Synthesis, Characterization and Use of Polymer-Supported Phase Transfer Catalyst in Organic Reactions

Inderjeet Kaur, Vandna Kumari, Poonam K. Dhiman

Department Of Chemistry, Himachal Pradesh University, Shimla-5

ABSTRACT: A polymer-supported (PS) phase transfer catalyst, polyethylene-g-quaternary ammonium salt (PE-g-Q_N^+), is prepared through a three-step graft copolymerization of maleic anhydride (MAn) onto polyethylene (PE) by photochemical method using 1% benzophenone (Bz) as photosensitizer. Post grafted acid hydrolysis of polyethylene-g-maleic anhydride (PE-g-MAn) results in the preparation of PE-g-succinic acid which on further treatment with tetrabutylammonium bromide (TBAB) under basic conditions in tetrahydrofuran (THF) gives PE-g-Q_N^+. Optimum conditions pertaining to maximum percentage of grafting have been evaluated as a function of concentration of maleic anhydride, amount of photosensitizer, and time of reaction. Maximum percentage of grafting (25%) was obtained using 3.57 mol of MAn and 0.5 mL of 1% Bz in 120 min. The PE and graft copolymers, PE-g-MAn, and PE-g-Q_N^+ were characterized by FTIR Spectroscopy and thermogravimetric analysis (TGA). The ionic nature of quaternary ammonium salt, PE-g-Q_N^+ has also been confirmed by conductance measurements. PE-g-Q_N^+ reagent have been used successfully for polymerization, amidation, and esterification reactions. The products obtained were characterized by FTIR and H^1NMR spectral methods. The reagent was reused for the further reactions and it was observed that the polymeric reagent polymerize, amidate, and esterificate the compounds successfully but with little lower product yield. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3185–3191, 2011

Key words: polyethylene; maleic anhydride; polymer-supported phase transfer catalyst; tetrabutylammonium bromide; polymerization; amidation; esterification; thermogravimetric analysis

INTRODUCTION

Basically, phase transfer catalysis is a method, which allows carrying out the reaction between a substrate soluble in organic solvent and an ionic reagent insoluble in this. Phase transfer catalyst is thus an instrument in transporting the reactant from one phase to another. Thus, phase transfer catalysis offers a variety of conceptual and practical advantages when performing carbonylation for example, malonic esters can be made by phase transfer catalytic carbonylation of ethyl chloroacetate at 1 atm CO at 25°C in the presence of cobalt carbonyl.[1] Oxidation of p-methyl benzyl alcohol by sodium hypochlorite[2] has been achieved with high yields in short reaction time at room temperature. Epoxidation,[3] chiral epoxidation,[4] cyanation,[5] Michael addition,[6] chiral alkylation[7,8] are some other reactions that have been studied using phase transfer catalyst with high yields at moderate reaction conditions and avoiding use of hazardous chemicals.

Phase transfer catalysts have also been used in polymerization reactions. The kinetics of phase transfer agents assisted free radical polymerization of o-tolyl methacrylate using potassium peroxydisulfate as water soluble initiator and tributylbenzylammonium chloride as the phase transfer catalyst was conducted in ethylacetate-water biphase system at 60°C.[9] Synthesis of poly (amide-esters) derived from diphenols with the amide group in the side chains by using several quaternary ammonium salts was successfully carried out by Tagle et al.[10] Shigeo and Chonghui[11] synthesized high molecular weight polyesters having reactive group in the side chain chemoselectively by a water phase/organic phase interfacial polycondensation using phase transfer catalysts.

Choi and Lee[12] reported that the polymers, poly-(methyl methacrylate), prepared by phase transfer catalyzed polymerization, were found to have considerably high molecular weight and more uniform molecular weight distribution than the polymers prepared by conventional organic initiators such as AIBN (azobis isobutyronitrile) under similar reaction conditions. Polymerization of a water soluble monomer, acrylamide (AAm) and the graft copolymerization of AAm onto a water insoluble polymer backbone, isotactic polypropylene (IPP), using a water insoluble initiator, benzoyl peroxide (BPO), and a phase transfer catalyst, tetrabutylammonium bromide ($Bu_4N^+Br^-$), were carried out in a water/xylene binary solvent system by Kaur et al.[13]

Correspondence to: I. Kaur (ij_kaur@hotmail.com).

