

Catalytic Activity of Polymer–Montmorillonite Composites in Chemical Reactions

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Received 24 November 2004; accepted 4 January 2006

DOI 10.1002/app.24027

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polymer–clay composite material has been prepared by intercalation of polymeric ammonium salt onto the montmorillonite (Na–MMT) followed by grafted polymerization of hydroxyethyl methacrylate onto amine-terminated poly(butadiene-co-acrylonitrile)–montmorillonite (ATBN–MMT) intercalate. The hydroxyl groups were modified to chloromethyl groups followed by conversion to onium salts, which are suitable as phase transfer catalysis. The catalytic activities of the supported catalysts were investigated in nucleophilic reac-

tions of thiocyanate and cyanate ions with alkyl and aryl halides. The rates of the reactions have been investigated under different factors such as the nature and structure of the support, the amount of catalyst, the solvent, and the temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1121–1129, 2006

Key words: catalytic systems; polymer–montmorillonite composite; intercalated catalysis; rubber–clay composite; heterolytic catalysis; functional polymers

INTRODUCTION

The reactivity of the polymeric support catalysts and reagents in organic synthesis strongly depends on the structure of the polymer backbone, the structure and the amount of the active groups introduced into the polymer backbone. The solvent and the structure of the organic molecules are usually more important in heterogeneous than in the case of homogeneous reaction.^{1–6} However, the choice of the solid support is also an important factor, especially its stability under the reaction conditions. In spite of all the advantages in using organic polymers, the main disadvantages of their use as supports in the solid-phase technique include their limited mechanical strength and thermal stability. These difficulties, which are encountered in most petrochemical and other similar industrial processes, have hindered their commercial applications.

Composites and clay nanocomposites were used as catalysts.^{7,8} Natural clays were among the earliest solid acid catalysts used in the petroleum oil industry to promote cracking and isomerization reactions,⁹ since these are inexpensive material and have high mechanical strength and chemical resistance toward acid and alkali treatment. Quaternary onium salts immobilized on clays, by adsorption on, or intercalation, have been widely explored as triphase catalysts.^{10–12} Inherent disadvantages such as low swelling capability in organic solvents render these catalysts unsuitable for many reactions and preclude their use. The

applicability of these intercalated onium salts was limited to few reactions as phase transfer catalyst (PTC).¹³ In addition, the application of clays, containing covalently attached ammonium salts through silane derivatives, as catalyst in nucleophilic substitution reactions has also been reported.¹⁴ However, such surface modification processes, involving grafting of the reactive groups on the available hydroxyl groups on the clay surface through coupling agents leads to materials coated with a thin layer of reactive groups located only on the surface, thus accounting for low loading capabilities. Therefore, such clay supports are totally unsuitable for high capacity demands.

In continuation of our interest in the polymeric catalysts,^{15,16} the objective of the present work was directed toward the production of polymeric catalysts grafted onto clay interlayers on the molecular dimension scale by grafted polymerization of suitable monomers with a modified clay derivative. These novel organic polymer-inorganic catalysts exhibit the characteristic properties of the individual components because of specific chemical interaction between the polymer and smectic montmorillonite clay interlayer. Thus, this work is aimed at the preparation of potentially useful materials, which combine the advantage of both organic polymer and inorganic supports. This combination of properties is necessary for most of the industrial chemical reactions.

EXPERIMENTAL

Materials

The montmorillonite (Na–MMT) mineral was supplied by ECC America, Inc. (TX), under the trade

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name Mineral Colloid-BP, as fine particles with an average particle size of 75 μm , cation exchange capacity (CEC) of 90 mEquiv/100 g, and interlayer spacing of 9.6 Å. The polymer, amine-terminated butadiene acrylonitrile (Hycar[®] ATBN), was obtained from BF Goodrich Specialty Polymers and Chemicals Division, which was an ATBN polymer (1300 \times 16) with acrylonitrile content of 16% (by mol), a Brookfield viscosity of 2×10^5 mPas at 27°C, and a glass transition temperature of -51°C. The molecular weight of ATBN was determined by Perkin-Elmer GPC using UV detector. The number-average molecular weight was found to be 1.09×10^3 and the weight average was 7.34×10^3 , which gives rise to a polydispersity (M_w/M_n) of 6.75. Hydroxyethyl methacrylate (HEMA) was used as supplied from Fluka. Chloromethyl styrene (CMS) was obtained from Polyscience Inc., as a mixture of m/p-isomers (\approx 30:60%) and used without purification. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under vacuum at ambient temperature.

Measurements

Infrared spectra were carried out on Perkin-Elmer 1430 Ratio-recording infrared spectrophotometer, using potassium bromide disc technique in the wavelength range of 4000–200 cm^{-1} .

The thermal behavior of the intercalated systems was investigated by thermogravimetric analysis (TGA) using a Polymer Laboratories STA 625 DSC thermal analyzer. The heating rate was 10°C/min in all cases in the temperature range ~25–500°C.

The calcinations was carried out by taking a definite weight (about 0.1 g) of the intercalated sample in porcelain crucible and dried in an electric oven at 120°C overnight, cooled in a desiccator, and then weighed to give the dry weight. The dry sample was introduced into an ignition oven and the temperature was raised to adjust 1000°C for about 20 h, cooled, and then weighed. The loading of each sample is expressed as the weight loss by ignition per 100 g of the dry sample.

