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### Synthesis and Modifications of Dendrimers on Polymer System Supported on Montmorillonite and Their Use in Organic Synthesis

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## **SYNTHESIS AND MODIFICATIONS OF DENDRIMERS ON POLYMER SYSTEM SUPPORTED ON MONTMORILLONITE AND THEIR USE IN ORGANIC SYNTHESIS\***

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**Key Words:** Montmorillonite, Phase Transfer Catalysts, Dendrimers, Supported Catalysts, Phosphonium Salts, Ammonium Salts, Phase-Transfer Catalysts

### **ABSTRACT**

Molecules with dendrimeric structure (cascade molecules) were attached to a polymer-montmorillonite system. The supported dendrimeric molecules were modified to produce ammonium and phosphonium salts. The catalytic phase-transfer activities of these systems have been investigated. The results from the catalytic activity studies showed that the dendrimeric system is highly activating the selected organic reactions. This was attributed to the dendrimeric structure of the system which consequently increase the weight efficiency. It is worth mentioning that this is the first report in the literature describing the formation of dendrimers on polymer-montmorillonite system and their use as phase-transfer catalysts.

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## INTRODUCTION

Homogeneous catalysts often have the advantage of giving high selectivity and high activity. However, these types of catalysts are often difficult to separate from reactants and products. Also, some of the homogeneous catalysts often possess poor thermostability and some of them are air sensitive and thus, not easy to handle. These disadvantages limit the applications of homogeneous catalysts in the industry [1-5].

It would be ideal to attach these catalysts to organic polymers or inorganic supports. Consequently, the attachment of these species to a crosslinked or insoluble polymer support, with all the usual advantages of retention, isolation and recovery, is a highly attractive proposition. They have long been recognized and industrially exploited. Thus, reaction products are easily separated from the catalyst and the latter is available for reuse. Since polymer-supported catalyst was reported by Regen [6], there has been much interest in polymer supported catalysts and reagents. The attachment of phase-transfer catalysts to insoluble polymer supports greatly simplifies their use in many anions promoted organic reactions.

Quaternary ammonium and phosphonium salts immobilized on insoluble synthetic polymers and inorganic oxides have been widely explored as triphase catalysts [7, 8-10]. Inherent disadvantages, such as their limited mechanical strength, thermal stability, alkali instability and acid instability, respectively, with polymers, silica and alumina, render these catalysts unsuitable for many reactions [11]. Montmorillonite is the support of current interest for immobilized and anchored catalysts [12, 13]. In view of the natural abundance of montmorillonite clay, it is one of the most naturally abundant minerals and available as inexpensive materials that have high physical and mechanical strengths as well as high chemical resistance [14]. Also the montmorillonite-based catalysts are environmentally friendly catalysts and were shown to have remarkably high activity in many reactions without any of the environmental disadvantages of using toxic homogeneous catalysts and reagents [5, 15]. Recently, significant interest has developed in the preparation and investigation of dendrimers, also known as cascade molecules. Dendrimers are highly branched oligomer or polymer like molecules, also these are species incorporating multidimensional elements of repetitive symmetry [16-22]. The elaboration of such dendrimeric structures along an insoluble polymeric backbone supported on montmorillonite, would seem to be promising for the development of highly efficient catalysts and would have many other advantages due to the use of clay as support and use of cascade molecules. The newly developed catalysts would have advan-

tages such as increased weight efficiency and improved mechanical properties. The objective of the present work is to report the synthesis of the modified cascade molecules supported on poly(methyl methacrylate-chloromethylstyrene)-montmorillonite and the use of these catalysts in organic synthesis.

## EXPERIMENTAL

### Materials

Chloromethylstyrene was obtained from Polyscience as a mixture of *m*-/*p*-isomers ( $\approx 30:60\%$ ) and was used without further purification. Methyl methacrylate (MMA) was supplied from Merck and was de inhibited before use. Montmorillonite (MMT) was supplied by ECC America, Inc. under the trade name Meniral Colloid-BP with average particle size of 75 micron, the exchange capacity of this clay is 90 m equiv/100 g and the interlayer spacing of 9.6 $\text{\AA}$ . The minerals were purified and activated as previously described [23]. Triethylamine was supplied from Aldrich and was used as received. Chloroacetyl chloride was supplied by Aldrich and was used as received. Triphenylphosphine was supplied from Aldrich and was used as received. Triethanolamine was supplied by GERMED, Germany and was used as received. *p*-Toluenesulfonyl chloride (Tosyl Chloride) was supplied from Merck and was used without further purification. IR spectra were recorded on the range of 4000–400  $\text{cm}^{-1}$  using a Perkin-Elmer 983 IR Spectrophotometer from potassium bromide disc. Microanalyses were recorded on Perkin-Elmer 2400. The quantitative conversion of the reactants to the products was followed by GLC, Perkin-Elmer 8400 Instrument and the products were identified by comparison with authentic samples.