Ooi et al.[14] developed highly diastereo and enantioselective direct asymmetric aldol reaction of a glycinate Schiff's base with aldehydes catalyzed by chiral quaternary ammonium salts. Tetra-*n*-propyl and tetra-*n*-butyl ammonium bromates were used for the oxidation of a variety of aromatic amines to nitro compounds in high yields.[15] O'Donnell[16] studied the development and application of chiral phase-transfer catalysis for the enantio-selective synthesis of optically active α-amino acid derivatives using achiral Schiff's base esters. Tomoi et al. [17] discovered that polystyrene supported phosphoric triamides and polyacrylamides efficiently catalyzed phase transfer reactions (such as bromide/iodide and bromide/cyanide exchange), either as such[18] or properly substituted and quaternized,[19] were employed to promote ethers,[18] azidohydrins,[19] halohydrins,[20] and thiocyanohydrins[21] formation. Poly (ethylene glycols), (PEGs), have extensively been used as inexpensive and easily functionalized supports for the immobilization of reagents and the recovery and recycling of catalysts.[22]

Polymerization of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane with 4,4-isopropylidendiphenol (bis phenol-A) and 4,4-sulfonyl diphenol in a two phase system of water and dichloromethane in the presence of dibenzo-24-crown-8 has been carried out by Ahmed.[23]

Organic and polymerization reactions by phase transfer catalyst immobilized on the polymeric supports have not been explored by polymer supported PTCs. The supported catalyst can be easily recovered by simple filtration and reused. In this study we, therefore, report the synthesis of a polymer support from polyethylene graft copolymerized with maleic anhydride. Postgrafting reactions converting the anhydride moieties to free carboxylic groups followed by treatment with TBAB to yield polymer supported quaternary groups which are utilized to carry out polymerization, amidation and esterification reactions.

EXPERIMENTAL

Materials and methods

Commercial polyethylene beads of density, 0.92 g/L was purchased from Thukral Trading, Delhi, India. The beads were dissolved in xylene and precipitated by the addition of methanol. The precipitates were filtered and dried in an oven at 50°C. Benzophenone solution in acetone (1%) was used as photosensitizer for grafting reaction. Maleic anhydride (MAn) (Burgoyne Urbidges) was used as received. UV lamp (125 W) was used as the source for UV rays. Tetrabutylammonium bromide (TBAB) (Sisco), tetrahydrofuran (THF) (Laboratory Rasayan), potassium persulfate

(KPS) (Merck), ethylbromide (S.D. Fine Chem), benzamide (Laboratory reagent), sodium benzoate (Laboratory Reagent) were used as received. Monomers that is, styrene (Merck), methyl methacrylate (Laboratory Chemcials), and acrylonitrile (Merck) were washed with 5% aqueous NaOH, dried over anhydrous $MgSO_4$ and distilled before use.

Graft copolymerization

Preparation of polyethylene-g-maleic anhydride (PE-g-MAn)

Dried polyethylene (100 mg) was suspended in 10 mL of xylene in a beaker. A known amount of maleic anhydride in 5 mL of acetone and a definite amount of the sensitizer were added to the reaction mixture. The mixture was irradiated with the UV lamp for different time periods. To avoid the rise in temperature during the reaction, a constant flow of water was maintained outside the reaction vessel. After the stipulated time period, the reaction was stopped and excess methanol was added to the reaction mixture. The product was filtered through the dried and weighed Whatmann filter paper and washed thoroughly with water to remove any unreacted maleic anhydride. The grafted PE was dried to a constant weight. The percentage of grafting (Pg) was calculated from the increase in the initial weight of the PE in the following manner:

$$\text{Percentage of grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1, respectively, are the weights of the original PE and grafted PE after complete removal of the unreacted maleic anhydride. Percentage of grafting was determined as a function of monomer concentration, amount of photosensitizer, and reaction time, thus evaluating optimum conditions for preparation of PE-g-MAn (Resin I).

Preparation of PE-g-quaternary ammonium salt (PE-g-Q_N^+)

Hydrolysis of PE-g-MAn. Hydrolysis of the maleic anhydride grafted PE was carried out by refluxing the mixture of PE-g-MAn (Resin I) (0.100 g) with 20 mL of water and 0.5 mL of concentrated sulfuric acid at boiling temperature for at least 4 h. The product, PE-g-succinic acid (Resin II), was filtered, washed with water, and dried.

