

CLAY-POLYMER NANOCOMPOSITE-SUPPORTED BROMINATING AGENT

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Abstract—The conventional methods of direct bromination of organic compounds with elemental bromine have several major drawbacks such as handling difficulty, corrosive effect, and toxicity, in addition to over-bromination and problems with isolation of products from the reaction mixture. Supported catalysts and reagents have become popular in the synthesis of organic chemicals over recent decades because they have overcome almost all of the drawbacks noted above. In the present study, a new clay polymer nanocomposite (CPN)-supported brominating agent was prepared from montmorillonite (Mnt) and styrene-*co*-vinyl pyridinium polymer. The reagent was obtained by the direct interaction of a two-fold excess of poly(styrene-*co*-*N*-methyl-4-vinylpyridinium) bromide with Na-montmorillonite (NaMnt) through ion exchange between Na⁺ of the NaMnt and pyridinium ions in the copolymer to provide CPN3 with free methylpyridinium bromide side chains. The structure of the CPN3 prepared was characterized by infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. Treatment of the CPN3 with bromine using the bromide ions which remained led to the perbromide-supported reagent, CPN4. The activity of the resulting CPN4 brominating reagent was examined through direct bromination of some alkenes, arenes, and carbonyl compounds and compared with the effectiveness of a crosslinked polymeric perbromide reagent. The yields obtained from application of the reagent were moderate to excellent. The advantages of this reagent, such as stability at room temperature, ease of regeneration from the polymeric by-product, and the yields of the brominated products, confirm the viability of using a CPN-supported brominating agent as a reactive reagent in organic chemistry synthesis.

Key Words—Bromination, Clay-Polymer Nanocomposite, Montmorillonite, Poly(vinylpyridine).

INTRODUCTION

The use of polymer-supported reagents in organic chemistry synthesis has become increasingly common in both academic and industrial synthesis laboratories. Chemical reagents attached to a polymeric support were first used successfully in organic synthesis (Solinas & Taddei, 2007). The major advantages of using polymer-supported reagents are simple isolation of products from the reaction mixture by filtration and increased selectivity compared with the analogous homogenous reactions (Kirschning *et al.*, 2001; Solinas and Taddei, 2007). Organic halogen compounds represent an important group of organic intermediate compounds and play an important role in organic transformations (Gribble, 2003). Organic halogen compounds have been used widely in industrially important products and biologically active substrates as antitumor, antifungal, antibacterial, and antiviral compounds (Gribble, 2003; Rossberg *et al.*, 2011). Organic halogen compounds have also been used as solvents, pesticides, refrigerants (*e.g.* haloalkanes), fire-resistant oils, electrically insulating coatings, and as ingredients in plastics and sealants (Gribble, 2003).

Various methods have been used for the halogenation of organic compounds (Sasson, 2009). Conventional brominating procedures include the use of bromine in chlorinated hydrocarbons, acetic acid, *etc.*, in the presence of FeBr₃, or using *N*-bromosuccinimide (NBS) or pyridinium perbromide (Sasson, 2009). The main disadvantages of these procedures are the difficulty in preparing the reagent, as well problems with separation of the reaction product. Furthermore, the production of a complex mixture of mono-, di-, and tribromo derivatives is observed for reactive aromatic materials such as phenols and anilines.

To overcome such drawbacks, polymer-bound halogenation reagents have been developed (Solinas and Taddei, 2007). Most of these reagents are based on ion-exchange resins derived from polystyrene (Cainelli *et al.*, 1976; Sherrington *et al.*, 1977; Gelbard, 2002) and other synthetic polymers such as polymethyl methacrylate (Akelah *et al.*, 1988; Hassanein *et al.*, 1989), and are often loaded with perbromide making them suitable for bromination reactions. Supported polymers and copolymers of 4-vinylpyridine (Solinas and Taddei, 2007; Tamami and Borujen, 2009; Zarchi and Ebrahimi, 2012) formed various types of complexes with halogens, and bromination for a variety of organic compounds from such bromine complexes has been proved possible. These reactive agents are stable and can be stored conveniently. The polymer-supported reagents do, however, suffer from a major drawback which is their

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limited mechanical strength and thermal stability, which affects their long-term performance (Hodge, 2005). Major enhancements have been noted in the physical properties of polymers upon formation of layered silicate CPN as a consequence of their enhanced interfacial properties and changes in phase morphology (Nguyen and Baird, 2006; Wu *et al.*, 2012). Amounts of as little as 5 wt.% of a clay mineral added to a polymer were found to be sufficient to improve significantly some of the polymer properties (Bergaya *et al.*, 2013).

Clay minerals are hydrous aluminum silicates with a layer (tetrahedral and octahedral sheets) structure (Bergaya *et al.*, 2013). Ion exchange of inorganic cations in the clay interlayers by organic cations renders the clay organophilic (Ray and Okamoto, 2003). Such organophilic clays have found widespread applications in drilling muds, coatings, paints, inks, water treatment, and as catalysts in various types of organic reactions (Varma, 2002; Nagendrappa, 2011).

