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Hydrophilic Recognition by Polymer-Supported Phase Transfer Catalysts and Its Effect on Reaction Activity and Selectivity

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Cross-linked polystyrene latexes with surface-bound quaternary ammonium groups have been prepared by a two-step method. First the functional monomer vinylbenzyl chloride (VBC) was introduced into a partially polymerized concentrated emulsion of styrene and divinylbenzene (ST/DVB) in water and complete polymerization was carried out. Second the poly(ST/DVB) particles with surface-bound benzyl chloride groups were quaternized. The dual-surface characteristics due to the hydrophilic bound cations and hydrophobic polystyrene can be varied by controlling the partial polymerization time of ST/DVB and the amount of VBC introduced. The phase transfer catalysts thus obtained were employed in the alkylation reaction of isopropylidene malonate (Meldrum acid). The ratio of mono- to dialkylation products was observed to increase with decreasing accessible hydrophilicity of the supported catalysts. When the partial polymerization time is short, a part of VBC copolymerizes with styrene and another part homopolymerizes and is grafted to the surface of the particles. When the partial polymerization time is long, only homopolymers of VBC, which are grafted to the particles, form. The ammonium groups to which the benzyl chloride units are converted via quaternization are more accessible, for steric reasons, to the Meldrum acid and to the monosubstituted Meldrum acid when they are part of the grafted chains than when they are part of the copolymer. As a result, the activity for the conversion of the Meldrum acid increases as the partial polymerization time increases. However, the selectivity for the monosubstituted Meldrum acid increases with decreasing partial polymerization time of the concentrated emulsion, because the fraction of hydrophilic groups that are accessible decreases and the monosubstituted compound has more difficulty, for steric reasons, binding to the onium cations than the unsubstituted compound.

INTRODUCTION

We report here the preparation of polymer-supported phase transfer catalysts that contain various amounts of hydrophilic quaternary onium groups bound to the surface of hydrophobic cross-linked polystyrene particles. The dependence of the activity and selectivity of these catalysts on their degree of accessible hydrophilicity was investigated for the alkylation of isopropylidene malonate (Meldrum acid) with ethyl bromoacetate. The formation of ion pairs between the polymer-bound onium ions and the reactive (unsubstituted or monosubstituted) isopropylidene malonate anions and the transfer of the electrophilic molecules of ethyl bromoacetate from the organic solvent (chloroform) to the reactive ion pairs bound to the polymer represent the two processes involved in this nucleophilic substitution reaction. Both processes require hydrophilic and hydrophobic interactions, which provide the basis for reactant recognition by the polymer-supported catalyst. This reaction has been extensively investigated, but only under homogeneous conditions (*1*).

The strategy of using concentrated emulsions (*2*) has been employed for the preparation of the polymer-supported phase transfer catalysts. An oil in water (o/w) concentrated emulsion can be easily prepared by dispersing a hydrophobic liquid into a surfactant-containing hydrophilic liquid by mechanical stirring. The concentrated emulsion is stabilized by the adsorption of the

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surfactant on the surface of the dispersed droplets. The volume fraction of the dispersed phase is larger than 0.74, which represents the volume fraction of the most compact arrangement of spheres of equal radii and can be as large as 0.99. The concentrated emulsions have the appearance and behavior of gels and for this reason are easy to handle (*3*). When the dispersed liquid is a hydrophobic monomer that contains a suitable initiator, and the continuous phase is water, polymer latexes of micrometer size are obtained after polymerization. Functional groups can be bound to the surface of the insoluble supporting polymer particles by introducing hydrophobic functional monomer(s) into partially polymerized concentrated emulsions of a hydrophobic monomer (which will be called supporting monomer) in water (in the present paper, the mole ratio of functional monomer to the supporting monomer is in the range 7 to 19%) and polymerizing again. The composition and the structure of the functionalized surface layer of the polymer particles can be controlled by varying the time of partial polymerization. Thus, if the functional monomer is introduced into a concentrated emulsion that has experienced a short polymerization time, a part of the functional monomer molecules will copolymerize during subsequent polymerization with the supporting monomer, and another part will homopolymerize and be grafted to the polymer particles. On the other hand, if the functional monomer is introduced into a concentrated emulsion that has experienced a long polymerization time, most of the functional monomer molecules will homopolymerize and be grafted to the surface of the particles. In the present paper, styrene (ST) and divinylbenzene (DVB) were used as supporting monomers, and vinylbenzyl chloride (VBC) was used as the functional monomer. The surface-pendant benzyl chloride units were chemically transformed to quaternary ammonium cations. Two extreme types of catalysts were obtained. In one, copolymers of quaternary ammonium and phenyl groups as well as grafted polyquaternary ammonium chains form an active layer on the particles (type 1). In the other, only grafted polyquaternary ammonium chains are present on the surface of poly(ST/DVB) (type 2).

The alkylation of the Meldrum acid with ethyl bromoacetate was chosen to examine the effect of the accessible hydrophilicity of the supported catalyst on the activity and selectivity of this nucleophilic reaction. This choice was made because: (1) the reaction can generate both mono- and disubstituted Meldrum acid (Scheme 2), as a result of the nucleophilic attack of unsubstituted and monosubstituted anions on the alkyl halide; (2) intuition suggests that the type 2 catalyst, which has surface-pendant polycation chains, can bind the unsubstituted and monosubstituted anions more easily than the type 1 catalyst does, for steric reasons. Therefore, the conversion of the Meldrum acid and the selectivity for the disubstituted compound are expected to be higher for the type 2 catalyst.

If the reaction is catalyzed homogeneously by a quaternary onium salt or a lightly cross-linked polyquaternary onium salt, only the disubstituted compound is obtained, because, in contrast to the heterogeneous polymer catalysts with dual surface characteristics, there are no steric constraints for the two kinds of anions to approach the quaternary onium cations. The presence of styrene segments adjacent to cation segments in the type 1 catalyst generates steric constraints that are greater for the monosubstituted than for the unsubstituted anion. In the type 2 catalyst, the surroundings of the surface-pendant ammonium chains have much less steric constraints than in the type 1 catalyst. The hydrophobic steric constraints due to the polystyrene segments are responsible for the decreased recognition of the un- and monosubstituted anions by the type 1 catalyst.