Conversion of PE-g-succinic acid to PE-g-Q_N^+

Resin II was suspended in 20 mL of tetrahydrofuran with 0.5 mL pyridine in a dry round bottomed flask. To the mixture was added 0.200 g of tetrabutylammonium

bromide and refluxed the mixture for 4 h at the boiling point of THF. The product, PE-g-Q$_N^+$ (Resin III) was filtered, dried and used as a polymer supported phase transfer catalyst for different reactions.
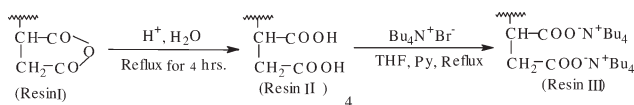
Polymerization reaction

For polymerization reactions the following general procedure was followed: A definite amount (1 mL) of the monomer (styrene/methyl methacrylate/acrylonitrile) taken in 10 mL of benzene was placed in a round bottomed flask. To it was added a solution of 0.350 g of potassium persulfate (KPS) in 10 mL of distilled water and 0.100 g of polymer supported phase transfer catalyst that is, PE-g-Q$_N^+$. The reaction flask was placed in water bath at a constant temperature (60°C) under constant stirring for 2 h. After the stipulated time, the flask was removed from the water bath and methanol was added to precipitate the homopolymer. The homopolymer and the polymer support were filtered and washed thoroughly with distilled water to remove any unreacted KPS. The residue was treated with an appropriate solvent [benzene for polystyrene, acetone for poly (methyl methacrylate) and dimethyl formamide for poly (acrylonitrile)] to dissolve the respective homopolymer and the polymer support was separated by filtration. The respective polymers [PS (23.3%)/PMMA) (8.51%)/PAN) (62.0%)] were reprecipitated by the addition of methanol. The recovered polymer supported PTC, Resin III, can be reused directly or after regeneration for polymerization reactions.

Amidation reaction

The following general procedure for amidation reaction of ethyl bromide to give N-ethyl benzamide using PE-g-Q$_N^+$ was carried out: Resin III PE-g-Q$_N^+$ (1 g) was suspended in 10 mL of water and kept for half an hour at room temperature for swelling. In a separate round-bottomed flask, benzamide (1.4 g) in 25 mL of 50% aqueous solution of NaOH was taken. To it was added benzene (25 mL) and the preswollen PTC. The reaction flask was kept for refluxing at boiling temperature of benzene. To this a definite amount of ethyl bromide (1 mL) in 5 mL of benzene was added drop-wise with efficient stirring. After the complete addition of ethyl bromide (1.5 h), stirring was continued for another 2.5 h at the refluxing temperature. After the stipulated time, the reaction mixture was cooled and 15 mL of water was added. The reaction mixture was filtered and the residue that is,

the polymer support was washed with ethanol. The organic phase of the filtrate was separated, washed with water (3 × 20 mL) until neutral and dried over anhydrous MgSO$_4$. The solution was decanted and evaporated to give a crystalline solid product, N-ethyl benzamide (0.32 g, 18.8%), with melting point 124°C.

Esterification reaction
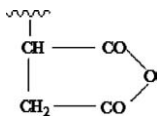
The general procedure used for the preparation of ethyl benzoate was as follows: A solution of sodium benzoate, 4.320 g (0.03 mol) and 0.100 g of PE-g-Q$_N^+$ in 20 mL of H$_2$O in a round-bottomed flask was kept for refluxing under continuous stirring. To it a solution of ethyl bromide, 2.2 mL (0.03 mol) in 20 mL of benzene was added drop wise from the dropping funnel. The refluxing was continued for at-least 4 h under constant stirring. Thereafter, the reaction mixture was cooled at room temperature, diluted with water (15 mL) and filtered to separate out the polymer support. The organic layer was separated and washed with H$_2$O (3 × 20 mL) until neutral and dried over anhydrous MgSO$_4$. The organic layer was decanted off and evaporated to give the product that is, ethyl benzoate (1.1 mL, 26.2%) having fruity smell. The product formed also gave the positive ester test.

Characterization

The characterization of Resin I and III that is, PE-g-MAn and PE-g-Q$_N^+$ and the products obtained from polymerization, amidation, and estrification reactions using Resin III have been made by spectroscopic and thermogravimetric methods. FTIR spectra were carried out on Beckman Spectrophotometer, H^{1}NMR on JEOL FT-NMR AL 300 MHz Spectrophotometer, and TGA on LINSEIS, L 81-11 Germany made, in air at the heating rate of 10°C/min.