Following community interest in polymer-supported reagents and catalysts (Akelah *et al.*, 1988; Hassanein *et al.*, 2005), the objective of the present work was directed toward the synthesis of a CPN perbromide reagent and its application in the bromination of carbonyl compounds containing α -hydrogen atoms, alkenes, and arenes. The results were also compared with a cross-linked polymeric perbromide reagent. The aim of the present study was to make the nanocomposite reagent prepared, which combines the advantages of both organic polymers and inorganic supports, valuable in applications in both academia and industry.

EXPERIMENTAL

Materials and reagents

Styrene (99%) and 4-vinylpyridine (95%) monomers were purchased from Fluka (Steinheim, Germany) and redistilled under reduced pressure before use. *N, N*-methylenebisacrylamide (Merck, 98%) (Darmstadt, Germany) was used as received. Methyl bromide (Sigma, 99%) (Steinheim, Germany) was used as received. Montmorillonite was obtained from Southern Clay Products Inc. (Gonzales, Texas, USA), and has a cation exchange capacity (CEC) of 114.8 meq/100 g. The d_{001} (interlamellar or interlayer) spacing, measured at ambient humidity is 12 Å, and 9.6 Å after drying in a vacuum oven (84.6 kPa) at 100°C for 12 h.

Synthesis of linear poly(styrene-co-4-vinylpyridine)1

In a 250 mL, two-neck, round-bottom flask, a mixture of 10.09 g (96 mmol) of 4-vinylpyridine, 9.9 g (96 mmol) of styrene, and 1 wt.% of benzoyl peroxide based on monomers in 40 mL of benzene was refluxed in a water bath for 10 h at 80°C. The polymer produced was precipitated in diethyl ether. The polymer produced was purified by dissolving it in 40 mL of chloroform, and reprecipitating it with diethyl ether (~300 mL), in two

repeated cycles. The final product was filtered and washed with diethyl ether, dried under vacuum (84.6 kPa) for 24 h at 40°C, and weighed, giving 17.8 g of dried linear co-polymer (89.4% yield). Elemental analysis gave C, 85.75%; H, 6.97%; and N, 6.43%. The relative viscosity (η_{rel}) was 1.1 (0.10 g, 10 mL acetone, 30°C).

Synthesis of polymeric pyridinium salt 2

A solution of poly(styrene-co-4-vinylpyridine)1 (10.0 g, 95.69 mmol) dissolved in 70 mL of methanol was treated with 10 mL of methanolic solution of methyl bromide (9.49 g, 100 mmol) and the mixture was stirred at room temperature for 24 h. The polymeric pyridinium salt was filtered, washed several times with methanol (50 mL), and dried in vacuum (84.6 kPa) for 24 h at 40°C, to give 13.0 g of product (89.4% yield). Elemental analysis gave C, 62.86%; H, 5.89%; and N, 4.42%. The amount of bromide, determined by the Volhard method (Jeffery *et al.*, 1989; Vogel's *Textbook of Quantitative Chemical Analysis*), was found to be 3.82 mmol of Br/g of dry co-polymeric salt.

Synthesis of CPN 3

To a dispersion of NaMnt (10 g, 11.48 meq Na) in 600 mL of distilled water, a solution of 6.98 g (23 mmol) of poly(styrene-co-*N*-methyl-4-vinylpyridinium bromide) dissolved in 50 mL of acetone was added in a dropwise manner and stirred at room temperature for 48 h. The reaction mixture was filtered and washed several times with distilled water. The product was vacuum dried (84.6 kPa) at 60°C for 12 h to give 14.4 g. The amount of bromide remaining, determined by the Volhard method, was 2.1 mmol of Br⁻/g of dry nanocomposite.

Synthesis of CPN perbromide reagent 4

Polymeric pyridinium bromide-clay nanocomposite (2.0 g, 8.54 mmol Br⁻/g) swelled in 90 mL of carbon tetrachloride for 24 h was treated with a solution of bromine (16.0 g, 100 mmol) dissolved in 20 mL of carbon tetrachloride at room temperature for 48 h. The reagent obtained was then filtered and washed thoroughly with carbon tetrachloride and methylene chloride until the filtrate became colorless. The reagent was then washed with diethyl ether, and dried under vacuum (84.6 kPa) for 12 h at 60°C to give 12.5 g of the dried reagent. The amount of the bromide present in the compound was determined by the Volhard method to give 4.27 mmol of Br/g.

Application with CPN4 perbromide reagent

In a 50 mL round-bottom flask, 2.0 g (8.54 mmol) of clay-polymer perbromide reagent was swelled in 30 mL of carbon tetrachloride for 24 h, then 5 mmol of the substrate, the material to be reacted with the clay perbromide reagent, dissolved in 5 mL of carbon

tetrachloride was added dropwise with stirring. The reaction mixture was then stirred magnetically under reflux conditions (Table 1). The progress of the reaction was followed by the thin-layer chromatography (TLC) technique (Vogel *et al.*, 1989) (two measurements each for 4 h reactions, three measurements each for 8 h reactions, and four measurements each for 12 h reactions; the eluent was a mixture of petroleum ether and ethyl acetate at 9:1 or 95:5). Read more about TLC in a document provided by the author and deposited at www.clays.org/JOURNAL/JournalDeposits.html. After completion of the reaction, the mixture was cooled to room temperature, filtered, and washed with carbon tetrachloride (2 × 5 mL) and methylene chloride (2 × 5 mL). The combined filtrates were evaporated on a rotary evaporator to obtain pure products which were identified by comparison of their melting points and their IR spectra with those of the original compounds.