X-ray diffraction (XRD) measurements were carried out using a Siemens Powder-Diffractometer D501 equipped with a Ni-filtered Cu-K radiation ($\lambda = 1.5418$) at stepping mode 0.02°, counter time 5 s., 40 kV, 30 mA, divergent slit 0.3°, and detector slit 0.15°.

The swelling degree was determined by taking a definite weight of the sample (about 0.2 g), which was introduced into a small sintered glass and allowed to imbibe in different solvents, such as distilled water, benzene, DMF, chloroform, and 1,4-dioxane, for 24 h. The excess solvent was removed by gentle centrifugation. The swelled sample was weighed and resuspended in the solvent. This procedure was repeated up to constant weight of the swelled sample. The

degree of swelling of each sample in different solvents is expressed as the amount of sorbed solvent per 100 g of dry sample.

Gas chromatographic analyses were carried out on Gas Chromatography, Perkin-Elmer 8410 Gas Chromatography instrument.

Intercalation of polymeric onium salts onto MMT (Scheme 1)

Preparation poly(chloromethylstyrene-co-hydroxyethylmethacrylate), I

A mixture of 0.3 g (2 mmol) CMS and 12.79 g (98 mmol) HEMA was heated at 70°C for 20 h in the presence of 0.1 g AIBN as initiator. The resulted product was dissolved in DMF and precipitated in benzene. The white precipitated product was filtrated, washed with benzene, and dried under vacuum at 40°C to give 9.5 g (72.6% yields) of white powder polymer (I).

IR (KBr): $\nu = 3424$ (—OH); 1727 (—C=O); 1455 (—CH₂); 1395 (—CH₃); 751 (phenyl rings); and 669 cm^{-1} (—CH₂Cl).

Elemental microanalysis: found: C (%) = 55.7; H (%) = 8.0; Cl (%) = 2.0 Cl \approx 5.682 mmol/100 g

Polymeric ammonium salt, II

A solution of 5 g of polymer I and 0.1 mL of triethylamine in 5 mL DMF was stirred at room temperature for 48 h. The resulted product was precipitated in benzene and filtrated off, washed several times with benzene, then dried under vacuum at 40°C to give the product II. The IR spectrum show absorption band at 1500 cm^{-1} for (Et)₃N.

Elemental microanalysis: found: N (%) = 1.6 N \approx 11.429 mmol/100 g.

Intercalation of polymeric ammonium salt onto montmorillonite III

The montmorillonite (5 g) was swelled in 150 mL distilled water under slow stirring for overnight, then was added 100 mL dioxane under vigorous stirring. A solution of polymer II (5 g in 100 mL DMF) was added dropwise to the stirred swelled clay suspension, and the stirring was continued at room temperature for 48 h. The suspension was precipitated in acetone and filtered off through sintered glass. The product washed several times with DMF to dissolve the adsorbed polymer followed by ethanol and finally dried at 40°C under vacuum to yield 7 g of intercalated MMT-polymer III.

IR (KBr): $\nu = 3424$ (—OH); 2938 (—CH); 1726 (—C=O); 1453 (—CH₂); 1397 (—CH₃); 795 (phenyl rings); and 1045, 522, 462 cm^{-1} (—Si—O).

Elemental microanalysis: found: C (%) = 23.3; H (%) = 3.5.

Chloromethylation of intercalated MMT-polymer IV

A solution of 1.5 mL (15 mmol) of chloroacetylchloride dissolved in 5 mL dry DMF was added under stirring to 6 g of polymer-MMT intercalate III swelled in 30 mL dry DMF in presence of 1.2 mL (15 mmol) of pyridine as base. The reaction mixture was stirred at room temperature for two days. The formed product was filtrated off, washed several times with DMF, distilled water, and finally with ethanol, then dried at 50°C under vacuum to give the product IV.

IR (KBr): $\nu = 2936$ (—CH); 1725 (—C=O); 1452 (—CH₂); 1387 (—CH₃); 795 (phenyl rings); 752 (—CH₂Cl); and 1045, 522, 463 cm⁻¹ (—Si—O).

Elemental microanalysis: found: Cl (%) = 1.8, ≈ 5.0704 mmol/100 g.

Preparation of polymer-MMT supported onium catalytic systems

To a swelled suspension of 1.5 g (IV) in 10 mL DMF, a solution of 5 mL triethylamine in 10 mL benzene was added under stirring at room temperature. After stirring for two days, the product was filtrated, washed several time with benzene, ethanol, and then dried under vacuum to yield 1.7 g the product V_a.

IR (KBr): $\nu = 2948$ (—CH aliphatic); 1726 (—C=O); 1663 (—C=C— aromatic); 1483 [—N(Et)₃]; and 1041, 523, 463 cm⁻¹ (—Si—O).

Elemental microanalysis: found: N (%) = 1.9, ≈ 13.5714 mmol/100 g.

The product V_b was prepared under similar conditions from 2.5 g (1.25 mmol of Cl) of IV and 2 g (7.6 mmol) of triphenylphosphine in 20 mL DMF to give 2.7 g of the dry product.

IR (KBr): $\nu = 2943$ (—CH aliphatic); 1724 (—C=O); 1658 (—C=C— aromatic); 1453 (P—Ph); and 1045, 521, 463 cm⁻¹ (—Si—O).

Elemental microanalysis: found: P (%) = 0.7, ≈ 2.2581 mmol/100 g.

