

SYNTHESIS AND APPLICATIONS OF CROSS-LINKED POLY(DIALLYLDIMETHYL AMMONIUM CHLORIDE) AND ITS DERIVATIVE COPOLYMERS AS EFFICIENT PHASE TRANSFER CATALYST FOR NUCLEOPHILIC SUBSTITUTION REACTIONS

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Abstract Cross-linked poly(diallyldimethylammonium chloride) and its derivative copolymers were synthesized and used as phase transfer catalyst in the nucleophilic substitution reaction especially halogen exchange reactions. In addition, the effect of hydrophilic-hydrophobic character of the polymers in the nucleophilic reactions was investigated.

Keywords: Poly(diallyldimethylammonium chloride); Phase transfer catalyst; Nucleophilic substitution reaction; Halogen exchange reaction.

INTRODUCTION

Phase transfer catalysts (PTC) facilitate inter-phase transfer of species and therefore make reactions between reagents in two immiscible phases possible. Phase transfer catalysts have been used widely in the synthesis of various organic chemicals in both liquid-liquid and solid-liquid systems^[1]. In the other words, this technique has been widely used in organic synthesis and also in industrial applications such as synthesis of dyes, pharmaceuticals, perfumes, flavorants, agricultural chemicals, monomers and also polymers^[2].

However, one of the most important problems in the applications of soluble phase transfer catalysts such as quaternary onium salts is separation of the catalyst from reaction mixture and also its subsequent reuse or disposal. Using insoluble phase transfer catalysts is a significant advancement for these problems, because of their easy separation and potential for recycling^[2]. During the last decades much interest have been focused on the applications of functionalized polymers as phase transfer catalysts because they provide great ease in separation of the catalyst and isolation of the products^[3, 4]. However, the higher cost, the lack of physical and chemical stability and lower activity are disadvantages of traditional insoluble polymer supported phase transfer catalysts^[5].

Poly(diallyldimethylammonium chloride) was first prepared in the 1950 s^[6]. The kinetics and mechanism of the polymerization process as well as the structure of the resulting polyelectrolyte from diallyldimethylammonium chloride were elucidated in these years^[7, 8]. Because of unique chemical structure of poly(diallyldimethylammonium chloride), the research about it and also its copolymer and derivatives has not diminished^[9–11]. Interestingly, the highly hydrophilic permanently charged quaternary ammonium groups provide the polymer with high water solubility and solution properties corresponding to those of strong polyelectrolytes^[12].

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Although the primary applications of this polymer remain in flocculation, dewatering, coagulation, retention, flotation and similar separation processes, some other emerging applications have been reported in recent years^[13]. One of the new applications is the using of poly(diallyldimethylammonium chloride) as phase transfer catalyst. Recently, we have reported the use of cross-linked poly(diallyldimethylammonium chloride) as an efficient polymeric phase transfer catalyst in chemo-selective and regio-selective reduction of aldehydes and ketones by NaBH₄ under solid-liquid system^[2] and also under solvent-free condition^[14].

In this article, a systematic study was carried out on the use of cross-linked poly(diallyldimethylammonium chloride) and its derivative copolymers as a very efficient phase transfer catalysts in nucleophilic substitution reactions.

EXPERIMENTAL

Materials and Techniques

Diallyldimethylammonium chloride (65%) was purchased from Fluka. *N,N'*-methylenebisacrylamide was used as crosslinking agent and was purchased from Merck. Solvents were distilled and used. Other reagents were purchased from Merck and used without further purifications. In order to obtain reaction yields, gas chromatography was used and recorded on a Shimadzu GC14-A. IR spectra were run on a Perkin-Elmer-IR-157.G spectrophotometer. NMR spectra were recorded on a Bruker Advance DPX instrument (300 MHz). TGA spectra were obtained by TGA-Q-50-V6.3 build 189.