Regeneration of CPN4 perbromide reagent

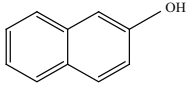
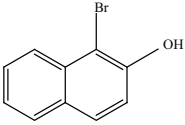
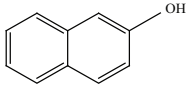
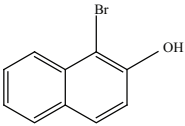
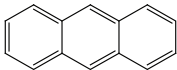
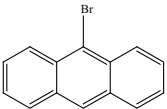
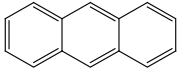
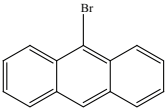
In a 100 mL two-neck flask, 5.0 g of the spent yellow clay-polymer perbromide reagent collected from different bromination reactions was swelled in 40 mL of carbon

tetrachloride for 4 h. Then, excess solution of bromine (6.4 mL, 19.9 g, 125 mmol) in 20 mL of carbon tetrachloride was added dropwise with stirring to the swelled, spent reagent. The reaction mixture was then stirred for 48 h at room temperature, filtered, and washed several times using carbon tetrachloride and diethyl ether until the filtrate became colorless. The reagent was dried under vacuum (84.6 kPa) to give 6.3 g of dried CPN4 perbromide reagent. The capacity of the regenerated CPN4 perbromide reagent was determined by the Volhard method and was found to be 3.93 mmol Br⁻/g.

Synthesis of crosslinked polymeric perbromide reagent 5

Crosslinked poly(4-vinylpyridine-*co*-styrene) with methylene bisacrylamide was prepared using the suspension polymerization method (Oadian, 2004). In brief: a solution of polyvinyl alcohol (6.0 g dissolved in 200 mL of H₂O) was placed in a two-neck, 1 L flask and heated at 90°C with stirring. Then, a monomer mixture of 4-vinylpyridine (26.4 mL, 245 mmol), styrene (28 mL, 245 mmol) and *N,N* methylene bisacrylamide as a crosslinker (1.5 g) were added under stirring in a solvent mixture of ethyl acetate/1-Pentanol (10:40 mL/mL).

Table 1. Bromination^a with clay polymer perbromide reagent (CPN4) and non-clay polymeric perbromide reagent 5.

Code	Substrate	Product	Yield obtained with polymeric clay reagent 4 ^b		Yield obtained with cross-linked polymeric reagent 5 ^b	
			Time (h)	Yield (%)	Time (h)	Yield (%)
1	C ₆ H ₅ COCH ₃	C ₆ H ₅ COCH ₂ Br	8	73.6	8	42
2	CH ₃ C ₆ H ₄ COCH ₃	CH ₃ C ₆ H ₄ COCH ₂ Br	8	61.7	8	46.3
3	ClC ₆ H ₄ COCH ₃	ClC ₆ H ₄ COCH ₂ Br	4	85.6	4	53.8
4	HOC ₆ H ₄ COCH ₃	HOC ₆ H ₄ COCH ₂ Br	12	92.3	12	72.7
5	H ₂ NC ₆ H ₄ COCH ₃	H ₂ NC ₆ H ₄ COCH ₂ Br	4	88.5	4	52.8
6	O ₂ NC ₆ H ₄ COCH ₃	O ₂ NC ₆ H ₄ COCH ₂ Br	4	78.9	4	48.3
7	O ₂ NC ₆ H ₄ COCH ₃	O ₂ NC ₆ H ₄ COCH ₂ Br	4	47 ^c	4	35.3 ^c
8	C ₆ H ₅ CH=CH ₂	C ₆ H ₅ CHBr-CH ₂ Br	2	82.4	4	66
9			8	65.5	8	51.2
10			8	59 ^c	8	39 ^c
11			12	58	12	33
12			12	39.8 ^c	12	27.8 ^c

^a Reactions were carried out in carbon tetrachloride at 75°C.

^b Yield percent of isolated products.

^c Yield obtained using regenerated reagent.

Polymerization was started by adding 1.0 g of benzoyl peroxide as an initiator. The reactor was heated at 90°C for 6 h with a mechanical stirrer. The resin produced was filtered out and washed repeatedly with 1 L of boiling water. The resin was finally dried under vacuum (84.6 kPa) and weighed, giving 47 g of the crosslinked polymer (91.8% yield).

The polymer was quaternized using methyl bromide (21.3 g, 150 mmol). The final product gave 17.0 g of dry resin (97% yields). Elemental analysis gave C, 43.97%; H, 4.38%; and N, 6.41%. The amount of bromide present in the compound was 4.12 mmol/g, as determined by the Volhard method.

