Preparation of Polymer-Supported Polyethylene Glycol and Phase-Transfer Catalytic Activity in Benzoate Synthesis

Baojiao Gao, Rubin Zhuang, and Jianfeng Guo
Dept. of Chemical Engineering, North University of China, Taiyuan, P. R. China

DOI 10.1002/aic.12019

The crosslinked polymeric microspheres (GMA/MMA) of glycyl methacrylate (GMA) and methyl methacrylate (MMA) were prepared by suspension polymerization. Polyethylene glycol (PEG) was grafted on GMA/MMA microsphers via the ring-opening reaction of the epoxy groups on the surfaces of GMA/MMA microspheres, forming a polymer-supported triphase catalyst, PEG-GMA/MMA. The Phase-transfer catalytic activity of PEG-GMA/MMA microspheres was evaluated using the esterification reaction of n-*chlorobutane in organic phase and benzoic acid in water phase as a model system. The effects of various factors on the phase transfer catalysis reaction of liquid–solid–liquid were investigated. The experimental results show that the PEG-GMA/MMA microspheres are an effective and stable triphase catalyst for the esterification reaction carried out between oil phase and water phase. The polarity of the organic solvent, the ratio of oil phase volume to water phase volume and the density of the grafted PEG on PEG-GMA/MMA microspheres affect the reaction rate greatly. For this investigated system, the solvent with high polarity is appropriate, an adequate volume ratio of oil phase to water phase is 2:1, and the optimal PEG density on the polymeric microspheres is 15 g/100 g. Triphase catalysts offer many advantages associated with heterogeneous catalysts such as easy separation from the reaction mixture and reusability. The activity of PEG-GMA/MMA microspheres is not nearly decreased after reusing of 10 recycles.* *AIChE J,* 56: 729–736, 2010

Keywords: polyethylene glycol, phase transfer catalysis, immobilization, polymeric microspheres, triphase catalyst, esterification

Introduction

Phase transfer catalysis (PTC) is now established as a versatile and important synthetic technique in organic synthesis chemistry.[1–4] It involves simple experimental operations, mild reaction conditions, and inexpensive and environmentally benign reagents and solvents,[5–7] so it has been widely used in industrial and organic chemistry. However, for liquid–liquid phase-transfer catalysis system in which soluble phase transfer catalysts are used, two major problems are always encountered, and they are: (1) the recovery and reuse of the catalyst; (2) the separation and purification of the final product.[8–10] Solid-supported phase transfer catalysts, also known as triphase catalysts, provide an attractive means of recovering the catalyst and separating the catalyst from the product mixture after the reaction. For the triphase catalysts, the phase-transfer catalysts are chemically bound to solid supports, such as silica gel, zeolites, polymers microsphere, etc.[11–13] Among various solid supports, polymeric supports are used most widely.

There are many types of phase transfer catalysts, such as quaternary ammonium and phosphonium salts, crown ethers,

---

Correspondence concerning this article should be addressed to B. Gao at gaobaojiao@126.com

and cryptands.[14–16] Except for these substances, polyethylene glycols (PEGs) and their derivatives (for example, podands) as open-chain crown ethers are also widely used as PTC catalysts.[17–19] Perhaps, they are less active than quaternary ammonium salts and crown ethers, but they have many advantages: they are relatively less costly, nontoxic and environmentally safe, thermally stable in the presence of strong bases, and easily biodegradable.[20–22] Furthermore, sometimes PEGs are very good PTC catalysts with better activities than that of crown ethers.[23]

For the most of the reported polymer-supported triphase catalysts, quaternary ammonium and phosphonium salts are commonly immobilized on the polymeric microspheres,[24,25] whereas for the polymer-supported PEGs and crown ethers, there have been a few instances in the literature. Furthermore, for those polymer-supported triphase catalysts, chemically modified crosslinked polystyrene is commonly used as the support.[26,27] In this work, a short cutting way to prepare a triphase catalyst of polymer-supported PEG was put forward via elaborately molecule-designing: glyceryl methacrylate (GMA) and methyl methacrylate (MMA) was firstly copolymerized in a suspension polymerization system in the presence of a crosslinker, ethylene glycol dimethacrylate (EGDMA), resulting in crosslinked copolymer microspheres GMA/MMA, and then PEG was grafted onto the surfaces of the microspheres GMA/MMA in coupling graft manner via the ring opening reaction of the epoxy groups of GMA/MMA microspheres (in this work, ring opening reaction of the epoxy groups was catalyzed by Lewis acid for the first time), leading to the immobilization of PEG and to obtain the triphase catalyst, PEG-GMA/MMA microspheres. In this article, the phase transfer catalysis property of PEG-GMA/MMA was investigated using the esterification of benzoic acid with *n*-chlorobutane as a model system. The effects of main factors on the reaction process were examined, and the mechanism of triphase phase-transfer catalysis was also studied. The experimental results indicate that this method put forward in this work is available and simple for preparing triphase catalysts of polymer-supported PEG, and the catalyst, PEG-GMA/MMA microspheres, has excellent phase-transfer catalysis activity. In this work, a new triphase catalyst, PEG-GMA/MMA, was designed and prepared successfully. As far as we know, similar study has not been reported.