Synthesis of Diallylbutylamine

Butylamine (0.1 mol, 7.31 g) in a three necked round bottomed flask was placed in an ice bath and agitated vigorously with magnetic stirrer. Allyl chloride (0.23 mol, 17.60 g) and a solution of sodium hydroxide (0.25 mol, 10.0 g) in 100 mL of water were added separately over a 1 h period. A thick white precipitate was formed. The slurry mixture was then heated at 36°C for 3 h and at 60°C for an additional 3 h. The mixture was cooled and the precipitate was filtered. The organic layer was separated and the aqueous phase was extracted with three 150 mL portions of ether. The organic extracts were combined, dried over 5 g NaOH and fractionally distilled at atmospheric pressure. The product (7.81 g, 51%) was collected as colorless oil. FTIR: 3084 cm⁻¹ (C=C-H), 2954 cm⁻¹ (C-H), 1641 cm⁻¹ (C=C), 1465 cm⁻¹ (CH₂), 1375 cm⁻¹ (CH₃), 720 cm⁻¹ (sequence CH₂); ¹H-NMR (300 MHz), CDCl₃/δ: 0.96 (3H, t), 1.28 (2H, m), 1.35 (2H, m), 2.3 (2H, t), 3.22 (2H, d), 3.4 (2H, d), 5.1 (2H, t), 5.77 (4H, m).

Synthesis of Diallylbutylmethylammonium Iodide (1)

To a solution of diallylbutylamine in ethanol (3 mol/L, 100 mL) placed in a 250 mL round bottom flask was added one equivalent of methyl iodide. The resulting mixture was allowed to stir at 60°C for 72 h. At the end of this time the solvent was removed under reduced pressure. The residue was dissolved in distilled water and extracted with diethyl ether (3 × 200) to remove un-reacted reagents. The aqueous solution was freeze-dried to isolate the methylbutylammonium iodide. The compound was obtained as waxy solids. FTIR: 3084 cm⁻¹ (C=C-H), 2954 cm⁻¹ (C-H), 1641 cm⁻¹ (C=C), 1465 cm⁻¹ (CH₂), 1375 cm⁻¹ (CH₃), 720 cm⁻¹ (sequence CH₂).

Synthesis of Diallylhexylamine (2a)

Diallylamine (0.24 mol, 23.32 g) and 1-bromohexane (0.06 mol, 9.90 g) in a 50 mL of ethanol were refluxed overnight under argon atmosphere. The solvent was removed and crude product was dissolved in 100 mL of CH₂Cl₂ and washed three times with aqueous NaOH (pH = 12). After evaporation of the solvent, brownish liquid was distilled under reduced pressure (1333.20 Pa) at 100°C to give 8.7 g (yield 80%) of colorless liquid. FTIR: 3084 cm⁻¹ (C=C-H), 2954 cm⁻¹ (C-H), 1641 cm⁻¹ (C=C), 1465 cm⁻¹ (CH₂), 1375 cm⁻¹ (CH₃), 720 cm⁻¹ (sequence CH₂); ¹H-NMR (300 MHz), CDCl₃/δ: 0.99 (3H, t), 1.25 (6H, m), 1.36 (2H, m), 2.51 (2H, t), 3.19 (2H, d), 3.29 (2H, d), 5.19 (4H, t), 5.75 (2H, m).

Synthesis of Diallyloctylamine (2b)

Diallylamine (0.2 mol, 19.43 g) and 1-bromooctane (0.06 mol, 11.59 g) were refluxed for 24 h in a 50 mL of ethanol under argon atmosphere. The solvent was removed and crude product was dissolved in 100 mL of CH_2Cl_2 and washed three times with aqueous NaOH (pH = 12). After evaporation of the solvent, brownish liquid was distilled under reduced pressure (1333.20 Pa) at 160°C to give 9.55 g (yield 76%) of colorless oil. FTIR: 3084 cm^{-1} (C=C-H), 2954 cm^{-1} (C-H), 1641 cm^{-1} (C=C), 1465 cm^{-1} (CH_2), 1375 cm^{-1} (CH_3), 720 cm^{-1} (sequence CH_2); $^1\text{H-NMR}$ (300 MHz), CDCl_3/δ : 0.96 (3H, t), 1.22 (10 H, m), 1.29 (2H, m), 2.49 (2H, t), 3.16 (2H, d), 3.25 (2H, d), 5.16 (4H, t), 5.73 (2H, m).