Application of polymeric perbromide reagent 5

The same procedure applied in the case of the CPN4 reagent was repeated for polymeric perbromide reagent 5.

Regeneration of polymeric perbromide reagent 5

The same procedure used for regeneration of the CPN4 reagent with bromine was used in the case of polymeric perbromide reagent 5.

Measurements. Elemental microanalysis was performed at the microanalysis unit (C, H, N analyzer) at Tanta University (Egypt). Infrared (IR) absorption spectra were recorded using a Perkin Elmer 1420 spectrophotometer (Boston, Massachusetts, USA). The spectra were collected using the potassium bromide disc technique in the solid state. Samples for X-ray diffraction (XRD) were dried in an oven and then mounted on a sample holder with a large cavity. A smooth surface was obtained by pressing the powder samples with a glass plate. The XRD measurements were performed at the central laboratory at Tanta University (Egypt) using a Philips (Eindhoven, The Netherlands) diffractometer (PW 1840) equipped with Ni-filtered $\text{CuK}\alpha$ radiation

($\lambda = 1.5418 \text{ \AA}$), operated at 40 kV and 30 mA, scanned from $3-25^\circ 2\theta$ at $2^\circ 2\theta/\text{s}$, with a divergence slit of 0.3° . Bragg's law ($n\lambda = 2d\sin\theta$) was used to compute the interlayer spacing.

The surface morphology of the CPN was examined at Scientific City, Alexandria, using a JEOL JSM-6400 (Tokyo, Japan) scanning electron microscope (SEM) operating at 20 kV and equipped with an energy dispersive X-ray (EDX) detector (EUMEX EDX with *SpectrumMono* software). Compressed samples were examined at their fracture surfaces. The specimens were sputter coated with palladium for X-ray mapping of Si and with gold for improved SEM imaging.

Transmission electron microscopy (TEM) analysis was carried out at the Faculty of Medicine at Tanta University using a JEOL JEM-100SX microscope (JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 80 kV. Thin films for use with TEM were prepared from dilute suspensions of 0.1 g of nanocomposite in 10 mL of CCl_4 , using an ultrasonic bath (Clifton ultra 8050-H, Weston-super-Mare, UK) and a drop of the suspension was placed on a 200 mesh carbon-coated Cu grid and the solvent evaporated at room temperature. Other TEM specimens were cut from the nanocomposite block using an ultramicrotome equipped with a glass knife. The ultrathin films (80 nm thick) were cut by moving the sample across a knife edge of glass. The ultrathin flakes floated onto a trough filled with water from where they were collected on 200 mesh copper grids and dried at room temperature.

RESULTS AND DISCUSSION

Synthesis of clay-polymer nanocomposites

The CPN reagent was prepared by a simple method. First, a copolymer was prepared from styrene and 4-vinylpyridine in equimolar ratios of both monomers

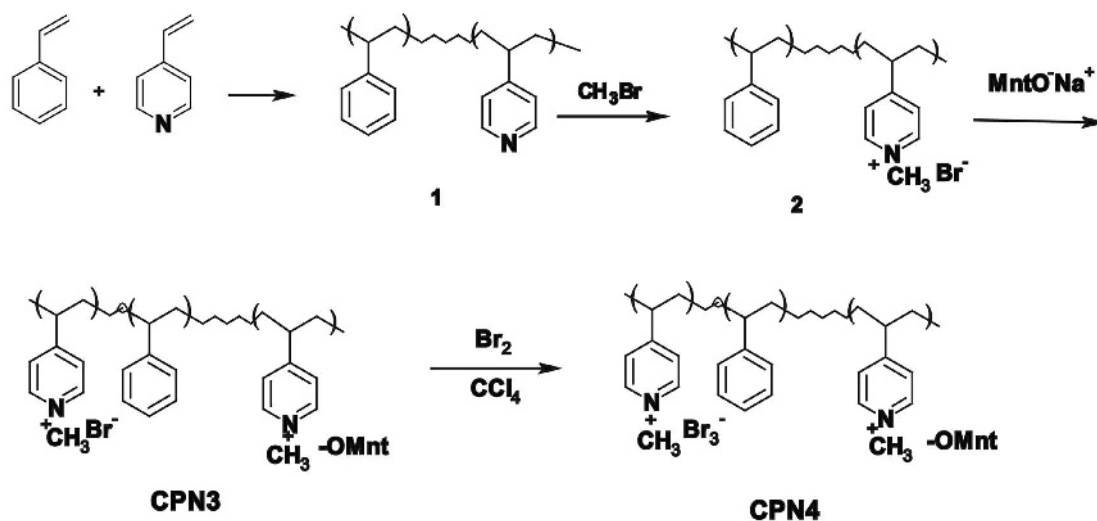


Figure 1. Synthesis of brominating reagent CPN4.