Experimental Section

Material and equipment

Glyceryl methacrylate (GMA, Suzhou Nanhang Chemical Engineering Ltd., Province Jiangsu, China), Methyl methacrylate (MMA, Tianjing Ruijinte Chemical Ltd., Tianjing City, China), and Ethylene glycol dimethacrylate (EGDMA, Yantai Yunkai Chemical Engineering Ltd., Province Shandong, China) were all of analytical grade and distilled under vacuum before use. Polyethylene glycol (PEG, Mr = 400, Beijing Chemical Engineering Plant, Beijing, China) was of analytical grade. Boron triflourid (BF_3, an ether solution of 50%; Tianjing Huadong Reagent Plant, Tianjing City, China) was of analytical grade. *n*-Chlorobutane (C_4H_9Cl, Tianjing Guangfu Fine Chemical Engineering Institute, Tianjing City, China) was of analytical grade. Benzoic acid (Tianjing Xinpein Chemical Engineering Ltd., Tianjing City, China) was of analytical grade. Other chemicals were all commercial reagents with analytical pure and were purchased from Chinese companies.

The instruments used in this study were as follows: Perkin-Elmer 1700 infrared spectrometer (FTIR, Perkin-Elmer Company, USA); 438VP scanning electron microscope (SEM, LEO Company, UK); HP 6890 gas chromatograph (Beijing Analytical Instrument Plant, China); TG16-WS high-speed centrifuge with desk top type (Xiangyi Group, Province Hunang, China).

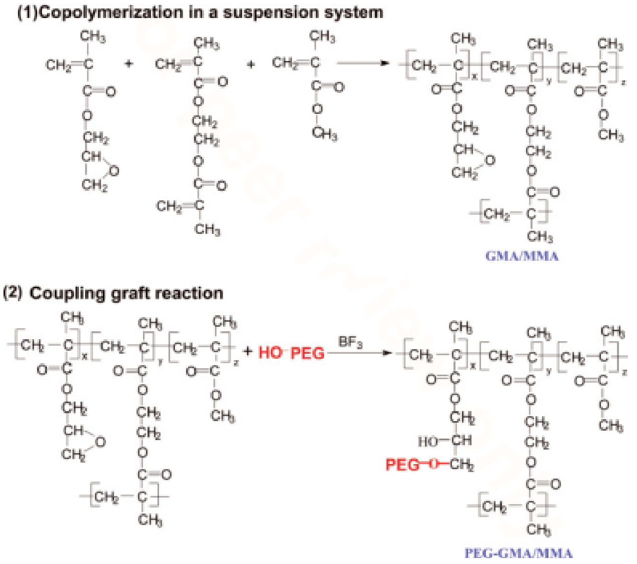
Preparation and characterization of triphase catalyst PEG-GMA/MMA

Preparation of Crosslinked Microspheres GMA/MMA. Crosslinked microspheres GMA/MMA were prepared by using suspension polymerization method. Two grams of polyvinyl alcohol (PVA) as disperser and 5 g of NaCl were dissolved in 100 mL of distilled water, forming water phase as continuous phase. The water phase was placed in a four-necked flask equipped with a mechanical agitator, a condenser, a N_2 inlet, and a thermometer. Three milliliters of GMA, 4 mL of MMA, and 2 mL of EGDMA were dissolved each other, constituting oil phase as dispersion phase. The oil phase was added into the flask and the system was stirred sufficiently so as to fully disperse the oil phase into the water phase. Simultaneously, N_2 was bubbled through the content of the flask for 30 min. The content was heated to 75°C, and 0.05 g of initiator, azobisisobutyronitrile (AIBN) dissolved in a little of toluene was added. The copolymerization was carried out at 75°C for 2 h with stirring under N_2 atmosphere, and then the temperature was enhanced to 85°C, and the reaction was performed for another 2 h. The white crosslinked microspheres GMA/MMA with translucence were obtained. Their structure was characterized by infrared spectrum (FTIR) and their morphology was examined with scanning electron microscope (SEM).

Grafting PEG on GMA/MMA Microspheres. Forty milliliters of *N,N*-dimethylformamide (DMF) and 1 g of the crosslinked microspheres GMA/MMA were placed in a four-necked flask, and the microspheres were allowed to be fully swell for 3 h. One milliliter of PEG and 0.5 mL of BF_3 solution of ether used as catalyst were also added into the flask. The grafting reaction was conducted at 60°C for 6 h. At the end, the resultant microspheres were filtered off, washed with ethanol and deionized water thoroughly, and dried under vacuum, and the functional microspheres PEG-GMA/MMA were obtained. The chemical structure of PEG-GMA/MMA microspheres was characterized by infrared spectrum and the grafting degree (g/100 g) of PEG on the microspheres was determined with weighting method. The PEG-GMA/MMA microspheres with different grafted degrees of PEG were prepared through controlling the graft reaction conditions.

Catalytic property of microspheres PEG-GMA/MMA in esterification

The esterification reaction of benzoic acid in aqueous phase with *n*-chlorobutane in organic phase was selected as



Scheme 1. Preparation process of PEG-GMA/MMA microspheres.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

a model system, and the triphase-transfer catalysis reaction of liquid–solid–liquid was conducted as follows. 0.62 g of benzoic acid (about 5 mmol) was dissolved in 20 mL of KOH aqueous solution (2 M), constituting water phase. The water phase was placed in a reactor equipped with a mechanical agitator and a reflux condenser, followed by adding 1 g of PEG-GMA/MMA microspheres. 0.35 mL of chlorobutane (about 3 mmol) was dissolved in 40 mL of chloroform, forming organic phase, and the organic phase was added in the reactor. The contents were agitated sufficiently at an agitation rate of 550 rpm to fully disperse the mixture. The phase-transfer catalysis reaction was performed at 55°C. Two milliliters of the reaction mixture was withdrawn periodically through the sampling port of the reactor. The sample was thoroughly separated by centrifugalization, and the obtained organic phase was filtered using a microporous filter. The content of butyl benzoate in the organic phase was quantified by gas chromatograph with internal standard method, and the conversion of *n*-chlorobutane was further calculated.

