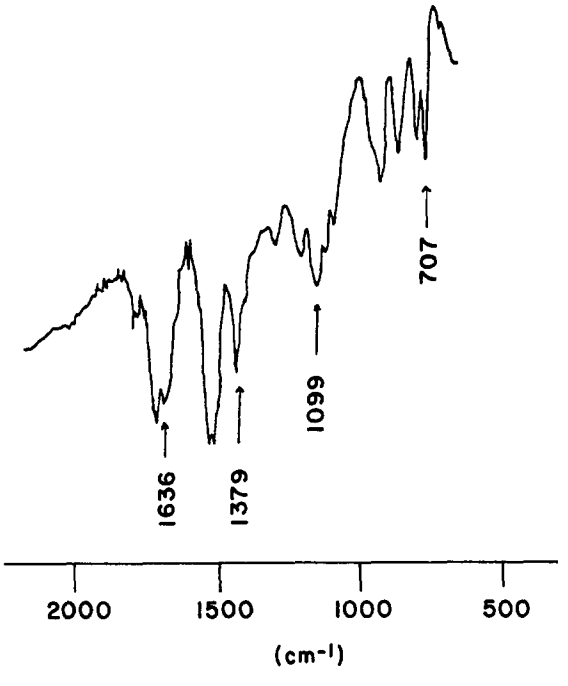
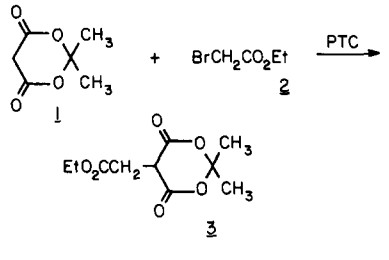


Figure 2 *FT*i.r. spectrum of poly(VBC)-supported ammonium salt of sample 1c (*Table 2*)



Scheme 2

1b provide higher yields than 1d. It is interesting to note that the catalysts 1a and 1b have numerous macropores (*Figures 1a* and *1b*), while catalyst 1d has a more compact morphology (*Figure 1d*). It is clear that the macropores facilitate the motion of the liquid phase toward the individual particles. *Table 3* also shows that the yield of the addition product *3* is higher for the poly(VBC)-supported quaternary ammonium chloride catalysts than for the unsupported phase transfer catalyst (VBAC). A similar observation was recently made by other authors[13] for a different reaction and substrate. This can be a result of either a cooperative effect among neighbouring quaternary ammonium sites on the polymer substrate, and/or of the hydrophobic microenvironment on the

Table 3 Comparison of the yields of monosubstituted isopropylidene malonate *3* (*Scheme 2*) in phase transfer catalyst reaction with various supported and unsupported ammonium salts[a]

Catalyst	Amount (g)	Ammonium salt (mmol)	Time (h)	Yield (mol%)
1a	0.50	1.21	4	64.3
1b	0.50	1.20	4	63.5
1c	0.50	1.22	4	61
1d	0.51	1.24	4	55
VBAC	0.41	1.22	4	54

[a]Ammonium salt (mmol): malonate *1* (mmol) = 1.20–1.24:5.0

polymer support, which facilitates the desorption of the hydrophilic product. It is important to note again that the ammonium salt catalyst is present in a large portion of the particle, which is also probably swollen with the reaction medium. The high concentration of catalyst in the swollen portion is probably responsible for the cooperativity effect. It should also be noted that the molecular ratio of the ammonium salt to reactant is 1.22:5 (*Table 3*), hence relatively large, and that the concentration of reagent in the swollen layer is also large. Both effects increase the reaction rate.

Characterization of polystyrene–poly(VBC) bound phase transfer catalysts with core–shell morphology

Polymer substrates with a core–shell morphology have been prepared by adding, under vigorous stirring, a precursor monomer (VBC in this case) to mildly polymerized concentrated emulsions of styrene in water (*Table 4*) and subjecting the systems to complete polymerization. The SEM micrograph (*Figure 3*) shows that in such cases a non-uniform shell of poly(VBC) coats a core of polystyrene. The e.d.s. analysis (*Figure 4*), indicates the presence of Cl in the superficial layer of the particles. The *FT*i.r. spectrum of the polystyrene–poly(VBC) presents a characteristic absorption band of the C–Cl group at 710 cm^{-1} over the background of the polystyrene absorption (*Figure 5*). After quaternization (*Scheme 3*), the content of substituted ammonium or phosphonium salt was determined by elemental analysis (*Table 4*).

In *Scheme 3*, y and z represent the content of VBC and onium salt units, respectively, in mol%: for $Z = N$, $y:z = 31:69$; for $Z = P$, $y:z = 62:38$.