EXPERIMENTAL

Main materials. Styrene (Aldrich, 99%), divinylbenzene (Aldrich, tech., 55%), butyl acrylate (Aldrich, 99 + %), and vinylbenzyl chloride (Kodak, *p* and *m*-isomeric mixture) were distilled under vacuum before use. Tributyl amine (Aldrich, 99%), tributyl phosphine (Aldrich, 92%), benzyl chloride (Aldrich, 0.25% propylene oxide), isopropylidene malonate (Aldrich, 98%), ethyl bromoacetate (Aldrich, 98%), sodium dodecyl sulfate (SDS) (Aldrich, 99%), and various solvents were used without further purification.

Instruments used. ^{1}H NMR spectra of the alkylation products were recorded on a VXR-400 spectrometer (400 MHz). Energy dispersive spectroscopy (EDS) surface analysis was performed on a PG/IMIX equipment (15 Kev). The morphologies of the polymer samples were investigated with scanning electron microscopy (SEM) (Amray 100A). Infrared absorption spectra of benzyl chloride groups bound on the polymer particles in different surroundings were obtained with a Mattson Alpha Centauri FT–IR instrument by using a KBr grate. The content of monoalkyl isopropylidene malonate was determined by HPLC (ISCO-2350 pump and ISCO – V_4 detector) using a column (4.6 mm × 25 cm) filled with Adsorbosphere C_8 of 5 μm. Elemental analyses for Cl, N, and P were carried out by Quantitative Technologies, Inc. (Bound Brook, NJ).

General Methods

Preparation of the cross-linked polystyrene particles with surface-attached benzyl chloride by the concentrated emulsion polymerization method. In a 100-ml round-bottom flask, a solution of SDS (0.30 g) in 4 ml of water was first prepared. Then, 12 ml of ST/DVB mixture (mol ratio = 10 : 1) containing 15 mg of initiator azobisisobutyronitrile (AIBN) was added dropwise to the aqueous solution, with mechanical stirring (about 500 rpm) using a Teflon blade, over a period of about 20 min at room temperature. The resultant gel-like concentrated emulsion (the volume fraction of the dispersed ST/DVB phase was 0.75) was polymerized at 40°C, for 4, 8, or 16 h. After the partially polymerized concentrated emulsions were cooled to room temperature, VBC (7.87 to 19.67 mmol) was added slowly with vigorous stirring (about 700 rpm). The emulsions charged with VBC were packed tightly by shaking, sealed in glass tubes, and polymerized for 48 h at 40–45°C. The polymers were ground and washed by stirring in refluxing methanol (30–40 ml) 3 times (1 h each time). After vacuum drying, the functionalized polymer powders (agglomerates of micrometer-size latexes) were analyzed for chlorine.

Preparation of the poly(ST/DVB)-bound benzyl tributyl ammonium chloride (P-BTAC). Tributyl amine was introduced into a suspension of benzyl chloride bound to cross-linked polystyrene (2.5 g) in 15 ml of DMF (5.6 eq tertiary amine for 1.0 eq bound chlorine). The mixture was stirred under a N_2 atmosphere, at 70–75°C for 72 h. After cooling, the mixture containing the quaternized polymer powder was introduced and stirred into a 60-ml mixture of ethyl ether and petroleum ether (v/v = 1/4). The filtered polymer powder was subsequently washed three times by stirring in the above mixture (30 min each time) and dried under vacuum at 50°C.

Preparation of poly(VBC)-supported benzyl tributyl ammonium chloride (P′-BTAC). Poly(VBC) cross-linked with 1.3 mol% DVB was first prepared starting from a concentrated emulsion of VBC (containing DVB) in water (volume fraction of the dispersed phase was 0.8). A total of 3.0 g of poly(VBC) powder (6.48 mmol of Cl/g polymer) and 5.56 g of tributyl amine was introduced in 30 ml of ethyl alcohol and held at 80°C for 48 h with stirring. After reaction, the quaternized polymer powder was purified twice by stirring in acetone under reflux. The obtained poly(VBC)-supported ammonium chloride contains 2.4 mmol of N/g polymer.

Synthesis of benzyl tributyl phosphonium chloride. Benzyl tributyl phosphonium chloride was synthesized by the reaction of benzyl chloride with tributylphosphine and then recrystallized from ether and chloroform according to the method of Ref. (*4*).

Alkylation reaction in the triphase reaction system. The alkylation reaction of propylidene malonate with ethyl bromoacetate was carried out under triphase (poly(ST/DVB)-supported BTAC 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 polymer-supported catalyst (containing 0.38 mmol of BTAC) were introduced into a flask (25 ml). Then, 10 ml of chloroform containing 2 μl of water and subsequently ethyl bromoacetate (1.24 g, 7.4 mmol) were added. The stirred slurry was held at 50–55°C under N_2 for 4 h. After reaction, about 20 ml of petroleum ether was added to precipitate the polymer catalyst. The filtered polymer was washed twice with a 20-ml mixture of ethyl ether and petroleum ether (v/v = 1) in a Buchner filter. The filtered liquid was collected and the solvent removed by evaporation. A total of 80 ml of petroleum ether was added, and the solution was cooled in a refrigerator overnight to allow crystallization of the products. The petroleum ether was gently drained out, and the remaining colorless solid washed by stirring for 30 min in 20 ml of water to remove the unreacted Meldrum acid. After vacuum drying, the isolated product containing the mono- and disubstituted Meldrum acid was subjected to thin layer chromatography (TLC) analysis (10 ml $CHCl_3$ and 4 ml CH_3CN as eluent, silica plate, Aldrich) and HPLC analysis (only the unsubstituted and the monosubstituted Meldrum acid has UV absorption at 248 nm).