To examine the effects of various factors on the triphase-transfer catalysis reaction, the reactions were conducted under different conditions, and these changed conditions include reaction temperature, solvent species, the ratio of oil phase to water phase as well as the grafting density of PEG on the surfaces of the solid catalyst, PEG-GMA/MMA microspheres. The duty-cycle operation property of the solid catalyst was also examined.

Results and Discussion

Reaction process of preparing triphase catalyst PEG-GMA/MMA

In a suspension polymerization system, the crosslinking copolymerization of two monomers, GMA and MMA, and crosslinker, EGDMA, was carried out, and the crosslinked microspheres GMA/MMA/EGDMA (denoted as GMA/MMA because GMA and MMA were the main units of the microspheres) were obtained. PEG molecules have end groups of hydroxyl groups. By the action of the catalyst (in this study, Lewis acid BF_3 was used as catalyst), the epoxy groups on the surfaces of PGMA/MMA microspheres are attacked by the end groups of hydroxyl groups of PEG, and the ring-opening and ether forming reaction is led to, so that PEG molecules are directly grafted onto PGMA/MMA microspheres in the coupling manner, forming the grafted microspheres, PEG-PGMA/MMA. The total reaction process to prepare PEG-PGMA/MMA microspheres is schematically expressed in Scheme 1.

Characterization of two microspheres

FTIR Spectra. Figure 1 gives the FTIR spectra of the two kinds of microspheres, PGMA/MMA and PEG-PGMA/MMA. In the spectrum of PGMA/MMA microspheres, expect for displaying the common characteristic absorptions of three monomer units as methacrylates, the characteristic absorptions of epoxy bond of GMA unit exhibit at 906 and 840 cm^{-1}. In the spectrum of PEG-GMA/MMA microspheres, the bands at 906 and 840 cm^{-1} have disappeared completely, and three new bands at 3430, 1050, and 1100 cm^{-1} have appeared. The bands at 3430 and 1050 cm^{-1} are attributed to the characteristic absorptions of the hydroxyl groups of PEG (another hydroxyl end groups), and the band at 1100 cm^{-1} should correspond to the characteristic absorption of ether bond, C—O—C, in PEG molecules. The aforementioned band changes reveal that PEG molecules have been grafted on the PEG-GMA/MMA microspheres in the coupling way via the ring-opening and ether forming reaction of epoxy groups on GMA/MMA, forming the functional microspheres PEG-GMA/MMA.

SEM Observation. Figure 2 displays the SEM images of GMA/MMA microspheres. It can be observed that the sphericity of GMA/MMA microspheres is fine and their size is

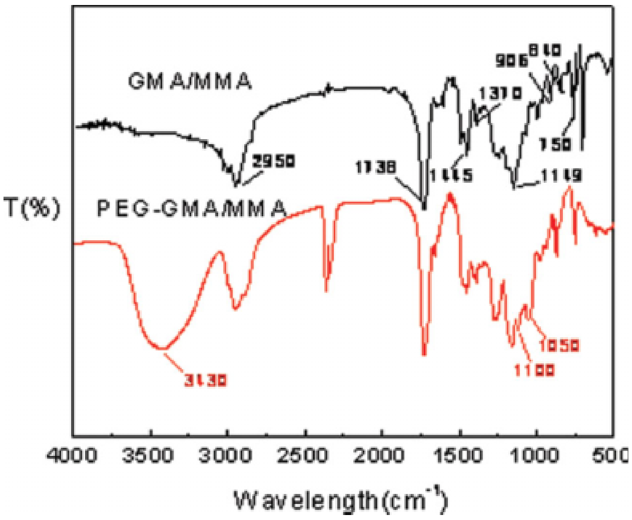


Figure 1. FTIR spectra of GMA/MMA and PEG-GMA/MMA microspheres.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

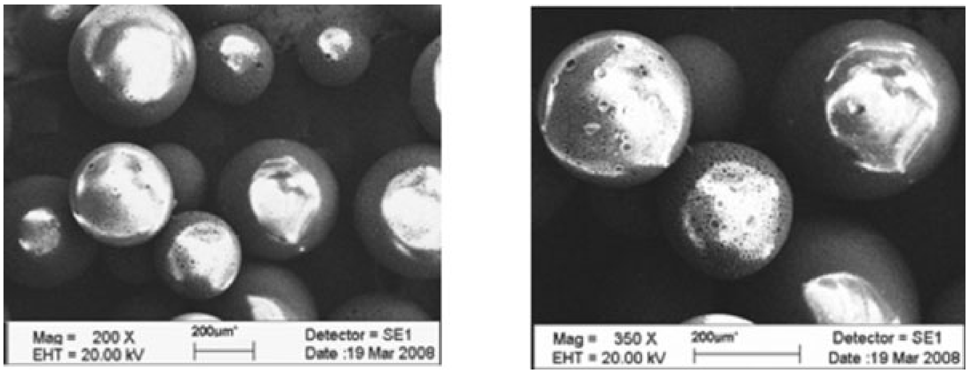


Figure 2. SEM images of GMA/MMA microspheres.

more uniform. The GMA/MMA microspheres with different grain sizes can be obtained via controlling the copolymerization conditions. The GMA/MMA microspheres used in this study have a mean diameter of 200 μm. It was found that the sphericity of the PEG-GMA/MMA microspheres still remains good after grafting reaction.