The polystyrene–poly(VBC)-supported quaternary benzyltributyl ammonium chloride 4a or benzyltributyl phosphonium chloride 4b catalysts listed in *Table 4* were employed as phase transfer catalysts in the alkylation reaction of isopropylidene malonate *1* (*Scheme 2*). Two

Table 4 The compositions of the concentrated emulsions used to prepare the core–shell polystyrene–poly(VBC) substrates and the elemental analysis of the substrates and of their quaternization products

Feed composition			Elemental analysis (mmol/g polymer)		
Dispersed phase			Cl	N	P
Styrene	12.49 g	polystyrene–poly(VBC) substrate	0.75		
DVB	2.73 g				
VBC	1.85 g				
AIBN	0.030 g	polystyrene–poly(VBC)-supported ammonium salt (catalyst 4a)		0.47	
Continuous phase					
SDS	0.34 g				
Water	2 ml	polystyrene–poly(VBC)-supported phosphonium salt (catalyst 4b)			0.27

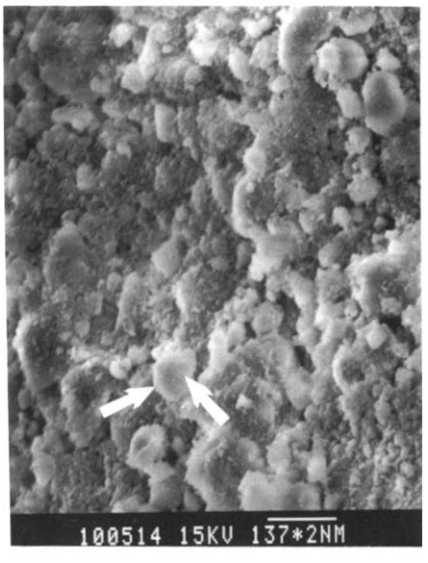


Figure 3 SEM micrograph of polystyrene (core)–poly(VBC) (shell) substrate. The arrows indicate the core and shell. The composition of the substrate is given in *Table 4*

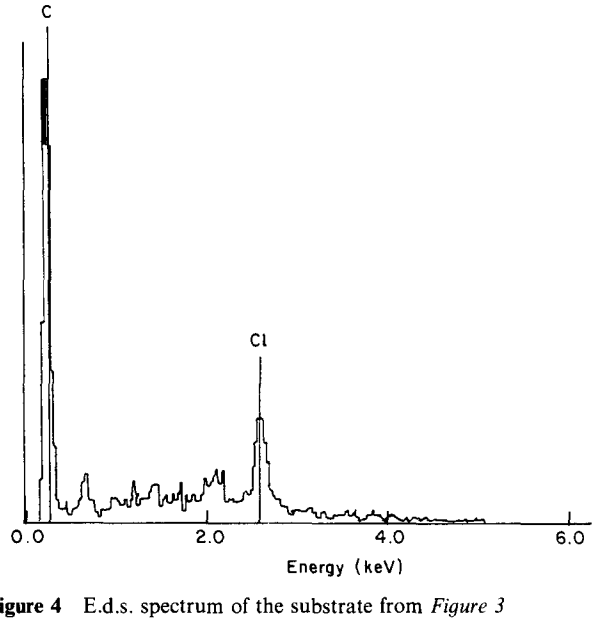


Figure 4 E.d.s. spectrum of the substrate from *Figure 3*

other catalysts, poly(VBC)-supported quaternary benzyltributyl phosphonium chloride 1e (*Table 2*) and the unsupported catalyst VBPC were also used for comparison (*Table 5*). The latter table shows that although