Grafting of polymeric onium salts onto ATBN-MMT intercalate (scheme 2)

ATBN-MMT intercalate, VI

A solution of 13 g of ATBN dissolved in 100 mL dioxane was added dropwise with stirring on 5 g of Na-MMT suspended in 120 mL distilled water, followed by addition of 1,4-dioxane by the same procedure reported in ref. 16 to give 14.8 g of ATBN-MMT intercalated product VI. The characterization of the product by spectra and analysis was identical as given in ref. 17.

IR (KBr): $\nu = 2848$ (—CH); 1664 (—C=C—); 1445 (—CH₂); 1039, 520, 462 cm⁻¹ (—Si—O).

Microanalysis found: C (%) = 14.6, H (%) = 3.1, and N (%) = 2.6.

Grafting of hydroxyethyl methacrylate onto ATBN-MMT, VII

A mixing of 4 g VI swelled in 20 mL dry benzene, 5 g HEMA dissolved in 10 mL dry benzene, and 0.2 g AIBN as initiator was heated at 80°C for 24 h. After cooling to room temperature, the product was suspended in 30 mL DMF under stirring for a few hours, followed by addition of an excess of benzene. After stirring for a few hours, the precipitated product was filtered off, washed several times with DMF and ethanol, and then dried under vacuum at 50°C to give 7.5 g (83.3%-yields) of the product VII.

IR (KBr): $\nu = 3426$ (—OH); 2928 (—CH); 1724 (—C=O); 1453 (—CH₂); 1397 (—CH₃); and 1057, 520, 464 cm⁻¹ (—Si—O).

Elemental microanalysis: found: C (%) = 39.0; H (%) = 5.3.

Chloromethylation of hydroxyethyl groups grafted onto ATBN-MMT, VIII

A solution of 2.5 mL (25 mmol) of chloroacetylchloride dissolved in 5 mL dried DMF was added dropwise to a mixture of 5 g VII swelled in 30 mL dry DMF and 2 mL (25 mmol) of pyridine as base using the same procedure described in chloromethylation of IV, to give 6 g of the dry product VIII.

IR (KBr): $\nu = 2957$ (—CH); 1729 (—C=O); 1452 (—CH₂); 1406 (—CH₃); 695 (—CH₂Cl); and 1054, 522, 464 cm⁻¹ (—Si—O).

Elemental microanalysis: found: Cl (%) = 8.3 (≈ 2.34 mmol/g).

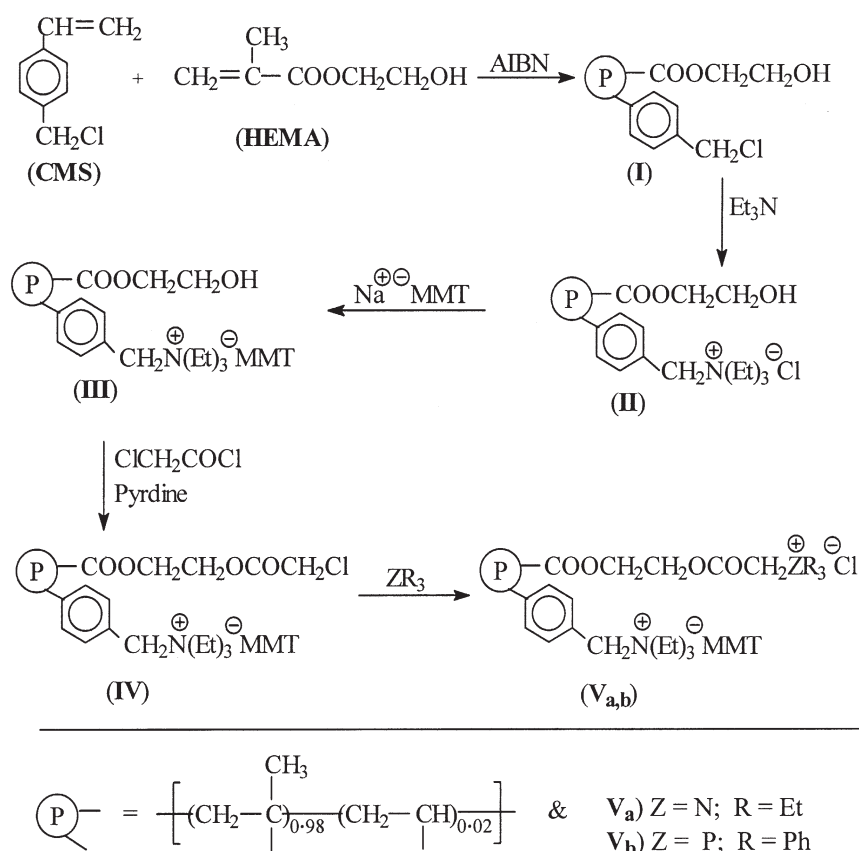
Preparation of onium catalytic systems grafted on ATBN-MMT

The ammonium salts grafted onto ATBN-MMT IX_a was prepared by the same procedure described in the preparation of V_a from 2 g of VIII swelled in 10 mL DMF and 0.5 mL of triethylamine dissolved in 5 mL DMF.

IR (KBr): $\nu = 2934$ (—CH aliphatic); 1729 (—C=O); 1663 (—C=C— aromatic); 1500 [—N(Et)₃]; and 1041, 522, 460 cm⁻¹ (—Si—O).

Elemental microanalysis: Found: N (%) = 2.5.