Catalytic activity of PEG-GMA/MMA in synthesis of butyl benzoate and catalytic mechanism

In Figure 3, the conversions of *n*-chlorobutane as a function of the time of the esterification reaction are displayed as different amounts of PEG-GMA/MMA microspheres with a PEG degree of 15 g/100 g are added into the reaction system. It can be seen clearly that in the absence of the catalyst, there is a little of reaction to occur, whereas in the presence of the triphase catalyst, PEG-GMA/MMA microspheres, the conversion of *n*-chlorobutane increases rapidly with increasing the added amount of the solid catalyst. This indicates that the PEG-GMA/MMA microspheres have obvious catalytic activity for the esterification reaction of *n*-chlorobutane with benzoic acid. The conversion of *n*-chlorobutane reaches 55% at 55°C in 6 h as only 1 g of PEG-GMA/MMA microspheres is added.

In water phase, benzoic acid reacts with KOH, forming negative benzoate ions. The PEG on the swelled PEG-GMA/MMA microspheres will associate with K^+ ions like crown ether, forming complexes positively charged on PEG-GMA/MMA microspheres, denoted as K^+-PEG-GMA/MMA. These positive complexes will combine with benzoate ions negatively charged, and at the same time, these anionic ions are transferred into the organic phase. The nucleophilic substitution between *n*-chlorobutane and the negative benzoate ion as attacking reagent is allowed to be carried out, resulting in the product, butyl benzoate. In the meantime, Cl atoms (in a form of anion) will be combined by K^+-PEG-GMA/MMA microspheres and are borne into water phase. Like this, the triphase catalyst PEG-GMA/MMA circularly plays a role in transferring negative benzoate ions from water to organic phase. The total reaction process of *n*-chlorobutane and benzoic acid as well as the mechanism of the triphase-transfer catalysis can be schematically expressed in Scheme 2.

Effects of various factors on triphase-transfer catalysis reaction

Effect of Temperature and Reaction Kinetics. Figure 4 gives the relationship curves of the conversion of *n*-chlorobutane and reaction time at different temperatures. The investigation results of some triphase catalysis systems[11,15] in which polymer-supported phase transfer catalyst were used, showed that there is no significant increase in conversion at agitation rates higher than 500 rpm. Therefore, to eliminate the external mass transfer resistance and to evaluate intrinsic kinetics, all experiments in this work were carried out at an agitation rate of 550 rpm. It can be observed in Figure 4 that the conversions of *n*-chlorobutane in the same period of time enhance remarkably with the reaction temperature, and it implies that the reaction rate is accelerated greatly by raising temperature. In general, in a phase transfer catalysis system, the mass transfer between two phases is rapid, whereas the reaction in the organic phase is usually a controlled step.[7,28,29] Because the nucleophilic reaction between *n*-chlorobutane and the negative benzoate ion in the organic phase has an activity energy with a certain value, warming will speed up the reaction.

Effect of Solvent Polarity. The triphase-transfer catalysis reactions were conducted using four solvents, CCl_4, $CHCl_3$,

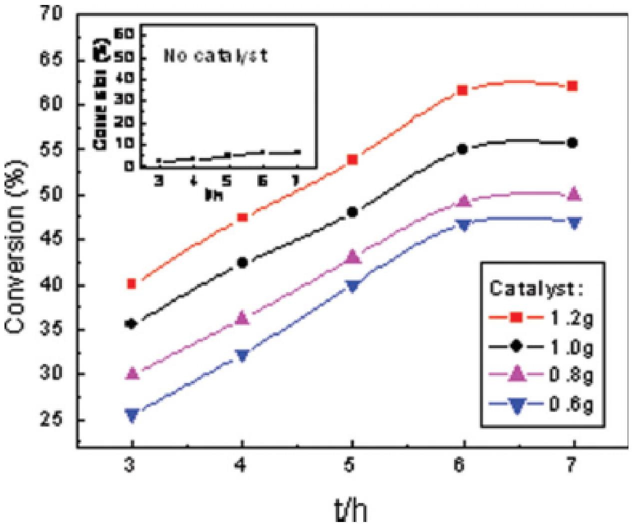
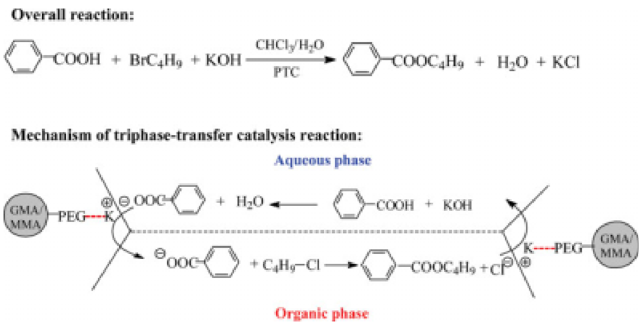


Figure 3. Variation curve of conversions of *n*-chlorobutane with time with different added amount of catalyst.