The ionic nature of quaternary salt, Resin III, has also been confirmed by conductance measurements. The conductance was made on Shedlousky Conductance Cell, Conductivity Bridge. The specific conductance of the aqueous solution of maleic anhydride grafted polyethylene (Resin I) was observed at 37 × 10^{-6} ohm^{-1} and that of aqueous solution of PE-g-Q$_N^+$ (Resin III) was higher and was observed at 47 × 10^{-6} ohm^{-1}. Conductivity and viscosity measurements have been made on tetra-n-butylammonium bromide - carbon tetrachloride solutions for the mole ratio range 1 : 40 to 1 : 2 at temperatures from 25 to 40°C by Denning and Plambeck[24] and it was observed that specific conductance first increases and then decreases with increasing mole fraction of TBAB. The maximum appears in the region of ∼ 1 : 5 mol ratio of TBAB to carbon tetrachloride. The rapid increase in viscosity with concentration brings about some decrease in conductivity.

<div style="text-align:center">

TABLE I
IR Spectral Data of PE and PE-g-MAn

</div>

Sample	Structure	C—H (υ cm^{-1})	C=O (υ cm^{-1})	C—O (υ cm^{-1})
PE	$-(CH_2-CH_2)_{\overline{n}}-$	2920.9		
		2850.2		
		1466.9 (def.)		
PE-g-MAn	CH—CO, CH$_2$—CO (anhydride structure)	1372.9 (def.)		
		2922.3	1835	1080.3
		2847.8	1795	1021.9

FTIR spectroscopy

The FTIR spectrum of PE-g-MAn (Table I) shows two peaks at 1795 and 1835 cm^{-1} due to C=O str. of anhydride group and peaks at 1080.35 and 1021.98 cm^{-1} of anhydride group due to C—O str. which confirms the formation of the graft copolymer, PE-g-MAn.

The FTIR spectrum of PE-g-Q$_N^+$ (Fig. 1) in addition to the regular bands due to υ_{C-H} str. at 2920 cm^{-1} of PE shows a characteristic peak at 2367.1 cm^{-1} due to ammonium salt. Other characteristic bands at 1628.9 cm^{-1} due to COO$^-$ asymmetric stretching and 1378.5 cm^{-1} due to COO$^-$ symmetric stretching of caboxylate ion also appeared in place of the $\upsilon_{C=O}$ str. band at 1710 cm^{-1} of the parent compound. Similar IR spectral pattern of PE functionalized by introducing succinic anhydride groups and their conversion to quaternary salt was observed by Sarkar et al.[25,26] The butyl groups attached to the nitrogen atom of the quaternary ammonium salt also shows two strong bands at 2920 and 2848.3 cm^{-1} due to υC—H asymmetric and symmetric stretching and peaks at 1467.1 and 1378.5 cm^{-1} due to υC—H asymmetric and symmetric deformation of CH$_3$.

Thermogravimetric analysis

The primary thermograms of PE, PE-g-MAn and PE-g-Q$_N^+$ are presented in Figure 2 and the initial decomposition temperature (IDT), final decomposition temperature (FDT) and decomposition temperature (DT) at every 10% weight loss are presented in Table II.

It is observed from the primary thermograms that the PE, PE-g-MAn and the polymer supported ammonium salt PE-g-Q$_N^+$ show single stage decomposition. The IDT (439.36°C) and FDT (504.35°C) of PE-g-MAn are higher than those for PE (423.91°C and 497.83°C, respectively). The decomposition for every 10% weight loss of grafted PE also occurs at higher temperature as compared to that of unmodified PE. Both the samples that is, the ungrafted and grafted polyethylene decompose almost at the same rate with small temperature difference between each 10% weight loss leaving behind no residue. Higher IDT, FDT, and DT values at every 10% weight loss of the

grafted samples indicate that the thermal stability of polyethylene increases upon grafting and this also confirms the formation of the graft copolymer of polyethylene and maleic anhydride.

The primary thermogram of PE-g-Q$_N^+$ shows that the initial decomposition begins at a lower temperature (394.8°C) and continues smoothly till 486.4°C from where begins the final decomposition. The lower IDT is due to the early decomposition of the pendant ammonium carboxylate groups evolving ammonia and carbon dioxide. The DT values for every 10% weight loss are also lower but the temperature difference between each 10% weight loss is more than either PE or PE-g-MAn indicating that the decomposition proceeds slowly. The decomposition is complete with no left over residue.