RESULTS AND DISCUSSION

Grafting Hydrophobic Functional Polymer Chains to the Surface of Cross-Linked Polystyrene Latexes—A Functionalized Polymerization Pathway

One of the characteristics of the concentrated emulsion polymerization (CEP) method is that hydrophobic functional groups can be attached either to the surface of cross-linked polystyrene latexes (*5a*) or of a macroporous network (*5b*). These two morphologies are obtained depending on whether the concentrated emulsion is prepared by dispersing ST/DVB into water or by dispersing water into ST/DVB. If the desired hydrophobic functional monomer(s) (here VBC) is introduced into a partially polymerized concentrated emulsion of ST/DVB in water, then during subsequent polymerization, the functional monomer(s) copolymerizes with styrene close to the interface between oil and water, and the rest homopolymerizes and is grafted to the surface of the particles. Two variables, the time of partial polymerization of the supporting monomers ST/DVB and the amount of functional monomer VBC, which affect the extent of copolymerization and homopolymerization, were varied in the present experiments (Table 1).

The samples with benzyl chloride groups attached to poly(ST/DVB) obtained for different partial polymerization times (denoted in Table 1 as SDC-1 to SDC-4) contain almost equal amounts of benzyl chloride groups. However, the SEM pictures show that their surface morphologies are different (Figs. 1a–1d). Sample SDC-1 (Fig. 1a) was prepared by polymerizing a concentrated emulsion of a mixture of ST/DVB and VBC in water without a partial polymerization of ST/DVB; in this case, the surface of the polymer particles is smooth. In contrast, samples SDC-2, SDC-3, and SDC-4 were prepared by introducing VBC in concentrated emulsions of ST/DVB in water that had already experienced 4, 8, and 16 h of partial polymerization, respectively. The SEM pictures (Figs. 1b to 1d) show that with increasing partial polymerization time the surface morphology of the polymer particles changes from a coarse layer (Fig. 1b) to a number of nodules attached to a relatively smooth surface (Figs. 1c and 1d). The surface compositions of samples SDC-1 to SDC-4 have been determined by EDS (15 keV, with a detection depth of about 100 Å) (Fig. 2). The average concentration of the

TABLE 1

Preparation of Poly(ST-DVB) Particles with Surface Copolymerized VBC and Surface-Grafted Poly(VBC) Chains by the Partially Polymerized CEP Method[a]

ST-DVB (mmol)	VBC (mmol)	Partial polymerization time (h)[b]	VBC (mmol)/g monomers	mmol of Cl/g polymer
SDC-1 87.9–14.3	7.87	0[c]	0.72	0.73
SDC-2 87.9–14.3	7.87	4	0.72	0.69
SDC-3 8.79–14.3	7.87	8	0.72	0.75
SDC-4 8.79–14.3	7.87	16	0.72	0.71
SDC-5 87.9–14.3	11.8	16	0.92	0.97
SDC-6 87.9–14.3	15.73	16	1.18	1.32
SDC-7 87.9–14.3	19.67	16	1.41	1.52

[a] The detailed procedure has been described under Experimental.

[b] The partial polymerization time of the concentrated emulsion of ST-DVB in water before VBC was introduced.

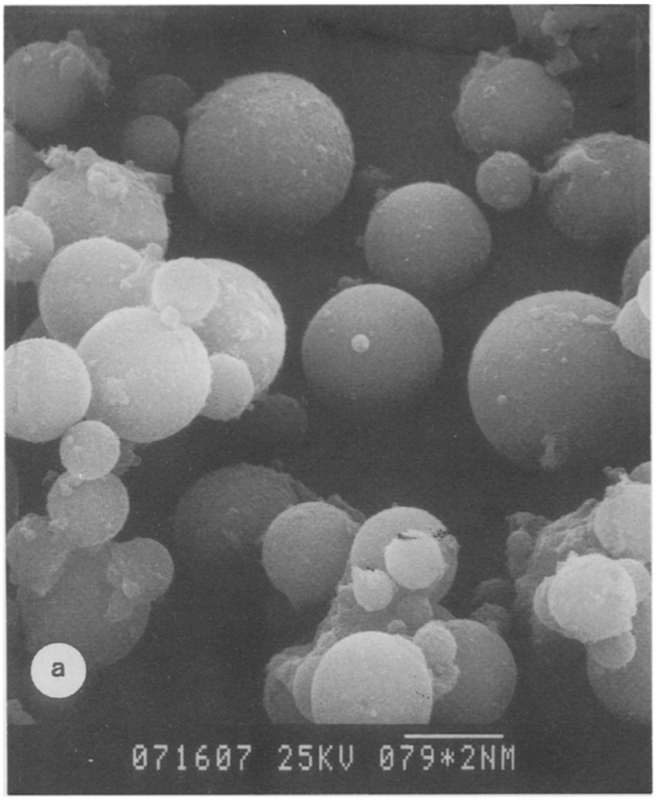
[c] In this experiment, the monomers VBC and ST-DVB were dispersed in water simultaneously to form concentrated emulsions.