Temperature: 55°C; Solvent: CCl_4; V(OP)/V(WP): 2/1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 2. Mechanism of phase-transfer catalyzed esterification of *n*-chlorobutane and benzoic acid using triphase catalyst GMA/MMA microspheres.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

toluene, and nitrobenzene, respectively. The conversion curves of *n*-chlorobutane in different solvents are shown in Figure 5. By analyzing the rate data Figure 5 with the integral analysis method, it can be found that the rate constants do not increase with the polarity of the organic solvents and are all close to 0.112 h^{-1}, namely, the polarity of the solvent does not change the intrinsic kinetics of the nucleophilic substitution reaction. However, the reactivity of these solvents is obviously different as shown in Figure 5, and their reactivity is in the order: $C_6H_5NO_2 > CHCl_3 > C_6H_5CH_3 > CCl_4$. The reactivity of the solvents is associated with their polarity. The dielectric constants of these solvents are listed in Table 1. It can be seen that the reactivity order of these solvents is consistent with their polarity, namely, the solvent with stronger polarity has higher reactivity. The reason for this can be explained as follows. The formation of dipole–dipole force between polar solvent and chloride group of *n*-chlorobutane is favorable for the separation of chloride group from the *n*-butyl group. Also, the higher the polarity of the organic solvent is, the easier it is that the negative benzoate ion leaves the positive complex, K^+-PEG-GMA/MMA. Therefore, the stronger polarity of the solvent is favorable for the benzoate ion to displace chloride group in the nucleophilic substitution reaction. Nevertheless, on the other hand, *n*-chlorobutane as one reactant is also solvated tightly by polar solvent, so those solvents with strong polarity hinder collision between the reactants, *n*-chlorobutane and benzoate ion. The aforementioned experimental facts show that for nitrobenzene with the highest polarity among four solvents, the result of the competition between dipole–dipole force and solvation action still makes it to be the most reactive.

Effect of Volume of Organic Solvent. In the reaction system described in the "Catalytic property of microspheres PEG-GMA/MMA in esterification," the total volume of oil and water phases remained to be 60 mL, and the reactions were performed with changed volume ratios of the organic solvent (CCl_4) to water, namely the ratios of oil phase to water phase, denoted as V(OP)/V(WP). Figure 6 gives the relationship curve between the conversion (in 6 h) of *n*-chlorobutane and the ratios of oil to water. It can be seen from Figure 6 that the conversion first increases and then declines with the increase of the ratios of oil to water, and there is a maximum conversion as V(OP)/V(WP) = 2/1. The possible reason for this is as follows. At the initial stage, because the amount of the organic phase is small, and it limits the solubility of benzoate ions (in fact, benzoate ions exist in a combining form with K^+-PEG-GMA/MMA), affect negatively the reaction in the organic phase. Along with the increase of the amount of the organic phase, the reaction is accelerated, leading to the enhancement of the conversion. However, as the amount of the organic phase is excessive, i.e., V (OP)/V (WP) is over 2/1, the reaction rate in the

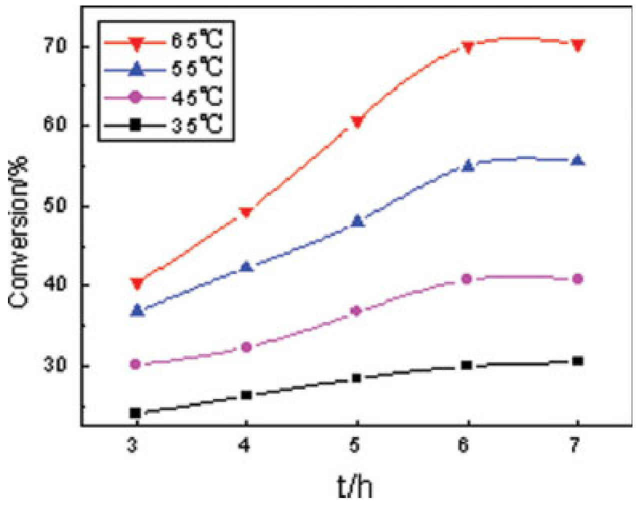


Figure 4. Variation curve of conversions of n-chlorobutane with time at different temperatures.

Solvent: CCl_4; V(OP)/V(WP): 2/1; amount of added catalyst: 1 g. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

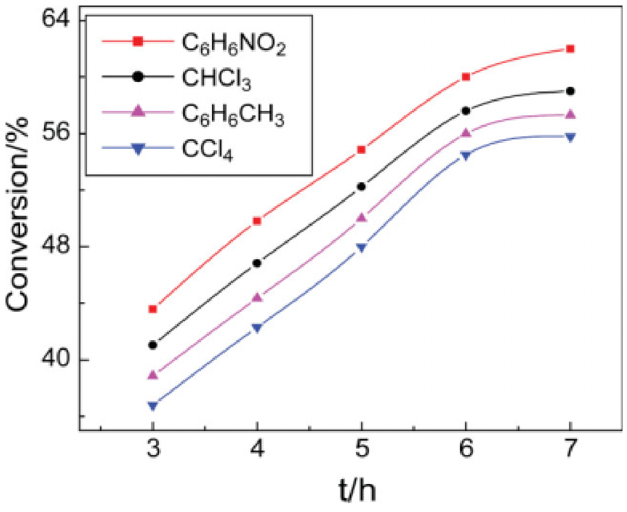


Figure 5. Variation curve of conversions of *n*-chlorobutane using different organic solvents.