### Preparation of (Chloromethyl Styrene and Methyl Methacrylate) Copolymer and its Ammonium Salt

This was synthesized as described previously by Akelah *et al.* [24] as follows: Copolymer of MMA and chloromethylstyrene (1:1) was prepared by bulk polymerization technique using AIBN as initiator. The ammonium salt of the produced copolymer was prepared by addition of 2% triethylamine to a stirred acetone solution of the copolymer, the stirring was continued at room temperature for 12 hours. The ammonium salt of the copolymer was purified by reprecipitation in ethanol and dried under vacuum (yield 91.7). The product was characterized by IR and elemental microanalysis (Table 1). The IR spectrum (II) showed the following peaks, 1607  $\text{cm}^{-1}$ , 1446  $\text{cm}^{-1}$ , (C=C aromatic), 1726  $\text{cm}^{-1}$  (C=O meth-acrylate),

TABLE 1. Elemental Microanalysis and Characteristics for Polymers and MMT-Polymers

Code	Analysis (%)						Cl m mol/g	N m mol/g
	C	H	N	Cl	P	S		
I	66.25	6.7	-	15.0	-	-	4.22	-
II	65.4	7.15	0.68	13.0	-	-	3.66	0.49
III	48.62	5.37	0.79	8.0	-	-	2.25	0.56
IV	50.87	6.17	4.38	-	-	-	-	2.857
V	49.2	6.0	4.0	11.1-11.2	-	-	3.154	2.86
VI	46.45	6.10	3.69	10.5-10.6	-	-	2.84	2.635
VII	53.1	7.1	3.7	10.1	0.8-1.0	-	2.845	2.64
VIII	52.9	6.0	4.1	9.0	-	4.7-5.1	2.535	2.93
IX	49.36	5.77	3.76	-	-	-	-	2.685
X	49.15	5.66	3.74	20.29	-	-	5.71	2.671
XI	48.34	6.02	6.6-6.9	18.3	-	-	5.15	4.928
XII	-	-	3.7	17.2	2.0	-	4.84	2.642

841, 1296  $\text{cm}^{-1}$  (1,4-disubstituted benzene ring), 2987  $\text{cm}^{-1}$  (CH aliphatic), 2928  $\text{cm}^{-1}$  (CH aromatic), 709  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}$ ), 1511  $\text{cm}^{-1}$  ammonium salt).

#### **Intercalation of Ammonium Salt of Copolymer (Methylmethacrylate-Co-Chloromethyl Styrene) with MMT**

This was carried out as described elsewhere [24-27] as following: 10 gm of Na-MMT was suspended and stirred overnight in 300 ml water and then 400 ml dioxane was added. A suitable amount of poly(methylmethacrylate/chloromethylstyrene) quaternary ammonium salt (15 gm) dissolved in 100 ml acetone was added to the stirred suspension portionwise. The stirring was continued for 24 hours at room temperature. The reaction product was recovered by filtration and was suspended in 200 ml DMF and allowed to stand overnight. Another solution of the ammonium salt of the copolymer in acetone (10 gm/75 ml) was added. The mixture was stirred for 24 hours at room temperature and the product was recovered

by filtration, dried under vacuum and purified by solvent extraction with acetone for 8 hours. The elemental microanalysis is shown in Table 1.

The IR spectrum for the product (III) showed the following peaks, C=C (aromatic  $1656\text{ cm}^{-1}$ ,  $1442\text{ cm}^{-1}$ , C=O (Methacrylate),  $1270$ ,  $843$ , (1,4-disubstituted benzene),  $2944\text{ cm}^{-1}$  (CH aliphatic),  $3051\text{ cm}^{-1}$  (CH aromatic),  $710\text{ cm}^{-1}$  ( $\text{CH}_2\text{C}$ ),  $1047$ ,  $523$ ,  $469$  (Si-O).

#### **Modification of the Intercalated Copolymer with Triethanolamine (IV)**

In a 100 ml flask containing 30 ml DMF, 4 gm of MMT-copolymer was added. The MMT-copolymer was allowed to swell overnight, then 20 ml of triethanolamine was added. The reaction mixture was stirred at  $90^\circ\text{C}$  for 4-days. The resultant material was filtered and washed successively several times with DMF and finally with ethanol and dried under vacuum to give 4.4 gm of IV. The characteristics of the product were as shown in Table 1.