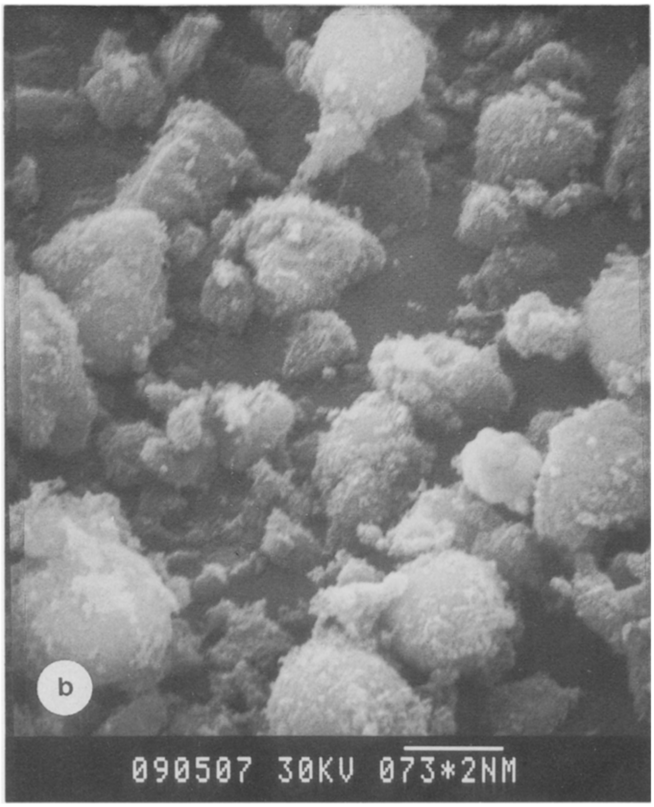
bound benzyl chloride groups within the surface layer of the functionalized particles (their diameters are below 10 μm) increases with increasing partial polymerization time. On the basis of SEM and EDS results, three kinds of surface compositions can be inferred. (1) In sample SDC-1, a mixture of ST/DVB and VBC was copolymerized; since VBC and DVB are more reactive than ST (*6*), much of benzyl chloride groups are buried inside the polymer particles, and the surface is rich in polystyrene. (2) In sample SDC-2, the coarse layer can be considered to contain the copolymer and chains of poly(VBC) grafted to the particles. (3) In sample SDC-4, the surface-attached nodules can be considered as poly(VBC) chains grafted to the particles, because when VBC is introduced into the concentrated emulsion, the primary poly(ST/DVB) network near the interface has already been formed. The VBC molecules will therefore homopolymerize and be grafted to the surface of the dispersed droplets. The surface morphology and composition of sample SDC-3 are similar to those of SDS-4. Samples SDC-5, SDC-6, and SDC-7 were prepared by increasing the amount of VBC introduced into concentrated emulsions that experienced the same partial polymerization time (16 h). Hence, their surface morphology and compositions are like those of SDC-4.

The FT–IR spectra (Fig. 3) of samples SDC-1 to SDC-4 show that the characteristic absorption band (*7*) of poly(VBC) at 607 cm^{-1} were observed only in samples SDC-3 and SDC-4, the absorption of the latter being greater than that of the former. Because there is no IR absorption band around 600 cm^{-1} for the 3 or 4-alkyl benzyl chloride compound (*7*), this absorption band can be assigned exclusively to poly(VBC). This result of FT–IR is in agreement with the above inference.

The polymer-supported PTC catalysts were prepared via the quaternization of the polymer supports SDC-*i* ($i = 2 - 7$) to obtain the series of P-BTAC catalysts that includes six types of catalysts (denoted SDC-

FIG. 1. Scanning electron micrographs of the benzyl chloride group-bound poly(ST/DVB) particles (SDC-*i* series, $i = 1$–4; Table 1). (a) SDC-1 sample; (b) SDC-2 sample; (c) SDC-3 sample; (d) SDC-4 sample.


a
071607 25KV 079*2NM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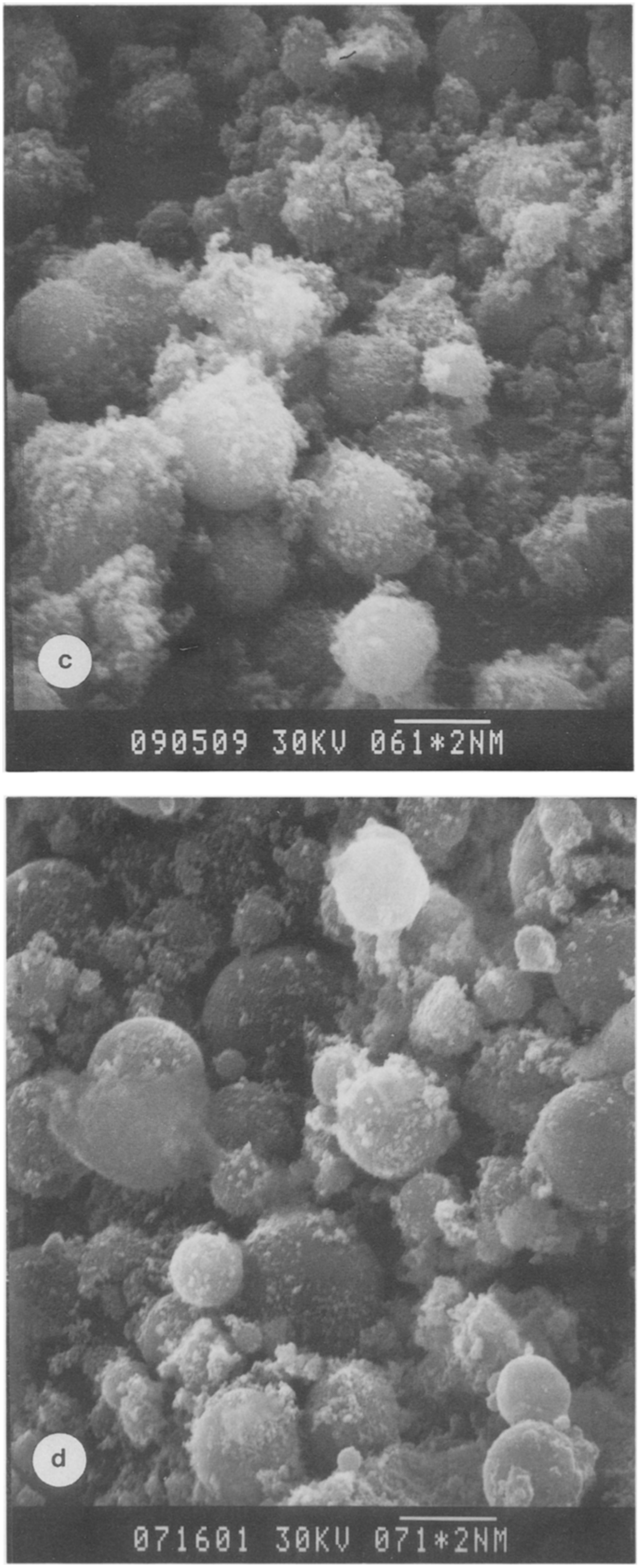