Temperature: 55°C; Solvent: CCl_4; V(OP)/V(WP): 2/1; Amount of added catalyst: 1 g. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 1. Dielectric Constant Data of Solvents

Solvent	CCl_4	$CHCl_3$	$C_6H_5NO_2$	$C_6H_5CH_3$
Dielectric constant (ε)	2.24	4.81	34.82	2.4

organic phase will decline due to diluting effect of the reactants. Perhaps, phase inversion will occur as V (OP)/V (WP) is over 2/1, and it affects the phase transfer catalysis greatly. By this token, for this investigated triphase-transfer catalysis system, the optimal volume ratio of oil phase to water phase is 2/1.

Effect of PEG Density on PEG-GMA/MMA Microspheres. The triphase-transfer catalysis reactions were conducted with different PEG-GMA/MMA microspheres on which the density of the supported PEG are different (i.e., different grafting degrees), but the total added amount of PEG into the reaction system remained identical (0.15 g). Figure 7 shows the conversion curves as used different PEG-GMA/MMA microspheres. To more clearly display the effect of the density of the supported PEG on the reaction in the organic phase, the conversion as a function of the density of the supported PEG on PEG-GMA/MMA microspheres is figured from the data in 6 h in Figure 7, as shown in Figure 8.

It can be observed clearly from Figure 8 that the conversion of *n*-chlorobutane first increases and then decreases with the increase of the density of the supported PEG on PEG-GMA/MMA microspheres, and there is a maximum conversion as the density of the supported PEG is 15/100 g. This fact reflects the effect of the hydrophilic and hydrophobic property of the polymeric carrier on the phase-transfer catalysis reaction. As the density of the supported PEG is low, the hydrophobicity of PEG-GMA/MMA microspheres is strong. Here, the microspheres cannot be fully swelled in water phase, and the grafted PEG cannot be revealed sufficiently but enwrapped inner the microsphere. This will lead to the decrease of the ability to bear the benzoate ions for the triphase catalyst and slow down the substitution reaction in the organic phase. However, if the density of the supported PEG is too high, the hydrophilicity of PEG-GMA/MMA microspheres is stronger, so that the swelled extent of the microspheres in organic phase will be poorer. This will lead to the phenomenon that the benzoate ions borne by the triphase catalyst are wrapped and cannot be released favorably. It will also slow down the substitution reaction in the organic phase. Therefore, this is an important finding for the triphase catalyst prepared using polymeric microspheres as

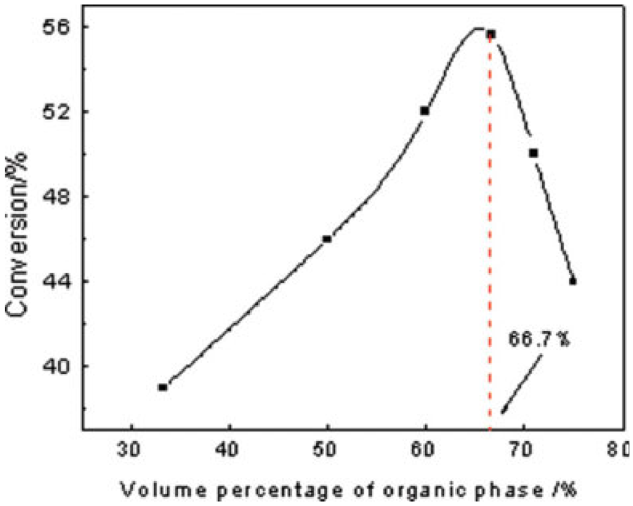


Figure 6. Variation curve of conversions of *n*-chlorobutane at different volume ratio of oil to water phase.

Temperature: 55°C; Solvent: CCl_4; Reaction time: 6 h; Amount of added catalyst: 1 g. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

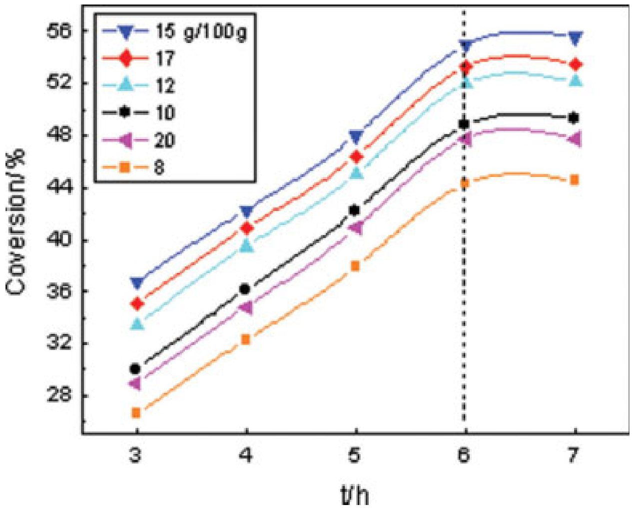


Figure 7. Variation curve of conversions of *n*-chlorobutane using triphase catalysts with different PEG densities.