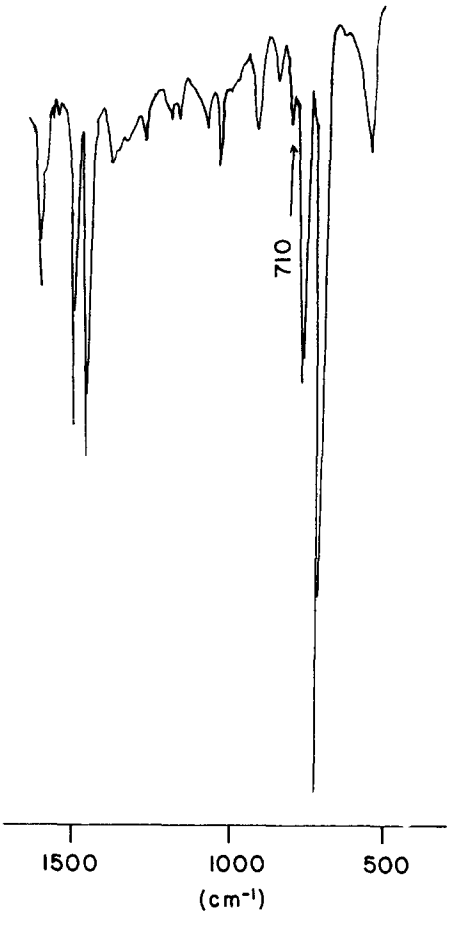
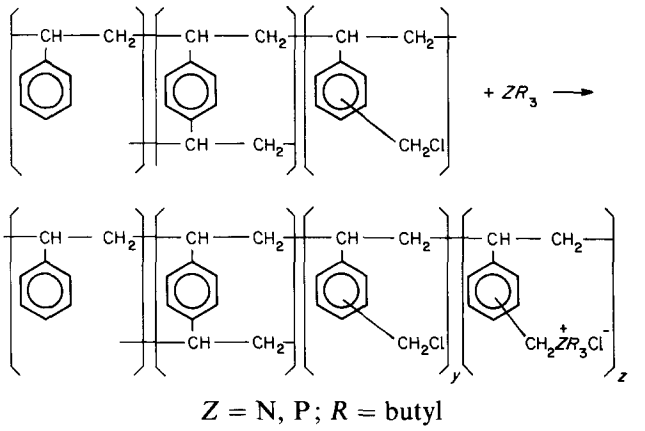


Figure 5 *FT*i.r. spectrum of the polystyrene (core)–poly(VBC) (shell) substrate



Z = N, P; R = butyl

Scheme 3

the molar amounts of phosphonium chloride contained by catalysts 4b, 1e and VBPC are the same, the yields of the product (5-substituted isopropylidene malonate *3*) are in the sequence: VBPC > 4b > 1e. Because VBPC is a low molecular weight catalyst which can dissolve in the reaction solvent, each of the molecules of VBPC can act as a reactive site; if the concentration of catalyst on the substrate is low and, consequently, the cooperativity effect is absent, the system which uses unsupported VBPC as catalyst should have the highest yield. This appears to be the case for the experiments presented in this section. One may note that the supported phosphonium chloride catalyst 4b provides a yield which is near that of VBPC and much higher than that of supported ammonium catalyst 4a. The low yield of the supported phosphonium chloride catalyst 1e (which has the same morphology as catalyst 1c of *Figure 1c*) is probably due to the deep penetration of the phosphonium catalyst in the polymer. Therefore a part of the catalyst is no longer available for reaction. It is important to note that in the present section, because of the smaller amount of catalyst, the molar ratio between the catalyst and reagent is 1:23, whereas in the previous section it was much larger, namely 1.22:5. Since there the amount of catalyst on the support was high, the cooperativity effect resulted in a higher activity of the supported catalyst than of the unsupported catalyst. The transition to cooperativity is now under investigation in our laboratory.

Polystyrene–supported onium salts prepared via their adsorption from the continuous phase on the surface of styrene droplets of a concentrated emulsion

In the third approach used for the preparation of phase transfer catalysts, a concentrated emulsion of styrene in water was prepared after the quaternary onium salt (*Scheme 4*) was dissolved in water. The onium salt is expected to be adsorbed upon the surface of styrene droplets with their vinylbenzyl group oriented towards the inside of the droplets. It is therefore possible that they will polymerize simultaneously with styrene. It is important to note that experiment has indicated that concentrated emulsions do not form for concentrations of quaternary onium salt greater than some critical values (*Table 6*). The instability of the concentrated emulsions containing quaternary onium salts is probably a result of the neutralization or screening of the net charge of the surface of the styrene droplets, by the formation of ion-pairs between the anionic surfactant and cationic quaternary onium ion. VBPC was used as a typical quaternary onium salt in experiments (*Table 7*). After polymerization, the samples were thoroughly washed to remove the unpolymerized onium salt. The amounts of elemental phosphorus in the samples prepared from concentrated emulsions for various volume fractions of styrene are given in *Table 8*. This table shows that with increasing volume fraction of the dispersed phase, the conversion of VBPC to surface-bound phosphonium salt increases. This is consistent with the increase in the available surface area. The angular e.s.c.a. analysis of sample 7b identified the presence of phosphonium cations on the surface of the polystyrene substrates (*Figure 6*). When this sample was used as a phase transfer catalyst in the alkylation reaction, only a small amount of product *3* (*Scheme 2*, *Table 5*) could be isolated. This can be attributed to the small amount of quaternary onium salt supported on the polymer substrate.