FIG. 1—*Continued*

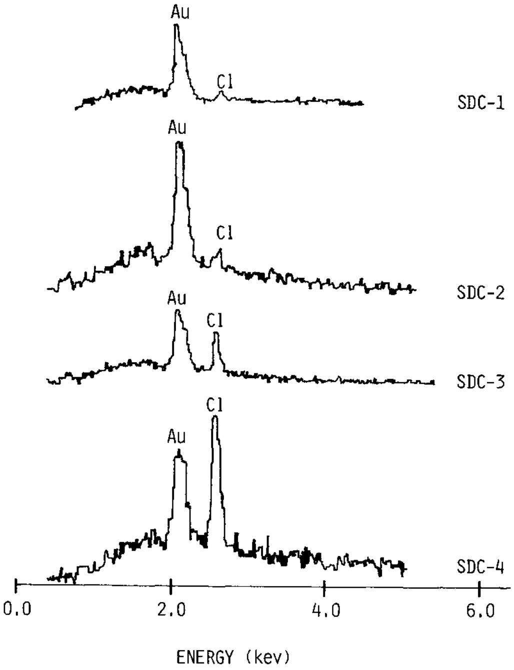


FIG. 2. Surface Analysis of the benzyl chloride group-bound poly(ST/DVB) particles (SDC-*i* series) by EDS; samples were coated with gold before analysis.

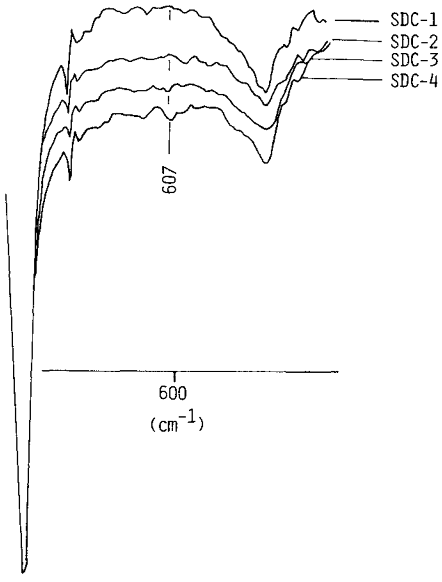


FIG. 3. FT–IR spectra of the benzyl chloride group-bound poly(ST/DVB) samples (SDC-*i* series).

TABLE 2

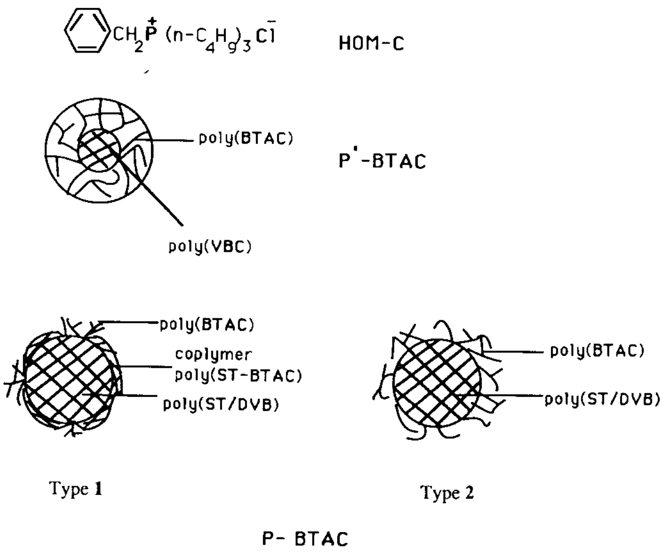
Quaternization of Benzyl Chloride Groups Grafted on the Surface of Poly(ST-DVB) Particles

Polymer-supported phase transfer catalysts P-BTAC	Content of pendant quaternary ammonium salt mmol of N/g polymer	Yield of quaternization (mol%)
SDC-2N	0.53	85
SDC-3N	0.59	88
SDC-4N	0.55	86
SDC-5N	0.74	88
SDC-6N	0.95	87
SDC-7N	1.09	90

2N to SDC-7N in Table 2). From the nearly equally high quaternization yields of SDC-2, SDC-3, and SDC-4 one can conclude that most benzyl chloride groups are present near the surface of cross-linked polystyrene particles and hence can react with the tributyl amine molecules. The poor ability of the quaternization medium (DMF) to swell the cross-linked polysytrene is in agreement with this conclusion.

The Effect of the Accessible Hydrophilicity on the Activity and Selectivity of the Alkylation of Isopropylidene Malonate

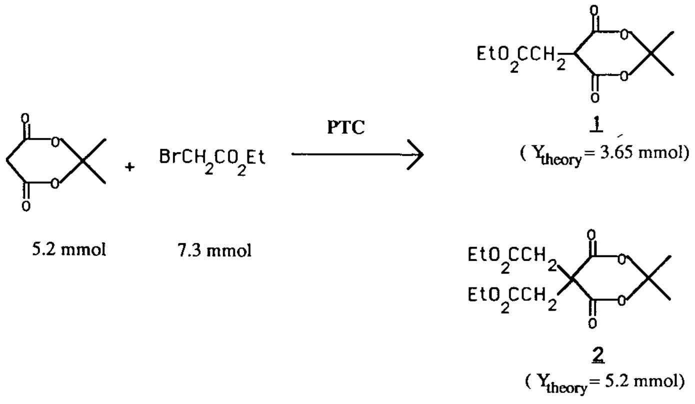
Three kinds of quaternary onium salts (depicted in Scheme 1) have been employed as PTC catalysts for the alkylation of isopropylidene malonate with ethyl bromoacetate (Scheme 2); see Table 3. They are: (1) the homogeneous catalyst benzyl tributyl phosphonium chloride (HOM-C), (2) poly(VBC)-supported poly(benzyl tributyl ammonium chloride) (P′-BTAC), which was prepared by the quaternization of poly(VBC) particles cross-linked with 1.3 mol% DVB (the molar yield of quaternization is 66%, other details have been described under experimental), and (3) the poly(ST/DVB)-supported benzyl tributyl ammonium chloride (P-BTAC) series. The P′-BTAC contains 2.4 mmol of quaternary ammonium per gram