Temperature: 55°C; Solvent: CCl_4; V(OP)/V(WP): 2/1; Amount of added PEG: 0.15 g. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

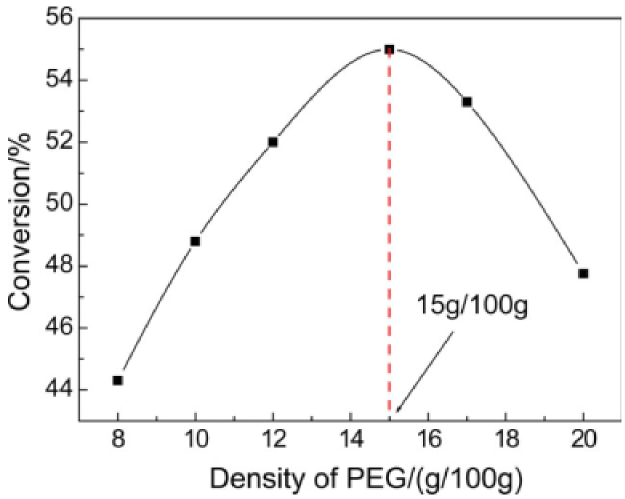


Figure 8. Effect of PEG density on triphase catalyst on conversions of *n*-chlorobutane.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

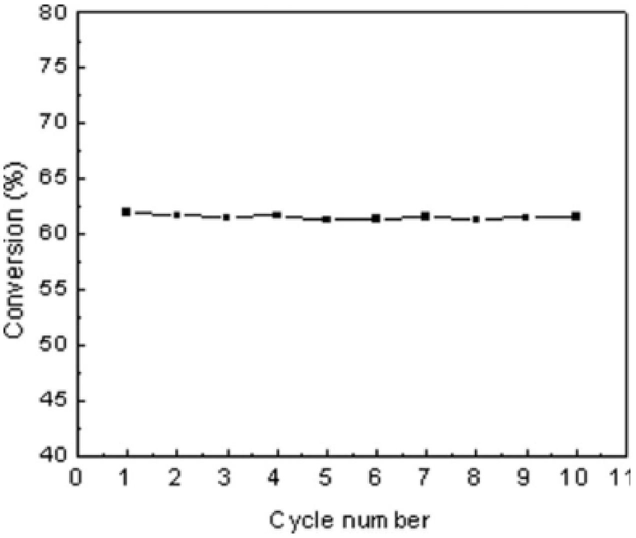


Figure 9. Effect of cycle number of reusing on catalyst activity.

Temperature: 55°C; Solvent: CCl_4; V(OP)/V(WP): 2/1; Amount of added catalyst: 1 g.

carrier, that is, the phase-transfer catalyst density on the carrier will change the hydrophilic and hydrophobic property of the polymeric carrier greatly, and will further affect the catalysis activity of the triphase catalyst. For the triphase catalyst prepared using polymeric microspheres as carrier, there is an optimal density of phase-transfer catalysis species. Perhaps, there is another possible reason. The hydrophobicity and hydrophilicity of PEG-GMA/MMA microspheres vary with the density of the supported PEG. The hydrophobicity and hydrophilicity of PEG-GMA/MMA microspheres affect its adsorption ability toward various species. Perhaps, as the density of the supported PEG is 15 g/100 g, PEG-GMA/MMA microspheres have the strongest associating action for K^+ ions, and have the strongest bearing ability toward benzoate ions, resulting in a maximum conversion of *n*-chlorobutane.

Recycle and reuse property of PEG-GMA/MMA microspheres

After use, to remove the absorbed substances, solid catalyst PEG-GMA/MMA microspheres were sufficiently soaked and washed with ethanol and distilled water in turn, and then dried under vacuum. The recovered catalyst was reused in the phase-transfer catalyzed esterfication of *n*-chlorobutane and benzoic acid. In each recycle experiment, the reaction conditions were fixed (55°C, 6 h and CCl_4 as organic solvent, and so on). Figure 9 shows the conversion of *n*-chlorobutane as a function of recycle number. It can be seen clearly that during the 10 recycle experiments, the activity of the triphase catalyst is not nearly changed, indicating that PEG-GMA/MMA microspheres have excellent reuse property and high stability.

Conclusions

In this work, PEG was grafted on the copolymer microspheres of GMA and MMA, and a new triphase catalyst, PEG-GMA/MMA, was prepared successfully. The triphase catalyst was used in the esterification of n-chlorobutane in organic phase with benzoic acid in water phase, and PEG-GMA/MMA microspheres has been confirmed to be an efficient and stable catalyst for this phase-transfer catalysis reaction of liquid–solid–liquid. For this investigated phase-transfer system, several important results were obtained: the organic solvent with high polarity has more reactivity; the density of the supported PEG on PEG-GMA/MMA microspheres has an obvious effect on the activity of the triphase catalyst; the optimal volume ratio of oil phase to water phase is equal to 2:1.