#### **Modification of MMT-Copolymer Supported Triethanolamine (IV) with Chloroacetyl Chloride**

In a 100 ml flask was added 4 gm of MMT-copolymer (IV) followed by the addition of 30 ml dry benzene. The MMT-copolymer was allowed to swell in the dry benzene for 24 hours. A solution of 10 ml pyridine in 10 ml DMF was added to the swelled MMT-copolymer. The reaction mixture was ice-cooled and stirred followed by dropwise addition of 10 ml of chloroacetyl chloride in 10 ml dry benzene. The stirring and cooling was continued for 3 days and the product was filtered, washed several times with ethanol and was dried under vacuum to give 5.0 gm of V.

#### **Preparation of MMT-Copolymer Supported Ammonium Salt Catalyst (VI)**

To a suspension of 1.5 gm of V, in 10 ml DMF, a solution of 10 ml triethylamine dissolved in 10 ml benzene was added dropwise under stirring. The stirring was continued at room temperature for 2 days and the product was filtered, washed several times with benzene and finally with ethanol, dried under vacuum to yield 2.0 gm of VI.

#### **Preparation of MMT-Copolymer Supported Phosphonium Salt Catalyst (VII)**

In 100 ml flask, 2 gm of MMT-copolymer (V) was allowed to swell in 15 ml benzene. A solution of 1.0 gm triphenylphosphine dissolved in 5 ml benzene was added under stirring. The reaction mixture heated at reflux for 2 days and was filtered, washed several times with benzene and finally with ethanol and dried under vacuum to yield 2.75 gm of VII.

### **Modification of MMT-Copolymer Supported Triethanol Amine (IV) with p-Toluene Sulfonyl Chloride**

To 3 gm of IV swelled in 20 ml pyridine was added dropwise a solution of 9.5 gm ( 50 mmol ) of tosyl chloride in 5 ml pyridine. The reaction mixture was stirred at room temperature for 48 hours, then the reaction mixture was heated at 80°C for another 48 hours. The product was filtered and washed many times with ethanol and dried under vacuum to yield 3.3 gm of VIII.

### **Modification of MMT-Copolymer Supported Tosyl Chloride (VIII) with Triethanol Amine**

To a suspension of 2.5 gm of VIII in 20 ml DMF was added a solution of 10 ml triethanolamine in 10 ml DMF. The mixture was stirred at room temperature for four days, followed by stirring at 90°C for 2 days. The product was filtered and washed many times with chloroform and finally with ethanol. The product was dried under vacuum to yield 2.9 gm of IX.

### **Modification of Triethanolamine “Balloon” Dendrimer Supported on MMT (IX) with Chloroacetyl Chloride**

Modified product IX (1.7 gm) was allowed to swell overnight in 10 ml dry DMF then 25 ml of pyridine was added to the suspension of the swelled IX. The reaction mixture was cooled and a solution of 25 ml chloroacetyl chloride in 10 ml DMF was added dropwise with stirring. The reaction mixture was stirred for 3 days and the product was filtered, washed many times with toluene and finally with ethanol. The product was dried under vacuum to yield 2.1 gm of X .

### **Modification of Dendrimers Supported on Montmorillonite (X) with Triphenyl Phosphine**

Modified dendrimers supported on MMT (X) (0.8 gm) was allowed to swell overnight in 10 ml dioxane. Then a solution of 2 gm of triphenyl phosphine in 5 ml dioxane was added dropwise to the reaction mixture. The reaction mixture was stirred and heated at 70°C for 3 days. The product was filtered and washed several times with chloroform and finally with ethanol. The product was dried under vacuum to yield 1.4 gm of product XII.

### **Modification of Dendrimers Supported on Montmorillonite (X) with Triethyl**

In 100 ml flask, 0.8 gm of chloroacetyl chloride modified dendrimers (X) was swelled in 10 ml dioxane, followed by dropwise addition of a solution of 10 ml triethylamine in 10 ml dioxane. The reaction mixture was stirred and heated at 70°C

TABLE 2. Nucleophilic Substitution Reactions using Polymer-MMT Supported Catalysts VII