SCHEME 1. Three kinds of phase transfer catalysts employed for the alkylation of isopropylidene malonate.

of polymer; hence the bound benzyltributyl ammonium chloride is present as a thick hydrophilic layer on a poly(VBC) core. In the P-BTAC series, hydrophilic quaternary onium groups are bound to the hydrophobic support, and therefore there are both hydrophilic and hydrophobic regions on the surfaces of the polymer particles.

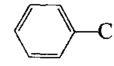
In the present experiments, the activity for alkylation of isopropylidene malonate is enhanced by: (1) using a highly polar and reactive compound, ethyl bromoacetate; and (2) adding a trace of water (about 1–2 μl, since too much water hydrolyzes the Meldrum acid) into the reaction medium (chloroform is the reaction medium and potassium carbonate the base). The trace amount of water provides carbonate anions for abstracting protons from the Meldrum acid and its monosubstituted compound.



SCHEME 2. Alkylation of isopropylidene malonate with ethyl bromoacetate under phase transfer conditions.

TABLE 3

Alkylation of Isopropylidene Malonate Catalyzed by Three Kinds of Quaternary Onium Salts (PTC Catalysts)[a]

Quaternary onium (PTC catalyst)	mmol of quaternary onium salt			
	0.62	0.38	0.19	0.095
	Alkylation yields (mol%)[b]			
$CH_2P^+(n\text{-}C_4H_9)_3Cl^-$	66	61	44	34
P'-BTAC	61	48	43	38
P-BTAC SDC-3N	37(7)[c]	40(8)	41(8)	—

[a] In a typical run, isopropylidene malonate (5.2 mmol), ethyl bromoacetate (7.3 mmol), K_2CO_3 (5 mmol), and quaternary onium salts (the amounts are given in millimoles) in 10 ml chloroform were stirred under N_2 at 55–60°C for 4 h.

[b] Alkylation yields for the bisalkyl-substituted product **2** as indicated in Scheme 1.

[c] Yields in parentheses for the monoalkyl-substituted product **1** as indicated in Scheme 1.

The results of the alkylation experiments show that when the HOM-C and the P'-BTAC catalysts are used, the disubstituted product **2** (Fig. 4a) is selectively generated, although small amounts of catalyst were employed. However, when the catalyst series P-BATC was employed, some monosubstituted products **1** were also obtained (Fig. 4b). The catalyst SDC-2N had the lowest yields of mono- and disubstituted products but the highest ratio of the two. For the other catalysts in the series, SDC-3N to SDC-7N, the alkylation yield increases but the mono-/di- ratio decreases (Fig. 5). This sequence is due to the increased accessibility of the pendant benzyl tributyl ammonium groups on the P-BTAC particles when the time of partial polymerization or the concentration of VBC increases. The strong tendency to form the disubstituted product **2** when the HOM-C and P'-BTAC catalysts are employed arises from the accessibility of hydrophilic catalytic onium cations that are involved in the ion-pair formation with the anions of both unsubstituted and monosubstituted Meldrum acid (Scheme 3). However, in the P-BTAC series, the copolymer bound cations are surrounded by phenyl groups. The proportion of copolymer bound cations is greater when the support SDC-*i* is prepared using a short partial polymerization time. The hydrophobic steric constraints around the quaternary onium groups, such as in the case of SDC-2N, decrease the capacity of the polymer catalyst for complexing the anions or adsorbing the polar halide molecules. As a result, the activity for the conversion of the Meldrum acid decreases as the partial polymerization time decreases. The decrease of the ratio of mono-/disubstituted products with increasing partial polymerization time can be explained as follows: the monoalkylated Meldrum acid bears three electron withdrawing groups and has a chair structure (*1a*), whereas the unsubstituted Meldrum acid bears two electron withdrawing groups and has a boat structure. The former is thus more susceptible to steric constraints than the latter and the steric constraints are greater for shorter partial polymerization times.

A kinetic study regarding the formation of the monosubstituted product **1** and its conversion to the disubstituted product **2** was also performed, by employing SDC-2N, SDC-4N, and P'-BTAC as catalysts (Fig. 6). In the reaction system involving P'-BTAC,