Literature Cited

1. Łęska B, Pankiewicz R, Schroeder G, Maia A. Application of a new class B-podands in solid-liquid phase transfer catalysis. *J Mol Catal A*. 2007;269:141–148.
2. Jayachandran PJ, Wang M-L. Applied Catalysis A: general selective dichlorocyclopropanation of dicyclopentadiene under controlled phase transfer catalysis conditions. 2001;206:19–28.
3. Yadav GD, Purandare SA. Novelties of selective synthesis of 3-methyl-4′-nitro-diphenyl ether under solid-liquid phase transfer catalysis. *J Mol Catal A*. 2005;237:60–66.
4. Łęska B, Pankiewicz R, Schroeder G, Gierczyk B, Maciejewski H, Marciniec B. New type of repeated Si-C-podand catalysts for solid-liquid phase transfer reactions. *Catal Commun*. 2008;9:821–825.
5. Hasegawa K, Arai S, Nishida A. Synthesis of α-diazo-β-hydroxyesters through a one-pot protocol by phase-transfer catalysis: application to enantioselective aldol-type reaction and diastereoselective synthesis of α-amino-β-hydroxyester derivatives. *Tetrahedron*. 2006;62:1390–1401.
6. Arai S, Hasegawa K, Nishida A. One-pot synthesis of α-diazo-β-hydroxyesters under phase-transfer catalysis and application to the catalytic asymmetric aldol reaction. *Tetrahedron Lett*. 2004;45: 1023–1026.
7. Landini D, Maia A. Phase transfer catalysis (PTC): search for alternative organic solvents, even environmentally benign. *J Mol Catal A*. 2003;204–205:235–243.
8. Baj S, Siewniak A, Socha B. Synthesis of dialkyl peroxides in the presence of polymer-supported phase-transfer catalysts. *Appl Catal A*. 2006;309:85–90.
9. Yadav GD, Badure OV. Selective engineering in O-alkylation of *m*-cresol with benzyl chloride using liquid–liquid–liquid phase transfer catalysis. *J Mol Catal A*. 2008;288:33–41.
10. Wu H-S, Wang C-S. Liquid–solid–liquid phase-transfer catalysis in sequential phosphazene reaction: kinetic investigation and reactor design. *Chem Eng Sci*. 2003;58:3523–3534.
11. Glatzer HJ, Doraiswamy LK. Rate enhancements due to autocatalysis and heterogenization in phase transfer catalysis: a comparative study. *Chem Eng Sci*. 2000;55:5149–5160.
12. Wu H-S, Lee C-S. Catalytic activity of quaternary ammonium poly(-methylstyrene-*co*-styrene) resin in an organic solvent/alkaline solution. *J Catal*. 2001;199:217–223.
13. Glatzer HJ, Doraiswamy LK. Triphase catalysis: a correlation for Sherwood number using the rotating disk contactor (RDC) developed earlier. *Chem Eng Sci*. 2001;56:3815–3827.
14. Grinberg S, Kas'yanov V, Srinivas B. Soluble polymer-bound phase-transfer catalysts. *React Funct Polym*. 1997;34:53–63.
15. Desikan S, Doraiswamy LK. Enhanced activity of polymer-supported phase transfer catalysts. *Chem Eng Sci*. 2000;55:6119–6127.
16. Li J-T, Liu X-F. An efficient and practical synthesis of 2,3-epoxyl-1,3-diaryl-1-propanone by combination of phase transfer catalyst and ultrasound irradiation. *Ultrason Sonochem*. 2008;15:330–333.
17. Sauvagnat B, Lamaty F, Lazaro R, Martinez J. Polyethylene glycol (PEG) as polymeric support and phase-transfer catalyst in the soluble polymer liquid phase synthesis of α-amino esters. *Tetrahedron Lett*. 1998;39:821–824.
18. Kang R, Ouyang X, Han J, Zhen X. A novel silica-polyglycol supported polymer-anchored bimetallic palladium-based catalyst for dechlorination of aromatic chlorides in water. *J Mol Catal A*. 2001;175:153–159.

19. Łęska B, Pankiewicz R, Schroeder G, Maia A. A new type of B-podand catalysts for solid–liquid phase transfer reactions. *Tetrahedron Lett*. 2006;47:5673–5676.
20. Jin G, Ido T, Goto S. Rate enhancement effect of third liquid phase on dibenzyl ether production in solid–liquid–liquid phase transfer catalytic system. *Catal Today*. 2003;79–80:471–478.
21. Łęska B, Siewniak PRA. Synthesis of dialkyl peroxides in the presence of polyethylene glycol or its derivatives as phase-transfer catalyst in liquid–liquid–liquid system. *Appl Catal A*. 2007;321:175–179.
22. Jin G, Ido T, Goto S. Effect of third-phase properties on benzyl-*n*-butyl ether synthesis in phase transfer catalytic system. *Catal Today*. 2001;64:279–287.
23. Naik SD, Doraiswamy LK. *Reactors, Kinetics, and Catal*. 1998;44:612–646.
24. Parvulescu V, Popa A, Davidescu CM, Vdlceanu R, Vass M, Luca C. Phase-transfer catalytic activity of polymer-supported ammonium and phosphonium salts in oxidation of benzyl alcohol with hydrogen peroxide. *React Funct Polym*. 1997;33:329–336.
25. Ghiaci M, Sedaghat ME, Kalbasi RJ, Abbaspur A. Applications of surfactant-modified clays to synthetic organic chemistry. *Tetrahedron*. 2005;61:5529–5534.
26. Chung H-T, Hsiao H-C, Weng H-S. Performance of the polymer- and oxide-supported triphase catalysts and effect of ultrasound on their stabilities. *J Chin Inst Chem Eng*. 2008;39:449–455.
27. Miyajima F, Iijima T, Tomoi M, Kimura Y. Aromatic nucleophilic fluorination with KF catalyzed by polymer-supported phosphonium salts under solid–solid–liquid phase transfer conditions. *React Funct Polym*. 2000;43:315–324.
28. Wang M-L, Tseng Y-H. Phase transfer catalytic reaction of *n*-bromobutane and sodium sulfide in a two-phase solution and its kinetics. *J Mol Catal A*. 2003;203:79–93.
29. Wang ML, Tseng YH. Phase-transfer catalytic reaction of dibromo-*o*-xylene and 1-butanol in two-phase solution. *J Mol Catal A*. 2002;179:17–26.

Manuscript received Jan. 30, 2009, revision received Apr. 13, 2009, and final revision received June 30, 2009.