Substrate R-X	Anion Y <sup>-</sup>	Reaction Conditions				Product	Yield
		Solvent	Temp. °C	PTC (%) ratio	Time (hrs)		
n-Bu-Br	SCN <sup>-</sup>	Bz/Wt	r.t	-	48	-	-
n-Bu-Br	SCN <sup>-</sup>	Bz/Wt	reflux	-	48	-	-
n-Bu-Br	SCN <sup>-</sup>	Bz/Wt	r.t	10	24	-	-
n-Bu-Br	SCN <sup>-</sup>	Bz/Wt	reflux	10	15	BuSCN	100
n-Bu-Br	SCN <sup>-</sup>	Bz/Wt	reflux	10*	15	BuSCN	96
n-Bu-Br	SCN <sup>-</sup>	Bz/Wt	reflux	10**	15	BuSCN	95.6
n-Bu-Br	SCN <sup>-</sup>	Ch/Wt	reflux	10	15	BuSCN	35
n-Bu-Br	SCN <sup>-</sup>	Ch/Wt	reflux	10	30	BuSCN	100
n-Bu-Br	SCN <sup>-</sup>	Bz/Wt	r.t	10	48	BuSCN	20
n-Bu-Br	SCN <sup>-</sup>	Bz/Wt	reflux	10	15	BuSCN	40
n-Bu-Br	SCN <sup>-</sup>	tol/Wt	reflux	5	9	BuSCN	70
n-Bu-Br	SCN <sup>-</sup>	Tol/Wt	reflux	10	9	BuSCN	75

Bz: Benzene; Wt: Water; Ch: Chloroform; tol: toluene.

r.t.: room temperature; \* : reused catalyst, \*\* : third trial for the use of the catalyst.

for three days. The product was filtered, washed many times with chloroform and finally with ethanol. It was dried under vacuum at 40°C to yield 1.2 gm XI.

### General Procedure for Nucleophilic Substitution Reaction

The anion substitution reactions were carried out by a batch technique by stirring of the polymer-MMT supported catalyst with the mixture of the substrate in organic solvent and a solution of the salt of the anion in water. Typical run is as follows: the ratio of the catalyst was added to the reaction mixture of alkyl or aryl halide (5 mmol) in organic solvent (5 ml) and reagent (5 mmol) in aqueous solution (5 ml) and the reaction mixture was stirred under conditions described in Tables 2 and 3.



TABLE 3. Nucleophilic Substitution Reactions using Polymer-MMT Supported Catalysts VI, XI, XII

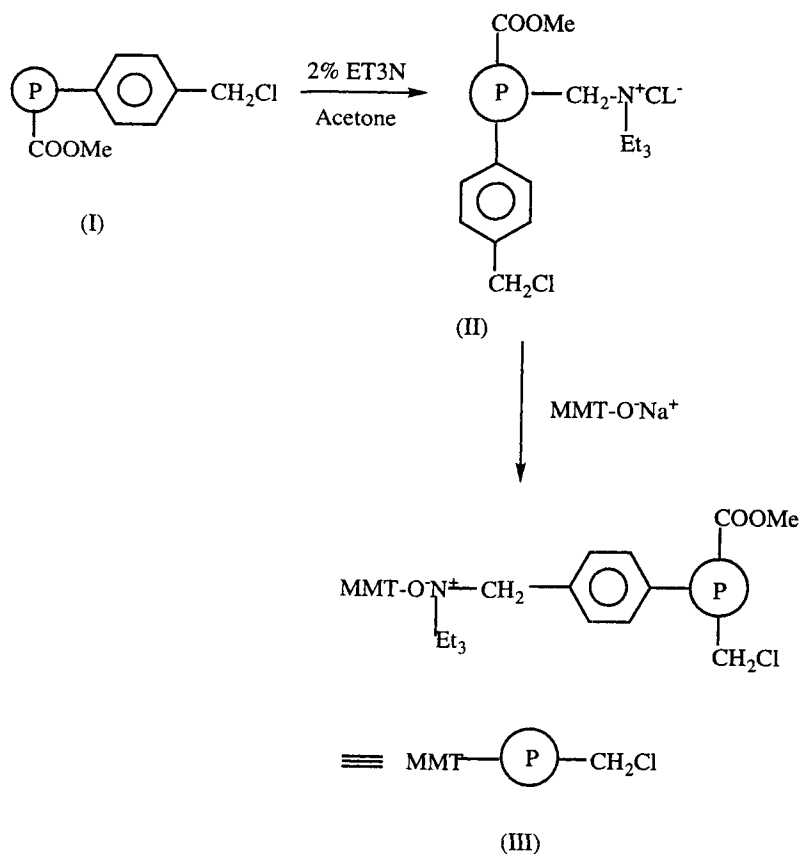
Substrate R-X	Anion Y <sup>-</sup>	Polymer- MMT code	Reaction Conditions				Product	Yield (%)
			Solvent	Temp.	PTC (%) ratio	Time (hrs)		
n-Bu-Br	SCN <sup>-</sup>	XII	Tol/Wt	80	5	15	BuSCN	92.5
n-Bu-Br	SCN <sup>-</sup>	XII	Tol/Wt	reflux	5	9	BuSCN	99
n-Bu-Br	SCN <sup>-</sup>	XII*	Tol/Wt	reflux	5	9	BuSCN	95
n-Bu-Br	No <sub>2</sub> <sup>-</sup>	XII	Tol/Wt	80	10	12	BuNO <sub>2</sub>	96
n-Bu-Br	CN <sup>-</sup>	VI	Bz/Wt	r.t.	10	48	BuCN	10
n-Bu-Br	CN <sup>-</sup>	VI	Bz/Wt	reflux	10	20	BuCN	43.3
n-Bu-Br	CN <sup>-</sup>	XI	Tol/Wt	80	9	15	BuCN	61