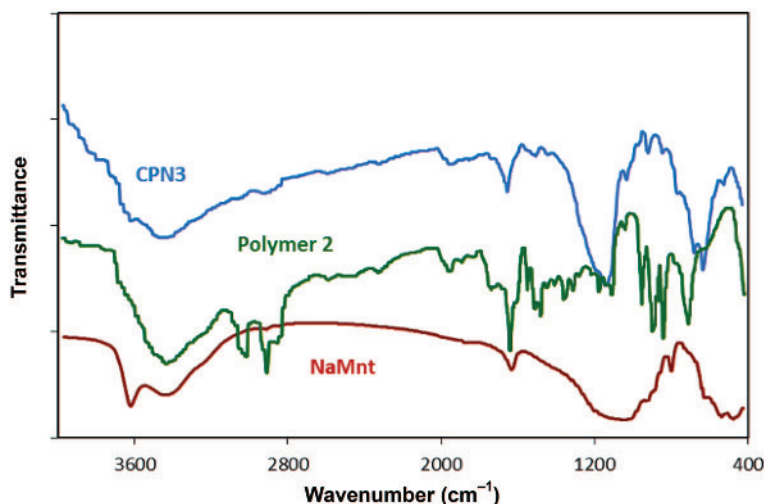


Figure 2. IR spectra of NaMnt, linear polymer 2, and CPN3.

by solution polymerization to give a linear co-polymer with a yield of 89.4%. Infrared spectra showed absorptions at 1603 cm^{-1} (CH=N pyridine unit), and 2920 cm^{-1} (CH₂ chain). The pyridine ring of the copolymer was then quaternized by reaction with methyl bromide to give polymeric pyridinium bromide salt 2 (Figure 1). The nanocomposite CPN3 was then prepared by reaction of styrene-pyridinium bromide copolymer salt 2 (Figure 1) in excess ratio (two-fold excess) with NaMnt, to provide the nanocomposite CPN3. The product (CPN3) was obtained following ion exchange between the Na⁺ ions of NaMnt and Br⁻ of the polymeric salt. The IR spectrum (Figure 2) of the

product showed a shift of the characteristic band of the 4-vinylpyridine from 1603 cm^{-1} to 1638 cm^{-1} due to formation of N⁺Br⁻ functional groups (Colthup *et al.*, 1990). The nanocomposite CPN3 was further reacted with bromine to give the CPN4 perbromide reagent. The IR spectra of CPN4 showed the same characteristic bands as noted in CPN3.

Characterization of nanocomposites

In order to examine the state of dispersion and proof of binding between the polymeric pyridinium salts and Mnt, the CPN3 and CPN4 were subjected to examination by XRD, TEM, and SEM. In general, the interaction of

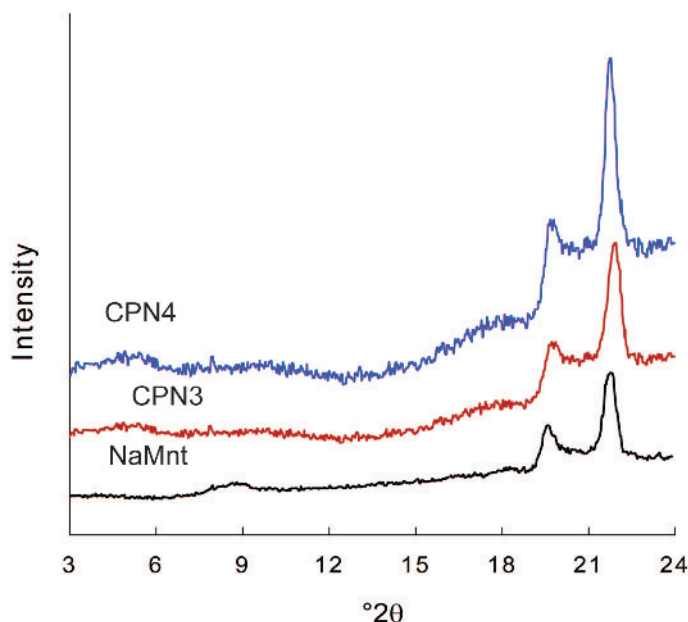


Figure 3. XRD patterns of NaMnt, clay-polymer nanocomposite 3 (CPN3), and clay-polymer nanocomposite 4 (CPN4) treated with perbromide reagent.

polymers and layered silicate structures results either in intercalation or exfoliation as observed for CPN (Han, 2009). Intercalation is observed when the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay:polymer ratio. In contrast, exfoliation is obtained when the layers of the clay are separated in a continuous polymer matrix by average distances that depend on clay loading and result in a greater surface area as a result of silicate layer expansion (Han, 2009). The results obtained from the XRD measurements (Figure 3) show that the characteristic peak of the (001) plane for the NaMnt is observed at $9.2^{\circ}2\theta$, while for CPN3 a broad peak was observed at $5.1^{\circ}2\theta$, and finally, a shoulder at $4.2^{\circ}2\theta$ for CPN4. The basal spacing was calculated, using Bragg's law, to be 9.6 Å and 17.3 Å for NaMnt and CPN3, respectively. The peak shift from a smaller d spacing to larger is due to the intercalation of the polymer into the

interlayers of Mnt. The broadness of the peak at low intensity suggests small stacks of silicate layers. From the width of the diffraction curve, the thickness of a particular set of reflecting planes is calculated using Scherrer's formula (Cullity, 1967).

$$t = 0.9 \lambda / \beta \cos \theta \quad (1)$$

where: t = thickness, $\lambda = 1.5418 \text{ \AA}$, and β = width of the diffraction curve in radians (radians = degree $\times \pi/180$).