Synthesis of Diallyldodecylamine (2c)

Diallylamine (0.16 mol, 15.55 g) and 1-bromododecane (0.04 mol, 9.97 g) were refluxed for 48 h in 75 mL of ethanol under argon atmosphere. The solvent was removed and crude product was dissolved in 200 mL of CH_2Cl_2 and washed three times with aqueous NaOH (pH = 12). Solvent and excess diallylamine were evaporated at ambient pressure (115°C) and the brownish residual liquid was distilled under reduced pressure (1333.20 Pa) at 185°C to give 8.81 g (yield 83%) of oil liquid. FTIR: 3084 cm^{-1} (C=C-H), 2954 cm^{-1} (C-H), 1641 cm^{-1} (C=C), 1465 cm^{-1} (CH_2), 1375 cm^{-1} (CH_3), 720 cm^{-1} (sequence CH_2); $^1\text{H-NMR}$ (300 MHz), CDCl_3/δ : 0.99 (3H, t), 1.30 (18H, m), 1.4 (2H, m), 2.45 (2H, t), 3.18 (2H, d), 3.31 (2H, d), 5.2 (4H, t), 5.75 (2H, m).

Preparation of Quaternary Ammonium Salts 2a, 2b and 2c

To a solution of (**2a**, **2b**, **2c**) (3 mol/L) in ethanol placed in a 250 mL round bottom flask one equivalent of methyl iodide was added. The resulting mixture was allowed to stir at 60°C for 72 h. At the end of this time the solvent was removed under reduced pressure. The residue was dissolved in distilled water and extracted with diethyl ether (3×100) to remove un-reacted reagents. The aqueous solution was freeze-dried to isolate the corresponding alkylmethylammonium iodide monomer. The monomer was obtained as waxy solids. Diallylhexylmethylammonium iodide **3**, -octylmethyl ammonium iodide **4** and -dodecylmethylammonium iodide **5** were obtained in near 94% yield. FTIR: 3084 cm^{-1} (C=C-H), 2954 cm^{-1} (C-H), 1641 cm^{-1} (C=C), 1465 cm^{-1} (bend CH_2), 1375 cm^{-1} (CH_3), 720 cm^{-1} (sequence CH_2).

Preparation of Cross-linked Poly(diallyldimethylammonium chloride) (PDADMAC)

An aqueous solution of diallyldimethylammonium chloride (6.0 g in 4.0 g deionized water, 60% W/W) and *N,N'*-methylenebisacrylamide as cross-linking agent (0.06 g, 0.39 mmol) was added to a three necked round bottom flask which equipped with a condenser, an argon inlet and an argon outlet. The solution was purged with argon for 45 min at room temperature and then was placed in an oil bath (65°C). An aqueous solution of ammonium persulphate (0.12 g, 2% W/W) was added slowly in 1.5 h to the monomer solution. After 24 h the mixture was poured in acetone and cross-linked polymer was filtered. This polymer was washed three times with acetone for separation of the monomer residue. Finally the polymer was dried under vacuum at 55°C (5.1 g, 83%). FTIR: 2954 cm^{-1} (C-H), 1664 cm^{-1} (amide C=O), 1465 cm^{-1} (CH_2), 1375 cm^{-1} (CH_3).

Preparation of the Cross-linked Copolymers

An aqueous solution of diallyldimethylammonium chloride (3 g) and corresponding comonomers (**1**, **2a**, **2b** and **2c**) (3 g) in deionized water (4 mL) and *N,N'*-methylenebisacrylamide as cross-linking agent (0.06 g, 0.39 mmol) was added to a three necked round bottom flask which equipped with a condenser, an argon inlet and an argon outlet. The mixture was polymerized in the presence of ammonium persulphate (0.12 g, 0.53 mmol) as the initiator at 65°C under argon atmosphere. After 24 h, the precipitated cross-linked copolymer was filtered easily and dried under vacuum condition at 50°C overnight. The yield of copolymers was as follow: copolymer **1** (4.5 g, 75%), copolymer **2** (4.9 g, 82%), copolymer **3** (3.6 g, 60%) and copolymer **4** (3.2 g, 53.3%). FTIR: 2954 cm^{-1} (C-H), 1664 cm^{-1} (amide C=O), 1465 cm^{-1} (CH_2), 1375 cm^{-1} (CH_3).