\* : reused catalyst.

## RESULTS AND DISCUSSION

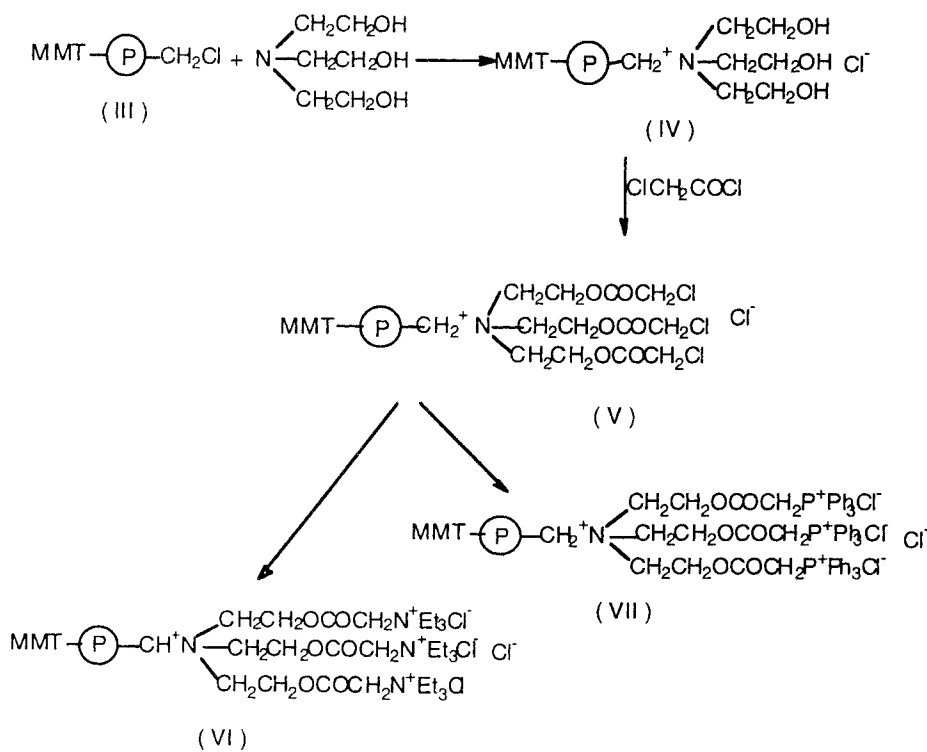
Synthesis of modified dendrimers supported on the polymer-clay system were described. The ammonium salt of chloromethylstyrene-methyl methacrylate copolymer was grafted onto montmorillonite interlayers by cations exchange process, (Scheme 1). The copolymer and its ammonium salt were prepared as described previously by bulk polymerization of the methylmethacrylate and chloromethyl styrene (ratio 1: 1). The ammonium salt of the copolymer was achieved by treatment with triethylamine (Scheme 2). The IR spectrum of the copolymer salt showed absorption band at 1500 cm<sup>-1</sup> (ammonium salt). The elemental microanalysis is as shown in Table 1.

The complexation of montmorillonite with copolymer with quaternary ammonium groups in the side chain was achieved by reaction of Na-montmorillonite with the ammonium salt of the copolymer at room temperature in acetone/DMF mixture (Scheme 1). After drying, the mixture was extracted with boiling DMF to remove the nongrafted polymers. Direct interactions between Na-montmorillonite and the copolymer ammonium salt seem to be at the first sight more versatile than the copolymerization on the functionalized inorganic surface.