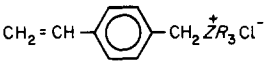
Table 5 Comparison of the yields of monosubstituted isopropylidene malonate *3* (*Scheme 2*) in phase transfer catalyst reactions with various supported and unsupported onium salts[a]

Catalyst	Amount polymer substrate (g)	Quaternary onium salt (mmol)	Time (h)	Yield (mol%)
4a (*Table 4*)	0.65	0.306	4	35
4b (*Table 4*)	0.80	0.219	4	52.8
1e (*Table 1*)	0.1	0.213	4	17.4
VBPC	0.078	0.219	4	59.2
7c (*Table 7*)	1.0	5.5×10^{-2}	4	Very small

[a]Phosphonium salt (mmol): malonate *1* (mmol) = 0.219:5.0

CONCLUSION

Polymer substrates of poly(VBC) and polystyrene–poly(VBC) have been prepared by the concentrated



Z = N, R = butyl, ethyl, methyl
Z = P, R = butyl, ethyl

Scheme 4

Table 7 Concentrations in the concentrated emulsions of styrene in water containing the quaternary onium salt VBPC

	7a	7b	7c	7d
Dispersed phase				
Styrene (g)	13.8	15.3	5.2	7.3
DVB (g)	0.28	0	0.105	0.148
AIBN	2.2×10^{-4} g/g monomer for all systems			
Continuous phase				
VBPC (g)	0.142	0.113	0.142	0.142
Surfactant (SDS) (g)	0.3 g for all systems			
Water	2 ml for all systems			

Table 8 Elemental analysis of the surface-supported phosphonium salts

Catalyst	VBPC ((mmol × 10^2)/g styrene)	Volume fraction, ϕ	P((mmol × 10^2)/g polymer)
7c	7.70	0.74	2.87
7d	5.48	0.80	2.75
7a	2.90	0.88	2.20

Table 6 Critical concentrations at room temperature of quaternary onium salts above which no concentrated emulsions form[a]

	VBPC	VBAC	VEPC	VEAC	VMAC
Concentration (M)	0.23–0.25	0.18–0.20	0.15–0.17	0.20–0.23	0.15–0.17

[a]Styrene (15 ml) was dispersed in the aqueous phase (0.30 g SDS + onium salt + 2 ml H_2O)

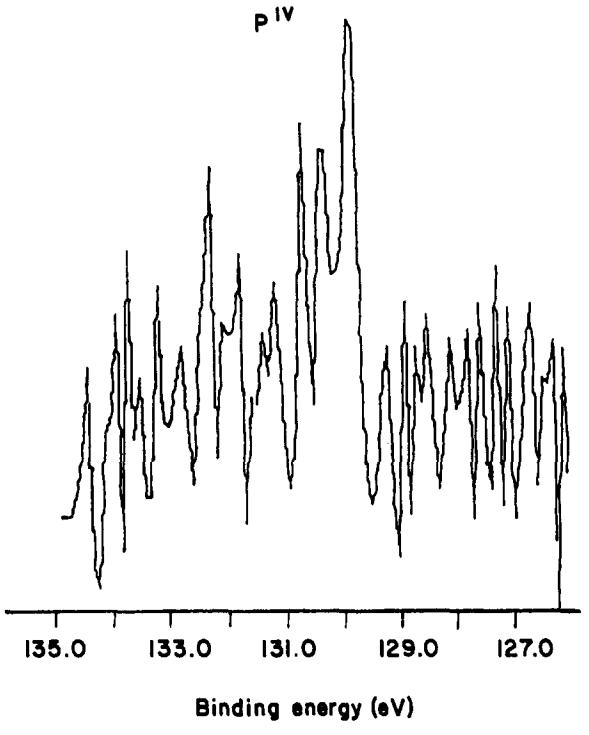


Figure 6 E.s.c.a. spectrum of sample 7b (*Table 7*). Atomic concentrations (%) of P^{IV} = 2.18. Binding energy of P^{IV} = 130.9 eV

emulsion polymerization method. The active quaternary phosphonium and ammonium chloride groups were subsequently introduced via quaternization reactions. Two kinds of phase transfer catalysts have been thus obtained: (1) poly(VBC)-supported onium salt, in which thick layers of bound onium salts were generated; (2) polystyrene–poly(VBC) bound onium salt, in which the substrate has a core–shell morphology with poly(VBC) covering a core of polystyrene. These two kinds of polymer-supported onium salts have been employed as phase transfer catalysts in the alkylation of isopropylidene malonate. Surface-bound quaternary onium salts were also prepared via the adsorption of the onium salt from the continuous phase on the surface of the dispersed phase of the concentrated emulsion. The adsorbed onium salts can be polymerized simultaneously with the styrene present in the droplets. The amount of supported onium salt thus obtained has been small. The latter approach needs further investigation.

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