General procedure for Anion Exchange in Polymers

The cross-linked copolymer (5.0 g) was added to the aqueous solution of NaCl (2 mol/L, 100 mL) and the

mixture was stirred for 12 h. Then the mixture was filtered and washed carefully with distilled water, ether and dried at 50°C under reduced pressure.

Nucleophilic Substitution Reactions

Reaction of octylbromide with potassium thiocyanate in the liquid-liquid-solid condition

The cross-linked copolymer (0.50 g), octylbromide (0.01 mol, 1.93 g), KSCN (0.02 mol, 1.10 g), CHCl₃ (10 mL) and water (5 mL) were charged in a round bottomed flask. Then, the reaction mixture was stirred at 60°C for 24 h. After this time, the copolymer was recovered by filtration and yield of the reaction was obtained by GC analysis.

Reaction of octylbromide with potassium thiocyanate in the solid-liquid condition

The cross-linked copolymer (0.50 g), octylbromide (0.01 mol, 1.93 g), KSCN (0.02 mol, 1.10 g) and acetonitrile (10 mL) were charged in a round bottomed flask. Then, the reaction mixture was stirred and refluxed for 12 h. After this time, the copolymer was recovered by filtration and yield of the reaction was obtained by GC analysis.

Reaction of octylbromide with potassium iodide in the liquid-liquid-solid condition

The cross-linked copolymer (0.50 g), octylbromide (0.01 mol, 1.93 g), KI (0.05 mol, 8.30 g), toluene (25 mL) and water (5 mL) were charged in a round bottomed flask. Then, the reaction mixture was stirred at 100°C for 24 h. After this time, the copolymer was recovered by filtration and yield of the reaction was obtained by GC analysis.

Reaction of octylbromide with potassium iodide in the solid-liquid condition

The cross-linked copolymer (0.50 g), octylbromide (0.01 mol, 1.93 g), KI (0.05 mol, 8.30 g), and acetonitrile (10 mL) were charged in a round bottomed flask. Then, the reaction mixture was stirred and refluxed for 12 h. After this time, the copolymer was recovered by filtration and yield of the reaction was obtained by GC analysis.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Functional Polymers

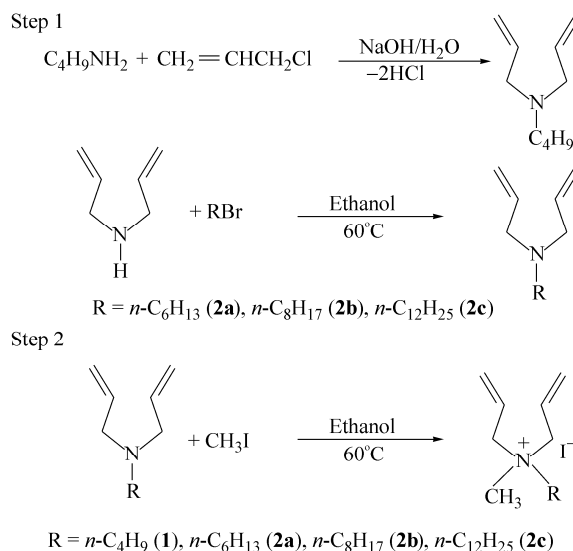
Polymerization of diallyldialkylammonium salts through an alternating intramolecular-intermolecular mechanism (popularly known as “cyclopolymerization”) is an established approach to prepare high molecular weight polymeric ammonium compounds containing five member cyclic rings along the polymer backbone^[15]. The modification of diallylamine to various diallyldialkylammonium salts and their free radical polymerization have produced a variety of functional polyammonium salts. By varying the nature of alkyl substituents, hydrophilicity and hydrophobicity affinity in polycations have been controlled^[16, 17]. These diallyldialkylammonium monomers have also been copolymerized with other monomers to produce novel polymeric structures that have found uses in various applications.