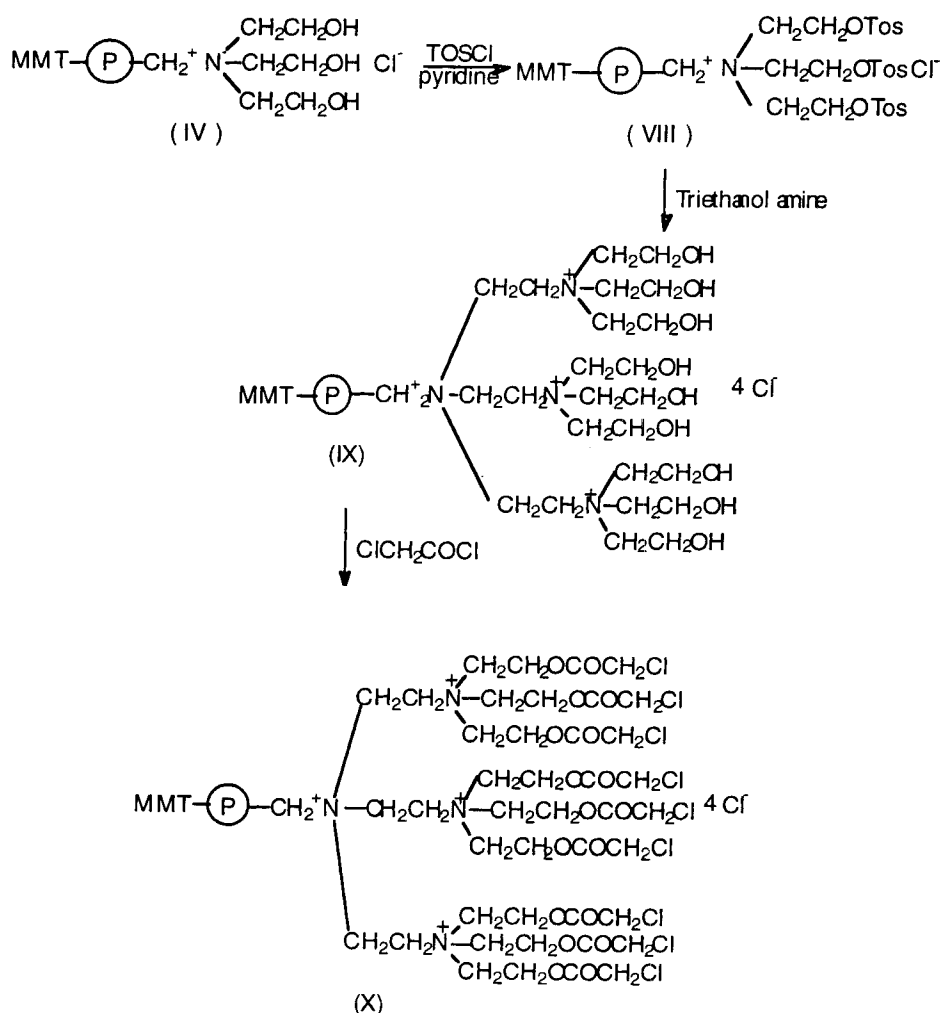
Scheme 1. Synthesis of Copolymer of Chloromethyl Styrene-Methylmethacrylate Supported on Montmorillonite.

The infrared spectrum of the polymer-MMT materials, showed absorption bands at  $3455\text{ cm}^{-1}$  ( $-\text{N}^+\text{Et}_3$ ), at  $1500\text{ cm}^{-1}$  (C-H stretching vibration of ethyl group and  $-\text{N}^+$  vibration). The presence of bands corresponding to the quaternary salts in the IR spectrum demonstrate the formation and the intercalation of the quaternary onium salts in the interlayers of montmorillonite. The intercalated copolymer was modified with triethanolamine in DMF at  $90^\circ\text{C}$  for four days. The triethanolamine modified MMT-polymer (IV) was divided into two parts. The first part was chloroacetylated using chloroacetyl chloride and with pyridine as base. The reaction was carried out under ice-cooling for three days and the conversion was high as indicated by elemental microanalysis for product (V) (Table 1). Tetraalkylammonium salt (VI) and tetraalkylphosphonium salt (VII) directly bonded to the chloromethylated