RESULTS AND DISCUSSION

Irradiation of polymeric backbone in the presence of UV light causes the formation of free radical sites where grafting of vinyl monomers can take place. The process is accelerated by the use of photosensitizer that leads to the generation of active sites. In the present work, graft copolymerization of maleic anhydride onto PE by photochemical method using benzophenone as photosensitizer was carried out. The following are the different steps that take place during photochemical grafting of maleic anhydride onto polyethylene.
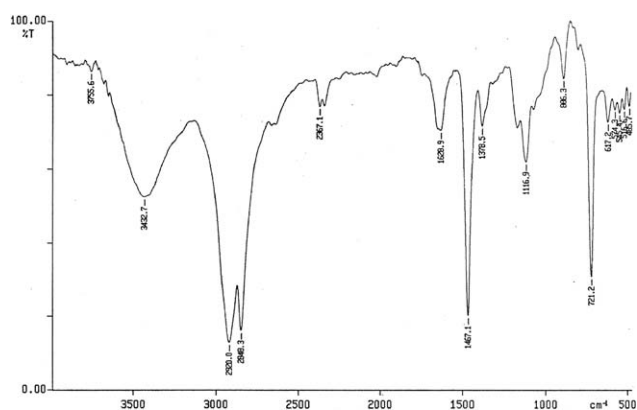

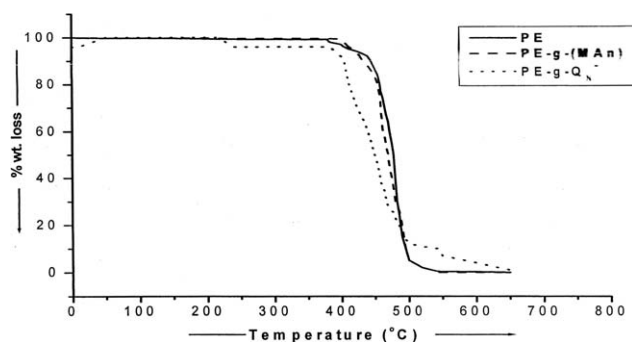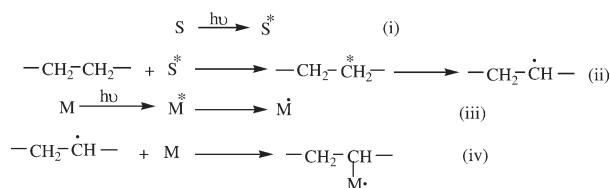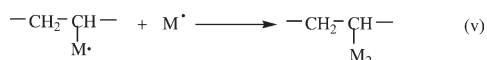**Figure 1**   FTIR Spectrum of PE-g-Q$_N^+$.

Figure 2 Primary Thermogram of PE, PE-g-MAn and PE-g-Q$_N{}^+$.

Initiation and propogation

$$S \xrightarrow{h\upsilon} S^* \qquad (i)$$

$$-CH_2{-}CH_2{-} \; + \; S^* \longrightarrow -CH_2{-}\overset{*}{C}H_2{-} \longrightarrow -CH_2{-}\overset{\cdot}{C}H{-} \quad (ii)$$

$$M \xrightarrow{h\upsilon} M^* \longrightarrow \overset{\cdot}{M} \qquad (iii)$$

$$-CH_2{-}\overset{\cdot}{C}H{-} \; + \; M \longrightarrow -CH_2{-}\underset{M\cdot}{C}H{-} \qquad (iv)$$

Termination

$$-CH_2{-}\underset{M\cdot}{C}H{-} \; + \; M^{\cdot} \longrightarrow -CH_2{-}\underset{M_2}{C}H{-} \qquad (v)$$

The effect of various reaction parameters on percentage of grafting of maleic anhydride onto PE was studied and the results are explained in the light of the mechanism.

Effect of amount of maleic anhydride

Figure 3 represents percentage of grafting as a function of concentration of maleic anhydride and it is observed that grafting percentage increases with increasing MAn, reaches maximum (25%) at MAn = 3.57 mol and decreases thereafter. At higher concentration, maleic anhydride undergoes [2 + 2] cycloaddition reaction thereby decreasing the concentration and percentage of grafting.