In the present study, the appropriate amphiphilic diallyldialkylammonium monomers were prepared in two steps. In the first step, desired alkyldiallylamines were prepared by reaction of diallylamine with a long chain alkyl bromide (hexyl, octyl and dodecyl bromide) but for butyldiallylamines by reaction of butylamine with allylchloride. Then, alkyldiallylamines were quaternized by reaction with methyl iodide (Scheme 1). These reactions are in general quite efficient and high yield (greater than 70% in each case).

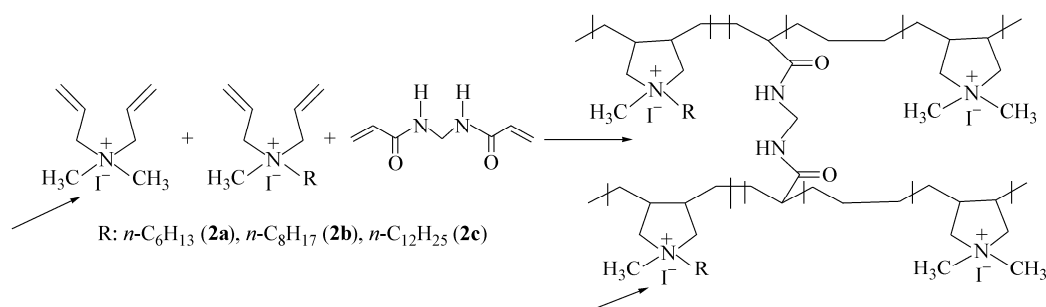
The regular increasing of hydrophobicity character of these monomers from butyl to dodecyldiallylamine was the main reason for their selection in this study. Furthermore, these monomers are water soluble and exhibit surfactant like properties in water.

Previous kinetic studies indicate that to achieve high conversion, high molecular weight and also low residual double bonds in the cyclopolymerization of diallyldialkyl quaternary ammonium monomers, the optimum monomer concentration should be 50%–65%^[18–20]. In addition, cyclocopolymerization of diallyl-quaternary ammonium monomers in such a high concentration has been reported to yield a random copolymer^[21].

With regard to the above information, the cross-linked copolymers were synthesized *via* reaction of the desired comonomers in 60%–95% concentration and in the presence of *N,N'*-methylenebisacrylamide as a cross-linking agent (Scheme 2).



Scheme 1 Synthesis of diallylmethylalkylammonium iodide monomers



Scheme 2 Copolymerization of monomers in presence of crosslinking agent

Following characteristic peaks were observed in FTIR spectra of the synthesized polymers and cross-linked copolymers: at 2954 cm⁻¹ for C–H, 1465 cm⁻¹ for CH₂, 1375 cm⁻¹ for CH₃ and 720 cm⁻¹ for sequence CH₂. In addition, the peaks at 3084 cm⁻¹ for C=C–H and 1641 cm⁻¹ for C=C related to monomers were completely absent. Furthermore, in the case of cross-linked copolymers a peak at 1664 cm⁻¹ for C=O (amide) related to the *N,N'*-methylenebisacrylamide was observed.

Thermal behavior and stability of the copolymers were investigated by thermo-gravimetric analysis (TGA). TGA curves of the polymers are shown in Fig. 1.

These curves show that the thermal stability of these copolymers decreases slightly with increase in the length of the alkyl chain. These results suggested that degradation occurred in side chain at first and moved to lower temperatures with increasing side chain length. The onset of main degradation steps are situated between 220°C and 300°C. The degradation for dodecyl side chain was initiated at 220°C and for other copolymers this temperature regularly increased to 300°C. Weight loss in the lower temperatures (< 150°C) is related to water existing in some of the copolymers.

Finally, degree of swelling of the cross-linked polymers in different solvents was determined (Table 1). As it can be expected the swelling percent of the cross-linked polymers were increased in apolar solvents with increasing of their alkyl side chain length and vice versa in polar solvents.