The thickness is measured using half of the difference between the two extreme angles at which the intensity is zero. The thickness calculated for CPN3 was found to be 44.11 Å which indicates the stacking of three layers intercalated with polymers. In the case of CPN4, a shoulder indicates that a substantial proportion of the clay mineral is only partially exfoliated. The peaks which appear at large angles ($19.5^{\circ}2\theta$, $21.5^{\circ}2\theta$) in all diffraction patterns correspond to the crystallographic

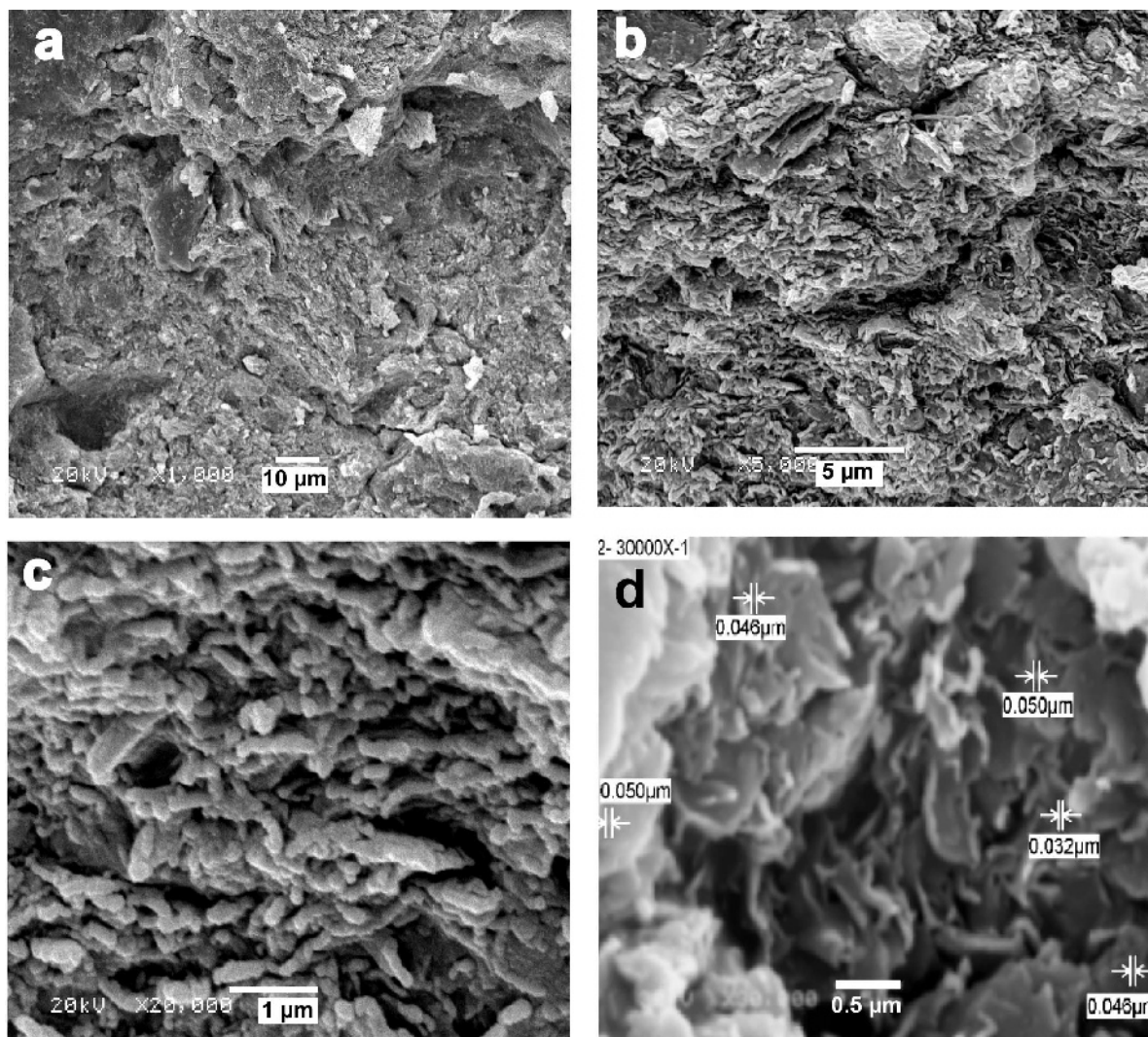


Figure 4. SEM images of CPN3 at various magnifications.

planes (110) and (020) of the clay minerals. A similar observation was reported by Kornmann *et al.* (2001) who attributed the appearance of these peaks to the ability of XRD analysis to detect the presence of clay in the nanocomposite.