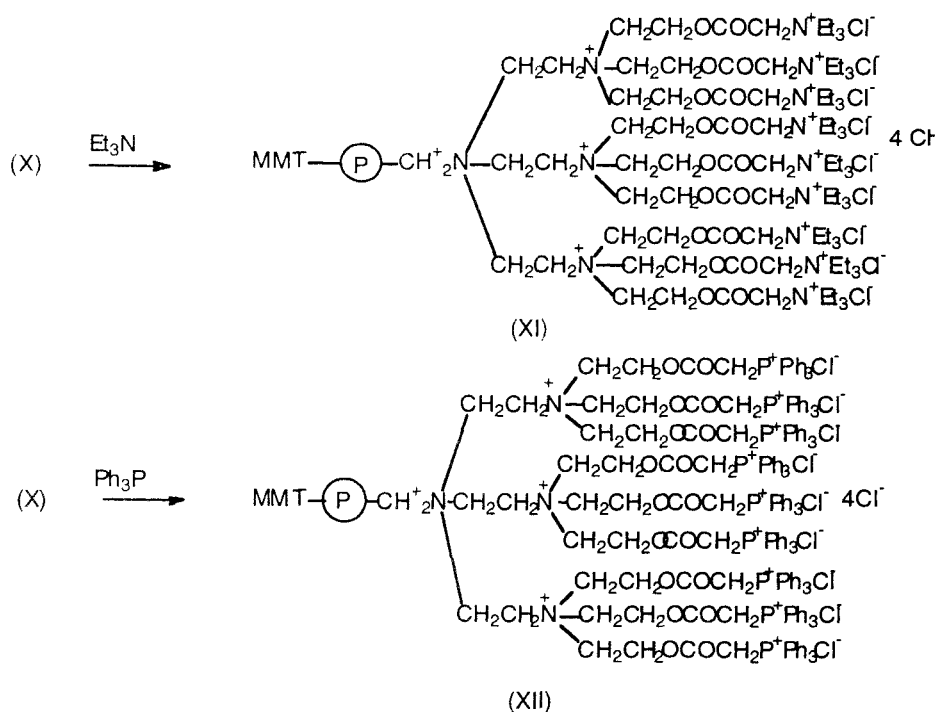
Scheme 2. Preparation of MMT-Poly(Chloromethyl Styrene-Methyl Methacrylate) Supported Phosphonium and Ammonium Salts Catalysts.

product (V) were prepared by reaction of triethylamine and triphenylphosphine with product V. The reactions were carried out by stirring the reactants in benzene at room temperature for product (VI) and at reflux temperature for product (VII). The elemental microanalysis of products VI and VII was shown in Table 1. Elaboration of the triethanolamine “balloon” dendrimer was accomplished with a two-step iterative procedure involving initial treatment of the second part of (IV) with *p*-toulenesulfonyl chloride in pyridine. The tosylation was carried out at room temperature for 48 hours, followed by heating at 80°C for another 48 hour. After separation and drying of the product, it was heated with an excess of triethanolamine in DMF. The characteristics of these products are as shown in Table 1. This sequence was performed to provide a “balloon” structure with cationic sites for each of substitutions on the polymer backbone. A schematic representation of the resultant structure is shown in Scheme 3. Again the product (IX) was modified



Scheme 3. Synthesis and Chloroacetylation of Cascade Molecules Supported on Montmorillonite.

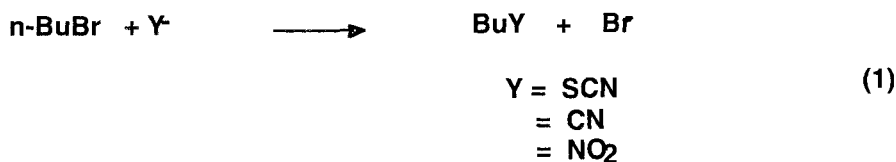
with chloroacetyl chloride as described previously in DMF and pyridine as base and the reaction was stirred for three days. Product (X) was quaternized either with triethylamine to afford product (XI), or with triphenyl phosphine to afford product (XII) (Scheme 4). All products were characterized by elemental microanalysis and infrared spectroscopy. The results of elemental microanalysis were as shown in Table 1. The weight gain for products was in agreement with the elemental microanalysis and in some occasions the weight gain was very small, the elemental



Scheme 4. Preparation of Ammonium and Phosphonium Salts (XI, XII) from Cascade Polymer Supported on MMT (X).