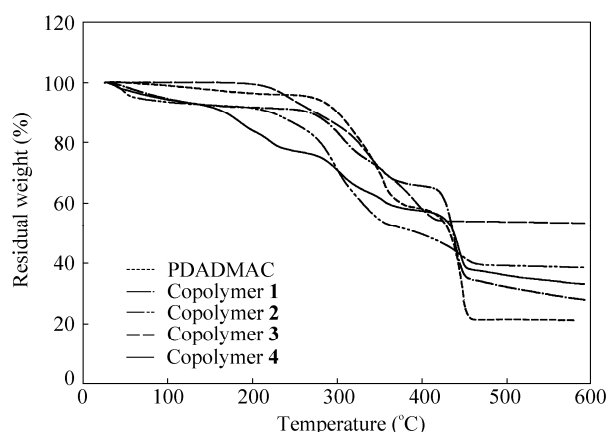


Fig. 1 Comparative TGA curves of the copolymers

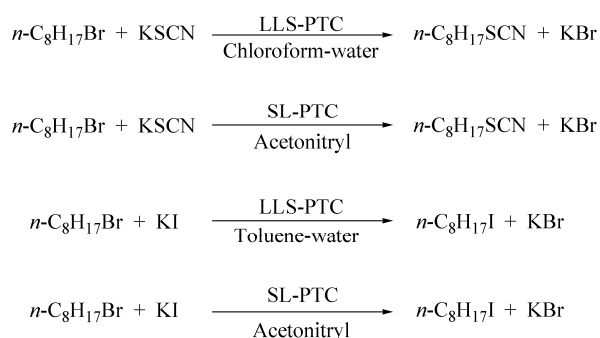
Table 1. The swelling percent of the cross-linked polymers in different solvents

Entry	Solvent	Homopolymer	Copolymer 1	Copolymer 2	Copolymer 3	Copolymer 4
1	H ₂ O	0.3	0.3	0.21	0.2	0.14
2	EtOH	0.52	0.45	0.4	0.31	0.26
3	Et ₂ O	1.6	1.6	1.8	2.1	2.5
4	THF	2.1	2.6	3	3.1	3.8

Applications

Nucleophilic reactions are an important method in organic synthesis. To accelerate the reaction of alkyl halides with metal salts, phase transfer catalyst is often used.

At first, for examination of catalytic behavior and efficiency of the synthesized functional polymers as phase transfer catalyst in nucleophilic substitution reactions, the reaction of potassium thiocyanate and potassium iodide with octylbromide was selected as a standard reaction. These reactions were performed in two different conditions involving liquid-liquid-solid (LLS) and solid-liquid (SL) conditions (Scheme 3).



Scheme 3 Nucleophilic reactions carried out with copolymers as PTC

The results of these reactions are summarized in Table 2.

As it is shown in Table 2, there is a remarkable difference between efficiency of these polymeric catalysts in LLS-PTC and SL-PTC conditions. Generally, it can be expected that the structure of phase transfer catalyst has a higher effect in LLS-PTC than in SL-PTC condition because of the non-polar character of organic solvents usually used in LLS-PTC. In reaction of octylbromide with KSCN under LLS-PTC system, the effect of PTC was more important and with increasing side chain length the yield of reactions was much improved. In the reaction of octylbromide with KI with regard to the size of iodide anions a more balance between hydrophilicity and hydrophobicity character of polymeric catalyst was needed and therefore the copolymer **3** which had octyl

side chains showed the best result and with dodecyl side chain also the yield of reaction was decreased. Interestingly in SL-PTC system with using acetonitril as an aprotic solvent because of high power of the solvent there is not a remarkable difference between the catalysts, and the yield of reactions of KSCN and also KI with all of them was almost the same.