Effect of amount of benzophenone

Percentage of grafting was studied as a function of amount of benzophenone, the photosensitizer, (1%
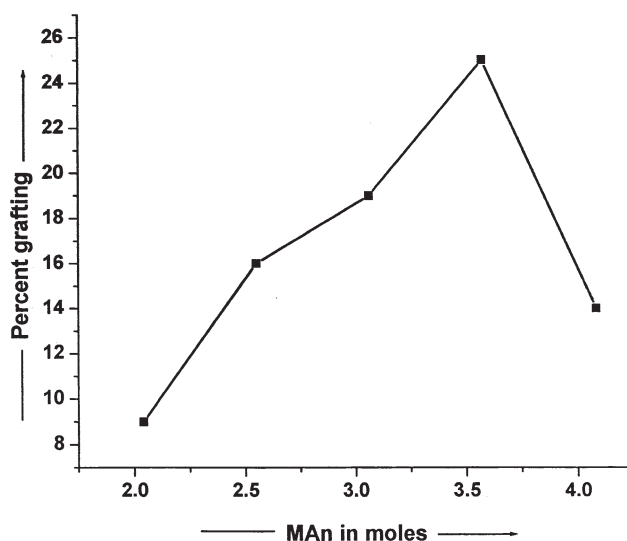

Figure 3 Effect of MAn on Pg.

solution in acetone), and the results are presented in Figure 4. Maximum grafting (25%) was obtained using 0.5 mL solution of benzophenone beyond which percent grafting decreases. The decrease in grafting at higher concentration of benzophenone is due the reason that under the conditions, it is photoreduced to benzhydrol thereby decreasing the activation process and hence percent grafting.

Effect of irradiation time

Figure 5 represents the effect of irradiation time on percentage of grafting and it is observed that percent grafting increases with increasing irradiation time reaches maximum (25%) in 120 min and decreases thereafter. Various chain transfer and termination reactions are promoted at longer time of irradiation that lead to decrease in grafting percentage.

Thus, polyethylene is successfully grafted with maleic anhydride introducing succinic anhydride grouping on the PE polymeric chains. These anhydride groups were opened to generate free carboxylic acids grouping of succinic acid that were converted to tetra ammonium groups on treatment with tetrabutylammonium bromide. Polymer supported quaternary salt was used as phase transfer catalyst for polymerization, amidation and esterification reactions and

TABLE II
IDT, FDT and DT at every 10% wt. loss of unreacted PE, PE-g-MAn and PE-g-Q$_N^+$

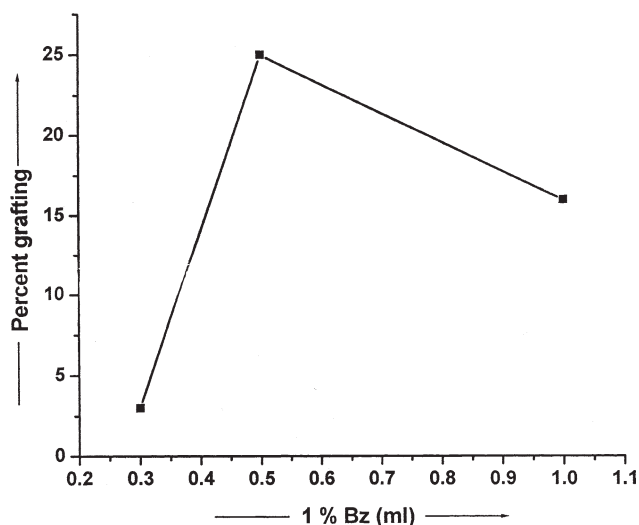| Sample	IDT (°C) at (% wt. loss)	FDT (°C) at (% wt. loss)	DT at every 10% wt. loss (°C)									Percent residue
			10%	20%	30%	40%	50%	60%	70%	80%	90%	
Unmodified PE	423.91 (4.29%)	497.83 (99.29%)	429.35	446.74	459.78	463.04	466.74	472.83	477.17	483.69	486.96	0.005%
PE-g-MAn	439.36 (3.93%)	504.35 (100.37%)	439.13	454.35	463.04	468.48	476.09	481.52	483.69	489.13	493.48	−0.445%
PE-g-Q$_N{}^+$	394.8 (6.75%)	486.4 (98%)	408.33	420.83	429.16	433.33	441.66	454.16	458.33	470.83	479.16	0%

Figure 4 Effect of amount of photosensitizer on Pg.

the products obtained in each case were characterized by FTIR and H^1NMR spectral data.

The formation of polystyrene (PS), polymethyl methacrylate (PMMA), and polyacrylonitrile (PAN) was confirmed by using IR and ^{1}HNMR and comparing with the known samples. The peak between 1640 and 1670 cm^{-1} due to $\nu_{C=C}$ str. present in the monomer is absent in the respective polymers confirming the conversion of the monomer to the polymer.