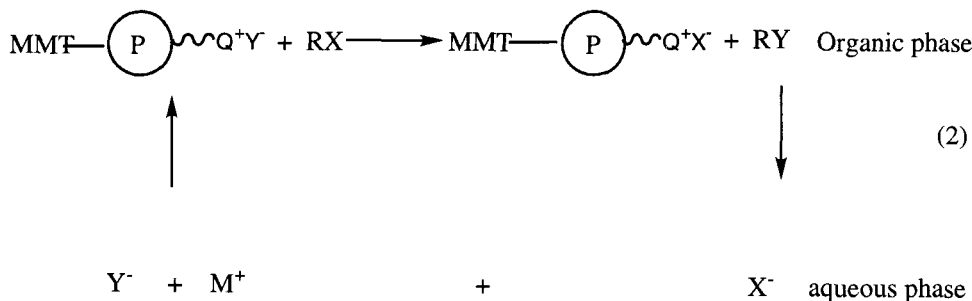
microanalysis indicated that the product contained substantial amounts of phosphine or nitrogen residues. Chemically the products behaved satisfactorily, similar results were reported previously [27].

The catalytic activities of the MMT-polymer supported catalysts VI, VII, XI, XII were tested for anions activation in nucleophilic substitution reactions (Equation 1):



In the presence of these catalysts, the alkyl thiocyanates, alkyl cyanide and nitroalkanes were prepared by the reactions of alkyl halides with thiocyanate, cyanide and nitrite anions carried out in liquid-liquid systems. The reactions were followed by GLC in comparison with authentic samples.

The mechanism of reactions in aqueous-organic media in the presence of supported quaternary salts may be represented as follows (Equation 2):



The above mechanism is similar to that shown for classical phase transfer catalysis [28-33]. Anion exchange at water-organic solvent interphase, with the inorganic  $\text{M}^+$  and the MMT-polymer supported quaternary cation  $\text{MMT}-\text{P}-\text{Q}^+$  as counterions in the aqueous and the organic phase. The catalytic activities for the prepared catalytic systems as phase transfer catalysts indicated that, the products were obtained in high yields and in shorter times than many other systems. It is worth mentioning that the experimental blank experiment gives no product at the same experimental conditions. The role of the polymer-MMT material is to stimulate the contact between the substrate and the anion and hence to improve the reaction yields [24]. The extra catalytic activities of these systems is attributed to the dendrimer molecules formed on the grafted polymer on MMT and consequently due to the high efficiency arising from the increase in the loading degree of the onium moiety. The percentage of the catalyst seems to be an important parameter for the rate of the reaction at which the anion undergoes. From Table 2, it could be noticed that the reactions of *n*-butyl bromide with  $\text{SCN}^-$  and catalyst VII in toluene/water gave higher yields at 10% than 5%. It was noticed also that the catalytic activities of the supported catalysts are higher at high reaction temperature and they had much lower activities at room temperature (Tables 2 and 3). In some instances, the reaction yields reaches 100% in a relatively short time at reflux temperature. This higher catalytic activity at reflux temperature is attributed to the high loading degree of the onium moiety and to the reduction of the time required for the swelling of MMT-polymer materials and the diffusion of reactants to the catalytic sites could occur. This demonstrated by reaction of  $\text{SCN}^-$  and *n*-butyl bromide at room temperature in benzene/water (Table 2). Also, the reaction of *n*-BuBr with  $\text{CN}^-$  and catalyst VII gave higher yield at reflux temperature than room temperature (Tables 2 and 3). The rate of the reactions in generally increased with

using phosphonium catalyst than in cases of ammonium catalyst under similar conditions, that indicate the effect of the structure of the active moiety on the reaction rates. The recyclability of these catalysts was tested and the results (Tables 2 and 3) showed that the reuse of these catalysts in another reaction gave higher yields with very slight loss of activities.

In all cases, the work-up of the product mixture was extremely simple and effective, requiring only the filtration of the solid catalyst followed by isolation of the product. Also there was no cross-contamination from the catalyst to the organic product and any organic contamination of the catalyst could be easily removed by washing with an organic solvent [16]. The major benefits of these catalysts that when it is in use at a laboratory scale and at industrial scale it could avoid many toxic homogenous catalysts and avoid many environmental disadvantages of using toxic materials. Also, in the industrial scale these catalysts can be recovered by simple filtration and reused without much loss in their activities.

## CONCLUSIONS

We found that the formation of dendrimeric structure could be achieved by modifications of functionalized polymer supported on montmorillonite. The dendrimeric molecules were modified to produce ammonium and phosphonium salts.

We investigated the catalytic activities of these systems and the results showed that they highly activated the selected organic reactions. The catalytic activities of these systems is attributed to the dendrimer molecules formed on the grafted polymer on MMT and consequently due to the high efficiency arising from the increase in the loading degree of the onium moiety. The recyclability of these catalysts was tested and the results showed that the reuse of these catalysts in another reaction gave higher yields with very slight loss of activities.

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