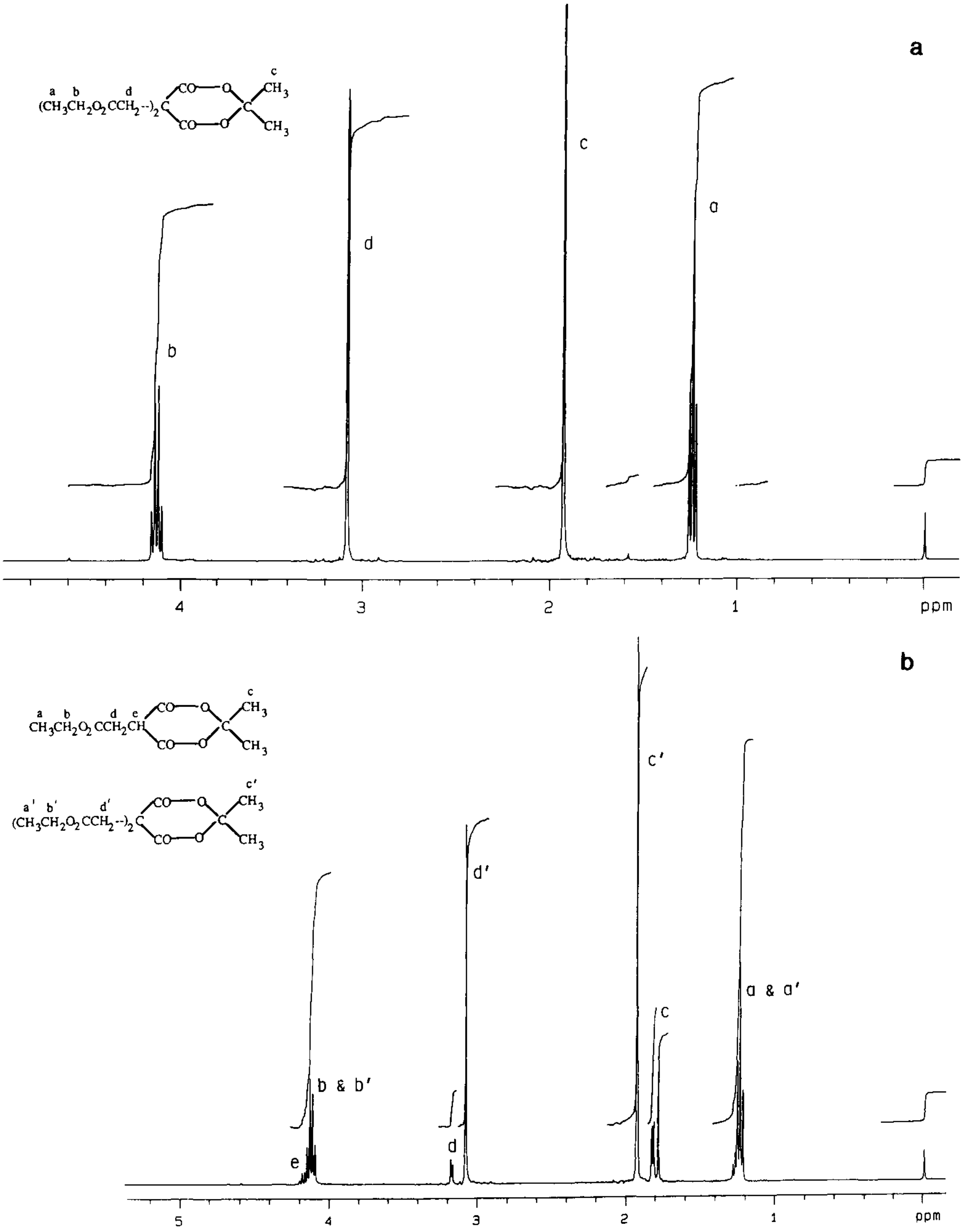


FIG. 4. H^1 NMR of the substituted Meldrum acid. (a) The disubstituted Meldrum acid, 5-di(ethoxy-carbonyl methylene) isopropylidene Malonate **2** obtained by using the catalyst P′-BTAC; (b) the mixture of disubstituted Meldrum acid and monosubstituted Meldrum acid, 5-(ethoxy-carbonyl methylene) isopropylidene malonate **1**, obtained by using the catalyst SDC-6N.

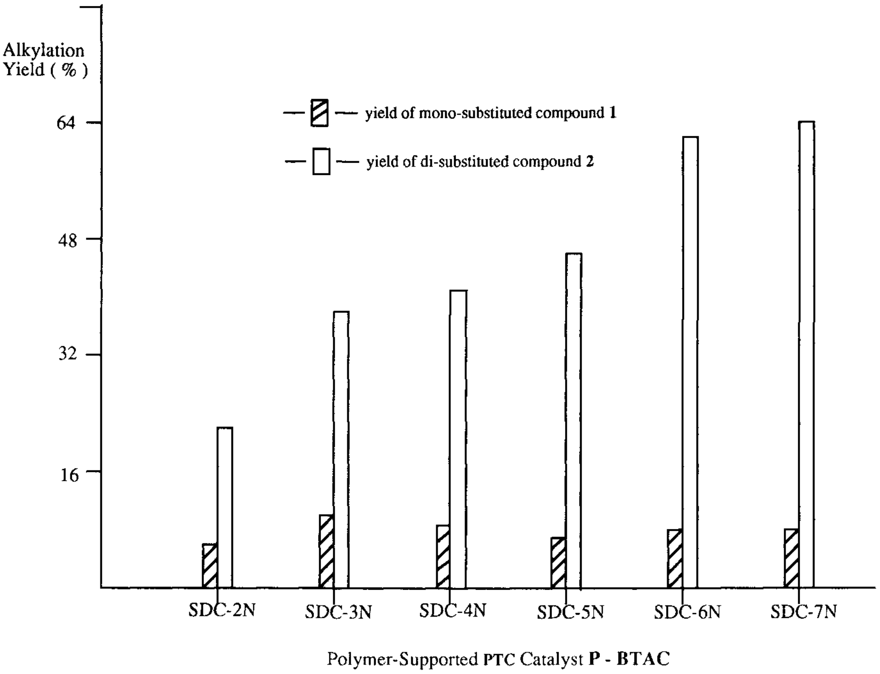
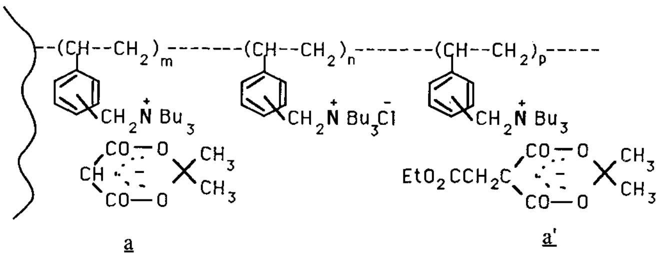


FIG. 5. Comparison of the ratios of mono-/disubstituted Meldrum acid in the products obtained by using catalysts SDC-*i*N (*i* = 1–7). The reaction conditions are specified under Experimental.

product **1** is more rapidly consumed than in the reaction systems involving SDC-4N or SDC-2N. This observation is in agreement with the high accessibility of the onium cations in the swollen layer of the P′-BTAC particles. In contrast, due to their dual surface properties, catalysts SDC-4N and SDC-2N show weaker tendencies to transform the Meldrum acid to products **1** and **2**. Although in Fig. 6 SDC-4N exhibits a higher yield for product **1** than SDC-2N, one can see from Fig. 5 that SDC-2N has a higher selectivity for product **1** than SDC-4N. This occurs, for steric reasons, since the former has less hydrophilic accessibility of onium cation than the latter. Because of this hydrophilic accessibility, SDC-4N leads to a higher yield of product **1** than SDC-2N. In summary, although SDC-2N has the highest selectivity for the monosubstituted product, it provides the lowest yields for the monosubstituted and disubstituted products.