Polymerization of vinyl monomers using polymer supported PTC has not been explored, however, polymerization of methyl methacrylate[27] and acrylonitrile and methyl acrylate[28] using tetrabutylammonium bromide as PTC has been carried out.

Characteristic peaks for the secondary amide group, a strong peak at 1669.8 cm^{-1} due to $\nu_{C=O}$ str., a single band (m) at 3445.5 cm^{-1} due to ν_{N-H} str. and a strong band at 1526.3 cm^{-1} due to ν_{N-H} def in
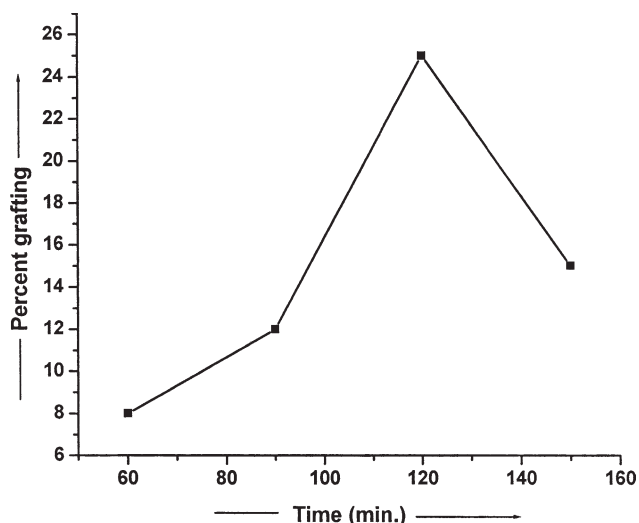

Figure 5 Effect of irradiation time on Pg.

the FTIR spectrum of N-ethyl benzamide and the absence of peaks due to the primary amide of benzamide confirms the formation of N-ethyl benzamide. N-alkylation of imides in the reaction of imide and alkyl halide using tertiary butylammonium bromide as PT catalyst has been recently investigated by Jaskowska and Kowalski.[29]

Peaks for $\nu_{C=O}$ str., conjugated with aryl group, at 1717.9 cm^{-1}, two ν_{C-O} str. bands near 1275.7 and 1108.4 cm^{-1} due to asymmetric and symmetric str. of C—O—C grouping and a band at 3044.8 cm^{-1} due to ν_{C-H} str. of aromatic ring and the presence of peak at 2927.2 cm^{-1} is due to ν_{C-H} str. of ethyl group confirms the formation of ethylbenzoate. Synthesis of cinnamyl acetate from cinnamy bromide and sodium acetate by solid–liquid phase PTC and its kinetic studies were carried out by Devulapelli and Weng using tertiary butyl ammonium bromide.[30]

H^1NMR spectral analysis

The H^1NMR spectra of the products obtained by polymerization, amidation, and esterification reactions of PS-phase transfer catalysis also confirms their formation.

The H^1NMR spectrum of polystyrene was found to overlap that of the authentic sample of PS confirming the polymerization reaction.

The H^1NMR spectrum of N-ethylbenzamide shows four types of signals for protons marked below:

$$\underset{(c)}{C}\underset{(b)}{ONH}\underset{(a)}{CH_2CH_3}$$

(d)
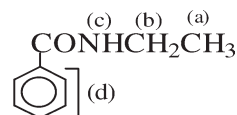
Methyl and methylene protons, marked (a) and (b), appearing as triplet and quartet, respectively, show peaks between 0.90–2.47 δ. However, the splitting of the peaks is not clear. The N—H proton marked (c) shows peak near 6.52 δ and the aromatic ring protons appear as singlet at 7.45 δ.

The H^1NMR spectrum of ethyl benzoate shows three types of signals for protons marked below:

$$\underset{(b)}{COO}\underset{(a)}{CH_2CH_3}$$

(c)
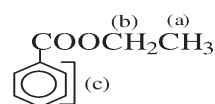
Methyl protons marked (a) shows a triplet at 1.12 δ and methylene protons marked (b) shows a quartet at 2.51 δ. A singlet near 7.81 δ due to aromatic ring protons marked (c) is also observed. All these peaks confirm the formation of ethyl benzoate.

From the foregoing discussion of FTIR and H^1NMR of the different polymerized, amidated and esterified products confirms phase transfer reactions take place successfully by using PE-g-Q_N^+ as PS-phase transfer catalyst.