The phosphonium salt product IX_b was prepared under similar conditions from 3 g (6.9 mmol of Cl) of VIII swelled in 15 mL of DMF and 2 g (7.6 mmol) of triphenylphosphine dissolved in 10 mL DMF to give 3.2 g of the dry product IX_b.



Scheme 1 Synthesis of onium catalytic systems by intercalation of preformed polymers onto montmorillonite interlayer.

IR (KBr): $\nu = 2935$ (—CH aliphatic); 1725 (—C=O); 1663 (—C=C— aromatic); 1450 (P—Ph); and $1043, 517, 449$ cm^{-1} (—Si—O).

Elemental microanalysis: found: P (%) = 1.8

Applications of catalytic systems for nucleophilic substitution reactions

The catalytic activity of the prepared onium salts intercalated onto MMT was investigated in the anion substitution reactions under different conditions, such as, solvents, temperatures, structures, and amounts of the catalysts. The study was carried out by stirring the intercalated supported catalyst (different ratios) with the mixture of 5 mmol of the substrate (alkyl or aryl halide) in organic solvent (5 mL) and aqueous solution of the anion (5 mmol/5 mL). The quantitative conversion of the reactants to the products was followed by gas chromatography and listed in Table II.

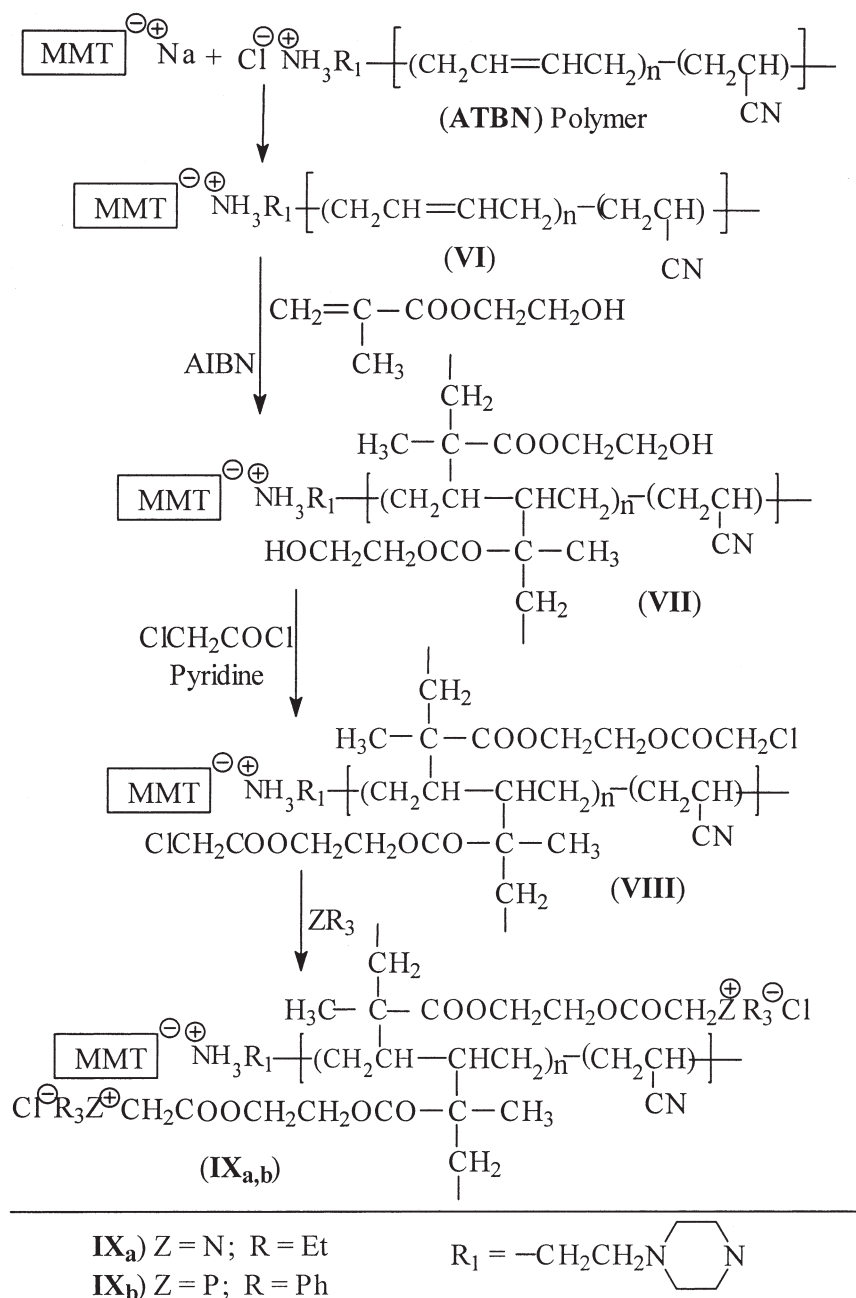
RESULTS AND DISCUSSION

Preparation and characterization of materials

The intercalation of polymeric systems onto montmorillonite clay has been achieved through two ways. The first way, outlined in Scheme 1, include the cation

exchange of preformed ammonium salt of poly(hydroxyethyl methacrylate-*co*-chloromethyl styrene) [poly(HEMA-CMS)], **II**, with the inorganic cations initially presented on the MMT interlayers. The product followed by the modification reaction with chloroacetylchloride, to introduce chloromethyl groups and finally conversion to onium salts to act as catalysis. The second way include grafting polymerization of HEMA onto ATBN-MMT intercalate followed by chemical modification (Scheme 2) as outlined in the first way.