SCHEME 3. Ion pairs between the pendant quaternary onium cations and the anions of unsubstituted a and mono-substituted a′ Meldrum acid.

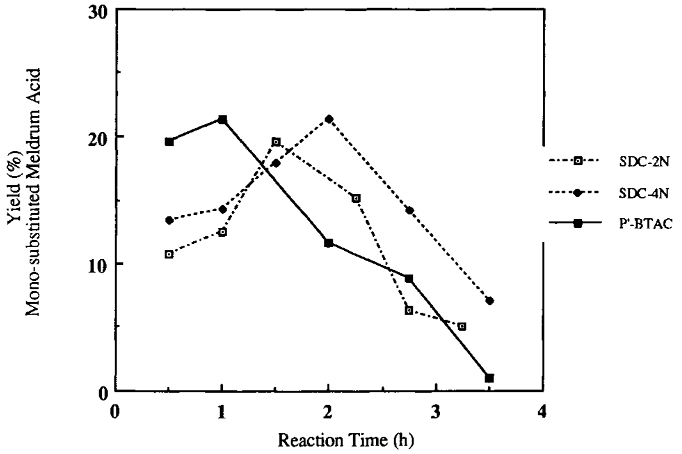


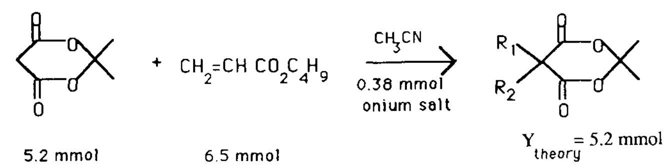
FIG. 6. Comparison of the activities of P'-BTAC, SDC-4N, and SDC-2N for the formation and conversion of the monosubstituted Meldrum acid. The measurements were carried out for the reaction conditions as specified under Experimental.

Hydrophobic and Hydrophilic Cooperations of Polymer-Supported Catalysts in Michael Addition

The SDC-7N and the HOM-C catalysts were also used for the nucleophilic addition (Michael addition) of Meldrum acid to butyl acrylate (Scheme 4). The polymer catalyst has a higher activity than the homogeneous catalyst probably because the hydrophobic butyl acrylate molecules are adsorbed on the hydrophobic region of the particle surface from where they can approach the hydrophilic quaternary onium groups that bind the Meldrum acid anions as ion pairs. From this experimental observation, one can conclude that if both hydrophilic and hydrophobic regions coexist on the surface of latexes, the dual functions can cooperate to generate a phase transfer pathway from the hydrophobic to the hydrophilic region.

SUMMARY

Benzyl chloride groups can be bound to the surface of poly(ST/DVB) latexes by introducing VBC into a partially polymerized emulsion of ST/DVB in water and polymer-



		Yield of the Alkylation (mole %)		
R_1	R_2	⌬$CH_2\overset{+}{P}(n\text{-}C_4H_9)_3\overset{-}{Cl}$	SDC-7N	H^1-NMR ($CDCl_3$/TMS) δ (ppm)
H	$CH_2CH_2CO_2C_4H_9$	7	31	0.96 (t, 3H); 1.35 (m,2H); 1.58 (m,2H); 4.08 (t,2H); 2.62 (t,2H); 2.38 (q,2H); 3.98 (t, 1H); 1.80 (t, 6H)

SCHEME 4. Michael addition of isopropylidene malonate to an electrophilic double bond.

izing again. The surface morphology and the surface composition of the prepared particles can be changed by varying the partial polymerization time and the amount of VBC introduced. If the partial polymerization time is short, VBC molecules copolymerize with styrene molecules on the surface and also homopolymerize and are grafted to the surface of the particles; if the time is long, VBC molecules homopolymerize and are grafted to the surface.

A polymer-supported phase transfer catalyst is obtained by transforming the surface bound benzyl chloride groups to benzyl tributyl ammonium chloride (BTAC) groups. Two extreme types of reactive environments can be obtained on the surface of the particles: (1), copolymer with BTAC and phenyl groups, and some polymer chains of BTAC grafted to the poly(ST/DVB) particles when the partial polymerization time is short; (2) chains of BTAC grafted to the poly(ST/DVB) particles when the time of partial polymerization is long. In the alkylation reaction of isopropylidene malonate with ethyl bromoacetate, the activity of type 1 catalyst is smaller because of the hydrophobic steric constraints for the anions of both unsubstituted and monosubstituted isopropylidene malonate due to the copolymerized fraction of BTAC. In addition, the ratio of monosubstituted to disubstituted product is increased, because the copolymerized fraction of BTAC has less recognition for the anion of monosubstituted isopropylidene malonate. In contrast, the type 2 catalytic environment promotes the activity of BTAC groups and generates the disubstituted product almost exclusively due to the accessibility of the grafted poly(BTAC) chains to both anions. The existence of separated hydrophilic and hydrophobic regions on the surface of type 2 catalyst stimulates the adsorption of both hydrophilic and hydrophobic reagents on the surface of the particles. The activity of the heterogeneous catalyst is much greater than that of the homogeneous catalyst when the Michael addition of the isopropylidene malonate to butyl acrylate is employed as a probe reaction.

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