Table 2. Reaction of octylbromide with KSCN and KI under LLS-PTC and SL-PTC conditions

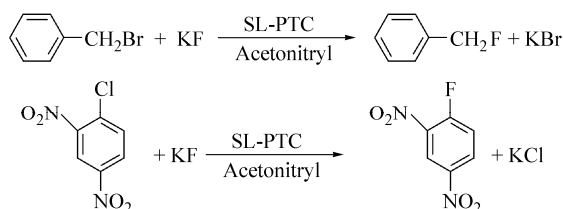
Catalyst	LLS-PTC		LLS-PTC		SL-PTC		SL-PTC	
	KSCN (at 60°C)		KI (at 100°C)		KSCN (at 80°C)		KI (at 80°C)	
	Solvent	Yield (%)	Solvent	Yield (%)	Solvent	Yield (%)	Solvent	Yield (%)
Homopolymer	CHCl ₃ /H ₂ O	1.39	Toluene /H ₂ O	6.5	CH ₃ CN	99.8	CH ₃ CN	98.2
Copolymer 1	CHCl ₃ /H ₂ O	14	Toluene /H ₂ O	46.4	CH ₃ CN	100	CH ₃ CN	98.7
Copolymer 2	CHCl ₃ /H ₂ O	22	Toluene /H ₂ O	80	CH ₃ CN	99.9	CH ₃ CN	98.6
Copolymer 3	CHCl ₃ /H ₂ O	80.7	Toluene /H ₂ O	100	CH ₃ CN	99.5	CH ₃ CN	99.9
Copolymer 4	CHCl ₃ /H ₂ O	95	Toluene /H ₂ O	11.1	CH ₃ CN	100	CH ₃ CN	99.5

In continuation of this research the synthesized copolymers were used in fluorine-exchange reactions. The phase-transfer catalysis fluorine-exchange reactions could only be carried out in the solid- liquid system because of the water sensitivity of these reactions, and potassium fluoride and also acetonitril must be quite dry before use. In addition, in this reaction the type of counter ion of the phase transfer catalyst is very important. As we observed, if the counter ion was iodide the reaction was not performed but with a change to fluoride the reaction was carried out.

The results of the reaction of benzyl bromide with potassium fluoride and also reaction of 2,4-dinitro-chlorobenzene with potassium fluoride under LS-PTC condition are summarized in Table 3 (Scheme 4).

Table 3. Fluorine-exchange reactions with KF under LS-PTC condition in acetonitrile

Entry	Catalyst	Substrate			
		Benzyl bromide		2,4-Dinitro-chlorobenzene	
		Temp (°C)	Yield (%)	Temp (°C)	Yield (%)
1	Homopolymer	80	43	80	29
2	Copolymer 1	80	47	80	26
3	Copolymer 2	80	57	80	37
4	Copolymer 3	80	71	80	64
5	Copolymer 4	80	85	80	62



Scheme 4 Nucleophilic reaction between benzyl bromide and 2,4-dinitro-chlorobenzene with potassium fluoride

As shown in Table 3, there is a remarkable difference between efficiency of the polymeric catalysts, and the best yield is obtained from the copolymer 4 which has the lowest hydrophilicity character.

In addition, comparison of results of SL-PTC system in Tables 2 and 3 shows that in the fluorine-exchange reactions there is a remarkable difference between the polymeric catalysts contrary to reaction of octylbromide with KSCN and KI. This is reasonable because of the more sensitivity of fluorine-exchange reactions to the

polarity of catalytic center and its environment.

Finally, in both catalytic systems (LLS-PTC and SL-PTC) workup of the reaction was easy and the polymeric catalyst can be removed from the reaction mixture *via* simple filtration. The filtered polymeric catalyst could be recovered several times and used without any loss in its capacity and efficiency.

CONCLUSIONS

In conclusion we have demonstrated that cross-linked copolymers of diallyl dimethylammonium chloride and its alkylated derivatives (butyl, hexyl, octyl and dodecyl) are useful and efficient polymeric phase transfer catalysts for the nucleophilic substitution reaction especially in fluorine-exchange reactions. In addition, it is shown that the action of these catalysts depends on some factors such as solvent, counter ion of the catalyst and structure of catalysts. These polymeric catalysts have the inherent advantages of a solid catalyst, including operational simplicity, filterability, and reusability.

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