The copolymer I was prepared by bulk free radical copolymerization of HEMA and CMS with mole ratio 98:2 to give product with a good yield (73%). The conversion of chloromethyl groups (IR absorbance band at 669 cm^{-1}) to ammonium salt moieties necessary for the attachment onto MMT interlayers was followed by the IR spectra [Fig. 1(a)] which showed an absorption band at 1500 cm^{-1} for —N⁺—. The intercalation of polymeric ammonium salt **II** on the MMT interlayer produced an ionic bond through the exchange of the sodium cations presented on the MMT with the positively charged ammonium groups of the polymer. This replacement leads to a marked reduction in the water uptake (134 wt %) of the product **III**. This was attributed to the change of an essentially hydrophilic surface to one with organophilic proper-



Scheme 2 Synthesis of onium catalytic systems through grafting polymerization onto ATBN-MMT composite.

ties. This behavior has made the intercalate **III** to exhibit greater affinity for organic solvents, ranging from 6.6 to 249.6 wt %. The solvent uptake for **III** evident from its swelling behavior in different solvents are listed in Table I. The IR spectra of **III** showed bands at 3424 cm^{-1} corresponding to $-\text{OH}$; and at 1045 cm^{-1} for $-\text{Si}-\text{O}$. The calcination of **III** showed that 0.563 g of polymer was intercalated into 1 g MMT interlayers. The TGA spectra have shown that this composite contain ~ 40 wt % of polymers intercalated into the clay and start decomposition above 250°C and take large scale $\approx 250^\circ\text{C}$ for complete decomposition as in Fig. 2.

The amount of polymer resident within the interlayer spacing was determined by WAXD through an increase in the (d_{001}) reflections. Fig. 3 shows typical WAXD traces of samples **III**, which indicated that the interlayer spacing of the silicate layers of MMT was increased to about 14.3 \AA for the products of intercalated samples when compared with the silicate layer (9.3 \AA) before intercalation in the montmorillonite itself.¹⁸

The second way of preparing polymer-MMT intercalate includes, the intercalation of ATBN rubber salt onto MMT interlayer by the same procedure as previously described.^{9,11} The IR spectra of VI [Fig. 1(b)] has

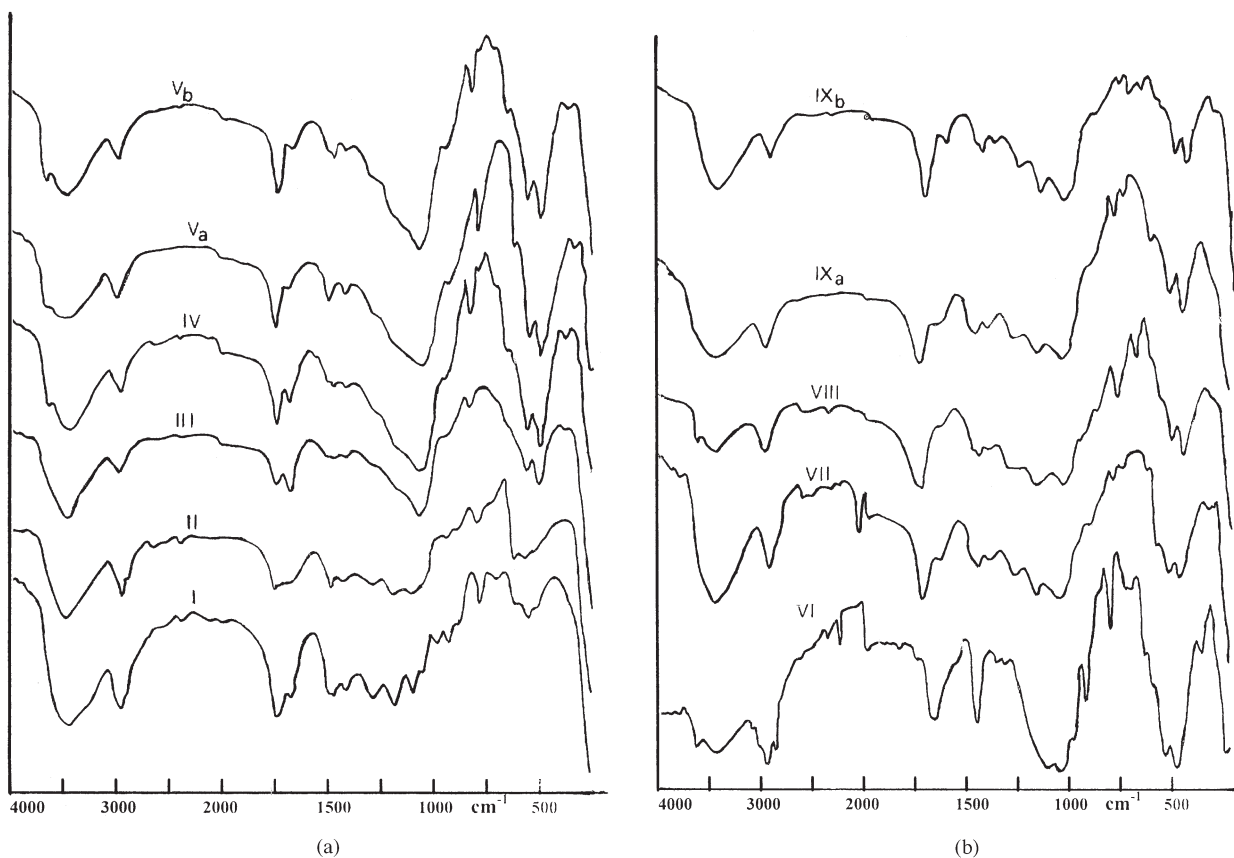


Figure 1 (a) IR spectra for onium catalytic composites I–V prepared by intercalation of preformed polymers onto montmorillonite clay interlayers. (b) IR spectra for onium catalytic composites VI–IX prepared by grafting polymerization onto ATBN–MMT.