The SEM images (Figure 4) were used to characterize the CPN3 surface. The images reveal clearly the absence of phase separation which indicates the formation of homogenous nanocomposite and the uniform dispersion of the Mnt layers across the linear polymeric salt matrix. Careful examination of SEM images of the fracture surface of CPN3 (Figure 4a–c) showed no inorganic

agglomerates, and an average size of 44.8 nm of the domain was observed at high magnification (Figure 4c–d) of the powder sample.

The identity of the particles was further explored using the SEM images and by means of X-ray elemental analysis. As shown in Figure 5a, on the fracture surface of CPN3 no mineral domains or agglomerates were visible. X-ray mapping of Si (Figure 5b, same magnification) showed almost uniform distribution of white dots, representative of Si in the polymer matrix. In the same images at higher magnification (Figure 5c), the same trend was also observed on the fracture surface

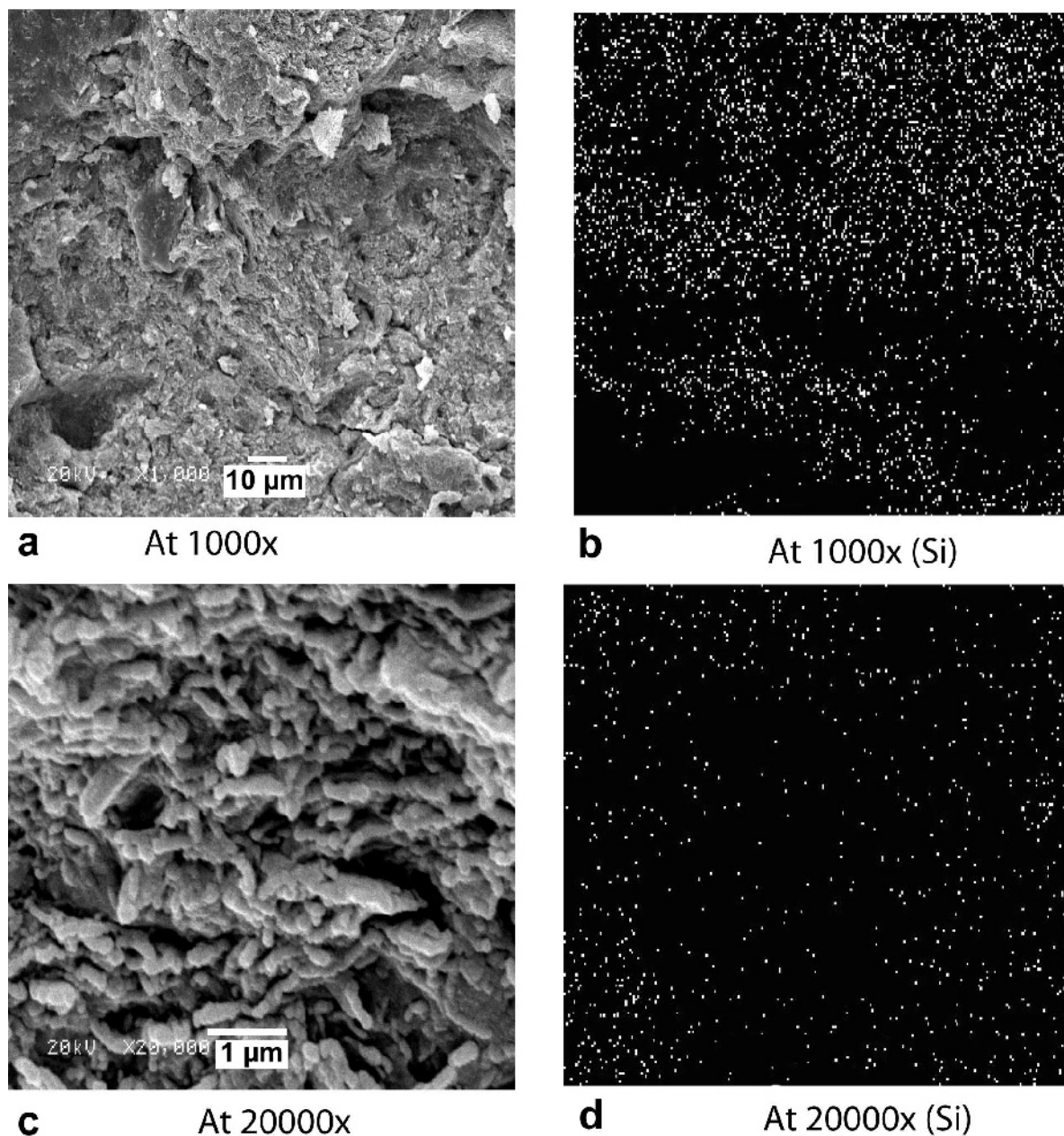


Figure 5. SEM images (a,c) with X-ray mapping (b,d) of CPN3.