Reusability/regeneration of PE-*g*-Q$_N^+$

The polymer supported quaternary ammonium salt after drying was reused for same phase transfer reaction without giving any treatment and it was observed that it efficiently formed the products although the yield is little low. For example, in case of polymerization of styrene, the percent yield was only 15.5%, as compared to that obtained with the fresh reagent (23.3%). The reagent, however, can be regenerated by washing the reagent with very dilute HCl solution followed by washing with very dilute NaOH solution and finally rinsing with distilled water. The washed polymer was hydrolyzed again to obtain PE-*g*-succinic acid and then refluxing with tetrabutylammonium bromide in THF and pyridine to give the regenerated PS-phase transfer catalyst that is, PE-*g*-Q$_N^+$. This can be used efficiently and effectively for the respective reactions as much as the fresh resin.

CONCLUSION

Successful synthesis of polymer supported immobilized quaternary salt on the grafted polyethylene backbone and its use as the polymer supported PT catalyst for the polymerization of styrene, methyl methacrylate, and acrylonitrile; amidation and estrification reactions has been achieved. The support can be still operative after its use and can also be easily regenerated for further polymerization, amidation, and esterification reactions.

References

1. Kantam, M.; Reddy, N.; Choudhary, B. Synth Commun 1990, 20, 2631.
2. Lee, G.; Freedman, H. U.S. Pat.4,079,075, 1978.
3. Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Nayori, R. J Org Chem 1996, 61, 8310.
4. Lygo, B.; Wainwright, P. Tetrahedron 1999, 112, 8595.
5. Dozeman, G.; Fiore, P.; Puls, T.; Walker, J. Org Proc Res Dev 1997, 1, 137.
6. Gestmann, D.; Lawrest, A.; Lawrent, E. J Fluorine Chem 1996, 80, 27.
7. Sabahi, M.; Irwin, R. U.S. Pat.5,347,043, 1994.
8. Corey, E.; Xu, F.; Noe, M. J Am Chem Soc 1997, 119, 12414.
9. Balakrishnan, T.; Muniraj, S. Proc IUPAC Int Symp Adv Polym Sci Technol 1998, 1, 153.
10. Tagle, L. H.; Diaz, F. R.; Cerda, G. O.; Penafiel, M. Polym Bull (Berlin) 1998, 40, 35.
11. Shigeo, N.; Chonghui, W. ACS Symp Ser 1997, 659, 231.
12. Choi, K. Y.; Lee, C. Y. Ind Eng Chem Res 1987, 26, 2079.
13. Kaur, I.; Singh, B.; Upasana J Appl Polym Sci 2004, 91, 2364.
14. Ooi, T.; Kameda, M.; Taniguchi, M.; Maruoka, K. J Am Chem Soc 2004, 126, 9685.
15. Das, S. S.; Nath, U.; Dob, D.; Das, P. J. Synth Commun 2004, 34, 2359.
16. O'Donnell, M. J. Acc Chem Res 2004, 37, 506.
17. Tomoi, M.; Ikeda, M.; Kakiuchi, H. Tetrahedron Lett 1978, 19, 3757.
18. Regen, S. L.; Mehrotra, A.; Singh, A. J Org Chem 1981, 46, 2182.
19. Tamami, B.; Mahdavi, H. Tetrahedron Lett 2001, 42, 8721.
20. Tamami, B.; Mahdavi, H. React Funct Polym 2002, 51, 7.
21. Tamami, B.; Mahdavi, H. Tetrahedron Lett 2002, 43, 6225.
22. Dickerson, T. J.; Reed, N. N.; Janda, K. D. Chem Rev 2002, 102, 3325.
23. Ahmed, I. K. J Appl Polym Sci 2004, 93, 651.
24. Denning, K. F.; Plambeck, J. A. Can J Chem 1972, 50, 1600.
25. Sarkar, N.; Bhattacherjee, S.; Sivaram, S. Langmuir 1997, 13, 4142.
26. Sarkar, N.; Sivaram, S. In Macro Molecules New Frontiers; Srinivasan, K. S. V., Ed.; Allied Publishers: Proceedings of International Symposium on Advances in Polymer Science and Technology. Macro-98, Jan 5–9, 1998; Vol. 1, p 421.
27. Osaitis, A.; Makuska, R. Polymer 1994, 35, 4896.
28. Vajjiravel, M.; Umapathy, M. J. Colloid Polym Sci 2008, 286, 729.
29. Jaskowska, J.; Kowalski, P. J Hetrocyclic Chem 2008, 45, 1371.
30. Devulapelli, V. G.; Weng, H. S. Catalysis Commun 2009, 10, 1638.