shown bands at 1089 cm^{-1} , 1038 cm^{-1} for Si—O and another band at 1650 cm^{-1} for C=C. The thermogravimetric analysis of pure composite sample **VI**, reveals that the polymer content is 27 wt % with improved thermal properties since the decomposition temperature was increased to about 470°C , as illustrated in Figure 2. This replacement brought a marked reduction in the water affinity (66% water uptake for the swollen composite sample) of the produced ATBN–MMT intercalate

VI due to the change of an essentially hydrophilic surface to one with organophilic properties. This behavior has made the ATBN–MMT intercalates to exhibit much greater affinity for organic solvents uptake, ranging from 84 to 264 wt %, which is evident from their swelling in different solvents (Table I). The grafting of hydroxyethyl methacrylate onto rubber–clay intercalate **VI** was carried out in benzene via radical solution polymerization with 83% yields of the product **VII**.

TABLE I
Characteristic Data for Polymeric–MMT Composites

Sample	X-ray data		Calcination		Microanalysis		Swelling degree (%)				
	2θ	d -Spacing	MMT (%)	Polym (%)	Element	(%)	CHCl_3	Benzene	Dioxane	DMF	H_2O
III	6.20	14.26	43.69	56.31	—	—	249.9	6.6	69.3	168.8	133.8
IV	—	—	40.80	59.20	—	—	91.7	133.4	23.8	293.0	45.3
V _a	—	—	—	—	N	1.9	116.3	168.0	124.5	345.6	69.8
V _b	—	—	—	—	P	0.7	179.6	77.0	105.2	345.6	80.0
VI	6.28	14.07	60.63	39.37	—	—	116.7	263.8	114.7	84.3	66.3
VII	6.12	14.44	72.22	27.78	—	—	32.8	95.5	112.5	260.3	117.3
VIII	—	—	81.38	18.62	—	—	163.8	60.0	295.0	475.0	63.0
IX _a	—	—	74.72	25.28	N	2.5	294.0	60.0	133.4	183.0	149.0
IX _b	—	—	71.50	28.50	P	1.8	278.0	20.0	94.8	233	183

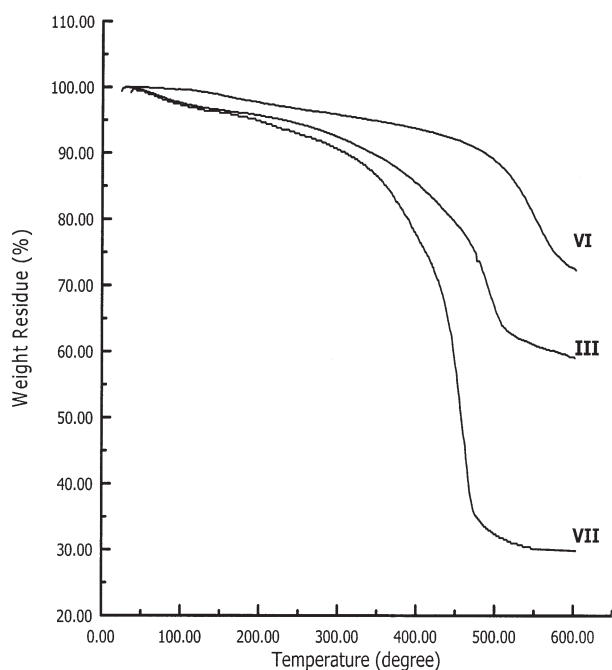


Figure 2 TGA thermograms for the composite materials III, VI, and VII.

The IR spectra of VII shows the absorbance band at 1750 cm^{-1} for $\text{C}=\text{O}$ and at 3424 cm^{-1} for $-\text{OH}$. The elemental microanalyses were determined and are listed in Table I. The determined thermal gravimetric analyses indicate that the polymer content was increased to about 70 wt % by grafting of hydroxyethyl methacrylate onto rubber-clay. The swelling study showed a high affinity of water, as the surface of the MMT became more hydrophilic due to the presence of OH groups as shown in Table I.

Also, Figure 3 shows typical WAXD traces of the intercalated sample VI and VII, which indicated that the interlayer spacing of the silicate layers of MMT was increased to 14.07 \AA and 14.44 \AA , respectively, and the relative intensity was decreased due to increasing the polymer content in the composites.

The composites III and VII were chemically modified by its reaction with chloroacetylchloride, to introduce the chloromethyl groups into the product. The product IV and VIII were characterized by the change in the swelling degree as shown in Table I. The IR spectra of IV and VIII showed absorption band at 710 cm^{-1} for CH_2Cl . The elemental analysis indicated that the percentage of halogen (Cl) was 1.8% and 8.3%, which corresponded to 0.507 and 2.3 mmol/g loading respectively.