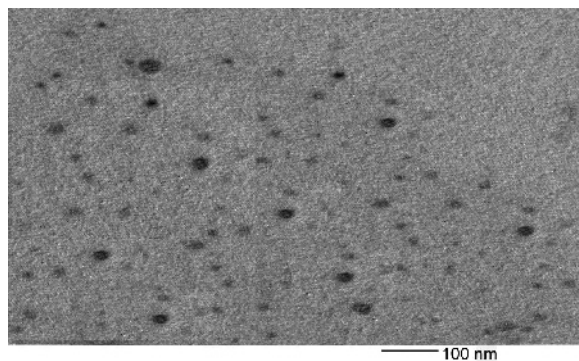


Figure 6. TEM image of CPN4 treated with perbromide reagent.

where no mineral domains or agglomerates could be seen, in addition to almost homogeneous distribution of Si in the polymer matrix.

Perbromide reagent CPN4

The supported perbromide reagent CPN4 was obtained by simple treatment of a cold dispersion of CPN3 in carbon tetrachloride with bromine solution in carbon tetrachloride (Figure 1). The XRD data for the CPN4 perbromide reagent obtained (Figure 3) show that the Mnt interlayer spaces had expanded from 9.6 Å (anhydrous Mnt) to 21.1 Å and indicated the formation of a shoulder of 11.71 Å. A thin film of a crude reagent CPN4 fabricated from a sample dispersion in carbon tetrachloride was examined by TEM (Figure 6). From the TEM images, the reagent CPN4 appears to be composed of mineral-rich spheres in which the polymer is bound to the mineral, dispersed in a polymer matrix. The spheres ranged in diameter from 11.6 to 21.7 nm with an average size of 16.6 nm. A similar morphology was reported for styrene-malic anhydride copolymer Mnt nanocomposite (Salahuddin and Akelah, 2002).

Applications of brominating reagent

The CPN4 perbromide reagent was used in the bromination of carbonyl compounds containing α -hydrogen atoms, alkenes, and arenes, as outlined (Figure 7).

The reactions were usually carried out in carbon tetrachloride under reflux conditions (Table 1). In general, excess clay-polymer perbromide reagent CPN4 was used to ensure complete bromination. The reactions generally gave moderate to excellent yields (62–92%) of the corresponding brominated derivatives. Reactions were easy to follow through the change of the orange reagent to yellow as its bromine content was consumed in the reaction. The yields of reactions were better than those obtained from the application of the crosslinked polymeric brominating agent (5) (Table 1). The observed (greater than expected) increase in yields could be due to the large surface area resulting from mixing of clay with the polymer matrix and the presence of chemically unbound bromine which is physically adsorbed and buried within the clay layers. The advantages of using clay-polymer reagent CPN4 include simple separation of products after completion of reactions and easy regeneration of the reagent by successive washings with organic solvent to extract the product followed by treatment with excess bromine. The regenerated reagent was used in further bromination reactions (see Table 1, codes 7, 10, 12) and gave moderate to excellent yields.

CONCLUSIONS

Clay-polymer nanocomposite (CPN)-supported perbromide reagent (CPN4) was prepared and used for the bromination of carbonyl compounds containing α -hydrogen atoms, alkenes, and arenes. The yields were better than when crosslinked polymeric reagent 5 was used. The advantages of using the former method to create the reagent are stability at room temperature and the ease of regeneration from the polymeric by-product as well as the yields of the brominated products. These advantages make it possible to use CPN based on styrene-*co*-vinyl pyridinium polymer and NaMnt as reactive reagents in synthetic organic chemistry. Transmission electron microscopy images indicated the formation of clay-polymer domains ~16.6 nm in size. Examination by SEM revealed no mineral agglomeration

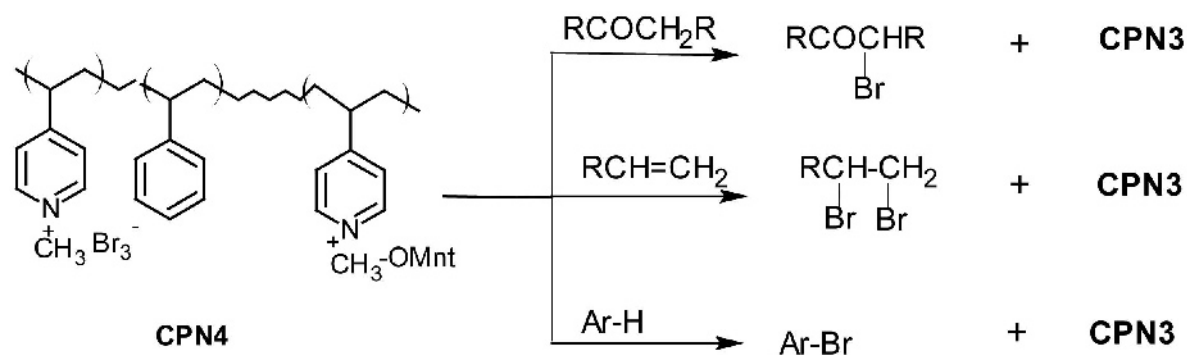


Figure 7. Bromination with reagent CPN4.

and Si mapping indicated that the clay minerals were dispersed homogeneously in the polymer matrix.

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