The products IV and VIII were converted to catalytic systems by quaternization of CH_2Cl groups to ammonium and phosphonium salts. The products V_{arb} and IX_{arb} were confirmed by IR which shows absorption bands at 1483 cm^{-1} for $^+\text{N}(\text{Et})_3$ and at 1453 cm^{-1}

for $^+\text{P}(\text{Ph})_3$. Also, the nitrogen and phosphorous contents were found 1.9% and 0.7% respectively.

Applications of catalytic composites as phase transfer catalysts

The catalytic activity of the prepared polymeric composites V_{arb} and IX_{arb} was examined by studying their applications as catalyst in the nucleophilic substitution reactions of alkyl and aryl halides with nucleophiles such as SCN^- and CN^- . The formation of alkyl and aryl thiocyanates as well as alkyl and aryl cyanates were carried out in liquid-liquid systems and followed by gas solid chromatography (GSC) in comparison with authentic samples of the reaction products. The obtained results were summarized in Table II, for catalytic reactions of alkyl halides and aryl halides. The results display the product yields as a function of reaction time, in comparison with the reaction in the absence of catalysts under the same conditions in which the product of the reaction was not detectable.

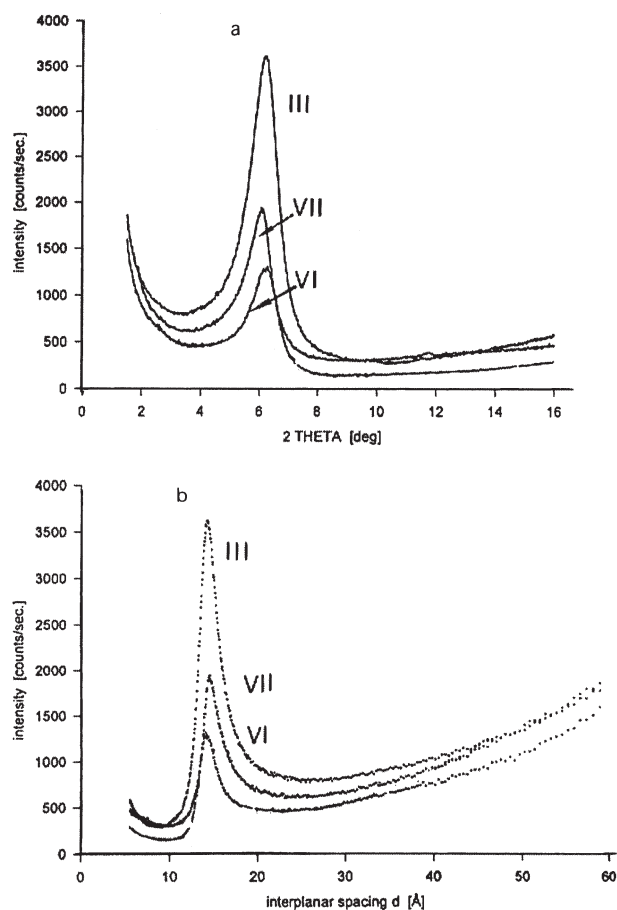
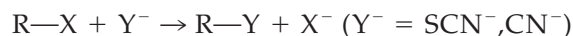


Figure 3 XRD patterns for intercalated composites III, VI, and VII; (a) 2θ (degree), (b) Interlayer spacing (\AA).

TABLE II
Nucleophilic Substitution Reaction Using Clay-Polymers Intercalates Supported Catalysts

Sample	Substrate R—X	Anion Y ⁻	Reaction conditions				Prod. R—Y	Yield (%)
			Solvent	Temp	Cat wt %	Time (h)		
Clay	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	r.t	4	48	—	—
Clay	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	60	4	24	<i>n</i> -Bu—SCN	4.4
Clay	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	60	4	48	<i>n</i> -Bu—SCN	8.6
Clay	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	60	4	72	<i>n</i> -Bu—SCN	13.3
Clay	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	60	4	96	<i>n</i> -Bu—SCN	15.8
Clay	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	60	4	120	<i>n</i> -Bu—SCN	18.6
Clay	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	Ref.	4	20	<i>n</i> -Bu—SCN	30
Clay	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	Ref.	4	40	<i>n</i> -Bu—SCN	70
V _a	<i>n</i> -Bu—Br	CN ⁻	DCM/W	Ref.	3	20	<i>n</i> -Bu—CN	20
V _b	<i>n</i> -Bu—Br	CN ⁻	DCM/W	Ref.	3	20	<i>n</i> -Bu—CN	25
IX _a	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	r.t.	9	24	—	—
IX _a	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	Refl.	9	20	<i>n</i> -Bu—SCN	40
IX _a	<i>n</i> -Bu—Br	CN ⁻	Bz/W	Refl.	9	20	<i>n</i> -Bu—CN	32
IX _a	<i>n</i> -Bu—Br	CN ⁻	Bz/W	Refl.	10	20	<i>n</i> -Bu—CN	40
IX _a	<i>n</i> -Bu—Br	CN ⁻	CHCl ₃ /W	Refl.	8	15	<i>n</i> -Bu—CN	50
IX _a	<i>n</i> -Bu—Br	CN ⁻	CHCl ₃ /W	Refl.	10	15	<i>n</i> -Bu—CN	43
IX _a	<i>n</i> -Bu—Br	CN ⁻	CHCl ₃ /W	Refl.	10	30	<i>n</i> -Bu—CN	70
IX _a	PhCH ₂ —Br	CN ⁻	CHCl ₃ /W	Refl.	9	20	PhCH ₂ —CN	43
IX _a	PhCH ₂ —Br	CN ⁻	CHCl ₃ /W	r.t.	10	72	PhCH ₂ —CN	2
IX _a	PhCH ₂ —Br	CN ⁻	CHCl ₃ /W	Refl.	10	20	PhCH ₂ —CN	40
IX _b	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	r.t	2	24	—	—
IX _b	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	Refl.	2	20	<i>n</i> -Bu—SCN	30
IX _b	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	r.t.	4	24	—	—
IX _b	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	60	4	20	<i>n</i> -Bu—SCN	11
IX _b	<i>n</i> -Bu—Br	SCN ⁻	Bz/W	Refl.	4	20	<i>n</i> -Bu—SCN	55
IX _b	<i>n</i> -Bu—Br	SCN ⁻	DCM/W	r.t.	2	24	—	—
IX _b	<i>n</i> -Bu—Br	SCN ⁻	DCM/W	Ref.	2	20	<i>n</i> -Bu—SCN	20
IX _b	<i>n</i> -Bu—Br	CN ⁻	Bz/W	Ref.	6	20	<i>n</i> -Bu—CN	40
IX _b	<i>n</i> -Bu—Br	CN ⁻	Bz/W	r.t.	9	24	—	—
IX _b	<i>n</i> -Bu—Br	CN ⁻	Bz/W	Ref.	9	20	<i>n</i> -Bu—CN	60
IX _b	<i>n</i> -Bu—Br	CN ⁻	CHCl ₃ /W	r.t	8	24	—	—
IX _b	PhCH ₂ —Br	CN ⁻	CHCl ₃ /W	r.t.	9	72	PhCH ₂ —CN	4

The effectiveness of these novel materials has been examined with the effect of several factors governing the rates of chosen chemical reaction, such as chemical composition of the polymer backbone, concentration of the active catalyst groups, chemical nature of the active moiety, nature of solvent, and temperature of reaction. Because of the marked increase in the organophilic nature of the intercalated catalytic systems V_{arb} and IX_{arb}, they attract the substrate molecules through swelling and act as active centers for reactions that make them viable and promising phase transfer catalysts for anionic substitutions.

The results of using these supported phase transfer catalysts indicate that the products were obtained in satisfactory yields in shorter time than the blank reactions. The natures of the supported catalysts play an effective role in the speed of reactions. For example, the reaction of *n*-Bu—Br with SCN⁻ in benzene/H₂O at reflux after 20 h using 9 wt % gave 32%-yield with IX_a and 60% yield with IX_b (another results can be seen in Table II).

Also, the effect of the solvent is the major factor that affects the anion activation in nucleophilic substitu-

tions. The interlayer distance can be increased remarkably in solvents, which have strong attractive forces and increase the contact between the intercalated substrate and anion which improve the reaction yields. The efficiency of the solvation of intercalated systems depends on the type of solvent mixture, and consequently affects the rate of reactions. It was observed that slow reaction occurred at reflux in chloroform/water mixture than in benzene/water mixture.

The intercalated systems were also characterized by their high reactivity at high temperature. Results in Table II, show that the temperature is an important factor affecting the reaction rate. The increase in the yield with temperature may be explained on the basis that the catalyst becomes more swellable and the miscibility of the solvents in the mixture increases. This facilitates the contact between the reacting species and catalyst leads to increasing the activation energy and consequently the reaction rate increases. The reaction of *n*-Bu—Br with SCN⁻ in benzene/H₂O mixture using 4 wt % of IV_b after 20 h gave 0, 11, and 55%-yield at ≈25°C, 60°C, and reflux, respectively. The reaction of PhCH₂Br with CN⁻ in chloroform/water using 10 wt

% of IX_a after 72 h gave 2%-yields at room temperature ($\approx 25^\circ\text{C}$); and after 20 h gave 40%-yields at reflux (another results can be seen in Table II).

Another important factor affecting the rate of reaction is the amount of the catalyst. The rate of reaction increased with increasing the amount of the catalyst in the reaction mixture as shown in Table II. This can be explained by increasing the number of active centers exposed to reacting species. The yield percentage is directly proportional to the amount of catalyst. For example, the reaction of *n*-Bu-Br with SCN^- in benzene/ H_2O at reflux in the presence of 2 wt % of IX_b , 30% of yield was detected after 20 h. When the amount of catalyst was increased to 4 wt % the yield was 55% at the same reaction conditions.

CONCLUSIONS

This study includes the production of polymer-clay catalysts through two ways. The first way includes the cation exchange of preformed ammonium salt of poly-(HEMA-CMS) with the cations initially presented on the MMT interlayers. The second way includes graft polymerization of HEMA onto ATBN-MMT intercalate. The obtained products were chemically modified with chloroacetylchloride and finally converted to onium salts to act as catalyst. Determination of the structural composition of the prepared polymer-clay materials has been studied by various techniques. The thermal properties of the intercalated polymer clay were investigated by TGA, which indicated that the contents of clay have an effect on the thermal properties. The chemical reactivity of the prepared functional polymers grafted onto MMT interlayers has been in-

vestigated in nucleophilic substitutions of thiocyanate and cyanate ions to enhance the efficiency of conventional chemical procedures. The effectiveness of these novel catalysts has been examined with respect to reaction rates, chemical composition of the polymer backbone, amount of catalyst, chemical nature of the active moiety, nature of solvent, and temperature of reaction.

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