

Influence of the Structure of the Onium Iodide Salts on the Properties of Modified Montmorillonite

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ABSTRACT: Dialkyl imidazoline, alkyl pyridine and alkyl quinoline containing salts have been synthesized and used as new surfactants for cationic exchange of layered silicates, such as montmorillonite (MMT) in order to evaluate their role in the formation of intercalated MMT clays. The new salts have been characterized by FTIR, ¹H, ¹³C-NMR spectra. These compounds have been intercalated into the layers of MMT via a solution dispersion technique and the extent of the interlayer space expansion was confirmed by using wide angle X-ray diffraction and FTIR spectra. Thermogravimetry analysis shows that these salts can be used in place of ammonium salts to produce organophilic clays with higher thermal stability than commercial alkyl ammonium-treated MMT. Moreover, the results also show that the imidazolium-modified clays have a greater thermal stability compared to the quinolinium and the pyridinium-modified clay. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: ionic liquid; imidazolium; pyridinium; quinolinium iodide; intercalated montmorillonite clays; thermal stability

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INTRODUCTION

The insertion of lamellar silicates in a polymer matrix may have beneficial effects on the final properties of the nanocomposite. Because clay nanocomposites can produce dramatic improvements in a variety of properties, it is important to understand the factors which affect delamination of the clay. These factors include the possible interaction of the intercalated silicate with the polymer, the exchange capacity of the clay, the polarity of the reaction medium, the thermal stability of organically modified silicate layer, and the chemical nature of the interlayer cations.^{1–22} By modifying the surface polarity of the clay, interlayer cations allow thermodynamically favorable penetration of polymer precursors into the interlayer region. The capability of the interlayer cations to assist in the delamination of the clay mainly depends on its chemical nature (polarity, bulkiness...). The correct selection of modified clays is essential to ensure effective penetration of the polymer or its precursor into the interlayer spacing of the clay resulting in the desired exfoliated or intercalated product. For the preparation of nanocomposites from high temperature engineering thermoplastics, a major limitation in the use of conventional interlayer cation modified

clays is the thermal instability of the alkylammonium species during processing.^{4–6,8,9,12–19,21,22} The nature of the interlayer cations also seems to play a crucial role on the degradation behavior of these materials.^{4–19,22} Ionic liquids, which are known to display high thermal stability, should therefore be advantageously used to overcome the lower thermal stability of organic modifiers that are used for dispersion and compatibilization. Recent approaches using aromatic cations, such as alkyl-imidazolium^{6,15,17,19–32} and alkyl-pyridinium^{4,5,19,33–36} do offer a viable alternate as they can survive much higher temperatures. Among the organic cations known to form ionic liquids, alkylimidazolium cations have been studied in detail. Generally, the imidazolium cations tend to be thermally more stable than the tetra-alkyl ammonium cations.³⁷ This is because alkylimidazolium-based salts usually exhibit low melting points and low viscosities that normally lead to high conductivities. These valuable properties of alkylimidazolium-based salts are often explained by charge delocalization on the aromatic five-membered ring. According to Zhang et al.,³⁸ thermal decomposition is also dependent on the anion nature; high thermal stability being provided by certain kinds of anions such as (CF₃SO₂)₂N[−] and

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(C₂F₅SO₂)₂N⁻. The given relative anion stabilities are as follows: PF₆⁻ > (C₂F₅SO₂)₂N⁻ > (CF₃SO₂)₂N⁻ > CF₃SO₃⁻ > BF₄⁻ > Me(CF₃SO₂)₃C > I⁻ > Br⁻ > Cl⁻.

In this work, a series of organic iodide salts based on long alkyl chain imidazolium, pyridinium and quinolinium have been synthesized and used in place of ammonium salts to produce organophylic montmorillonite (MMT). The long alkyl chains cause expansion of the interlayer distance. The aromatic groups are also crucial in helping to generate a better intercalation of the clay platelets because aromatic groups can be trapped in the hexagonal cavities of the layers. The choice of a similar anion (iodide) for all the salts has allowed comparing efficiently the various cations and the influence of the N-alkyl chain length, a rigorous study, which had never been performed before. Thus, to evaluate and to compare the potential of these molten salts as substitutes for the conventional alkyl ammonium salts, a detailed study was carried out using thermogravimetry analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy techniques. In addition, X-ray diffraction (XRD) has been used to characterize the layered structures of the modified clays. The XRD curves showed that as the alkyl group increased in length, the *d*-spacing increased. Study of the influence N-alkyl chain length on the thermal properties of the organophylic MMT clearly demonstrates that the best stability is obtained with the longest chains (C18) as probed by TGA.

EXPERIMENTAL

Measurements and Materials

¹H and ¹³C NMR spectra have been recorded on a Brüker DPX 250 (250 MHz) spectrometer with tetramethylsilane as internal standard reference for calibrating chemical shift. Data are given in the following order: δ , chemical shift in ppm, multiplicity (s, singlet; d doublet; t, triplet; q, quartet; hept, heptuplet; m, multiplet), coupling constants in Hertz, assignment broad band ¹H decoupling. FTIR absorption spectra were recorded on a Perkin Elmer Spectrum One FTIR Spectrometer with an ATR accessory. The IR absorptions were observed as strong bands and are given in cm⁻¹. High-resolution mass spectra (HRMS) have been obtained with a Waters Q-TOF Micro instrument in electrospray ionisation positive (ES+) or negative (ES-) mode and lockspray with orthophosphoric acid. These analyses have been performed with an infusion introduction of 10 μ L.min⁻¹, a source temperature of 80°C, a desolvation temperature of 120°C and an external calibration with NaI. XRD patterns were collected on a Philips Xpert MPD Pro diffractometer (40 kV, 40 mA), equipped with a graphite mono-chromatized Cu K α radiation, with a scanning rate of 2 s/step, and 0.01° 2 θ step size. Thermogravimetric analyses (TGA) were performed on a Perkin Elmer TGA 7 (alumel, nickel and perkalloyl calorimeter). The samples were heated from 30 to 800°C at a rate of 10°C /min, under nitrogen flow.

A sodic MMT, denoted *Nanofil 757* (MMT), i.e., an aluminosilicate with intercalated sodium was chosen as pristine clay and was provided by Süd Chemie (Germany). The *Nanofil 757* has a cation exchange capacity of 95 meq/100 g and is described by the following formula Na_{0.65}[Al, Fe]₄Si₈O₂₀(OH)₄. The organically modified MMTs with the dimethyl (benzylmethyl) tallow

quaternary ammonium (*Nanofil 919* namely DMBT-MMT) was commercial MMTs, provided by Süd Chemie. C18P-MMT was obtained by modification of MMTs with octadecyltriphenylphosphonium iodide.³⁹ Butyliodide, dodecylidide, imidazole, octadecylidide, pyridine, and quinoline were obtained from Aldrich and used without further purification.

Syntheses

Imidazolium (1a-1e), Pyridinium (2a-2b), and Quinolinium (3a-3b) Salts

General Procedure for the Synthesis of 1-alkyl-3-alkyl imidazolium iodides (1a-1e). These compounds are not commercially available, and their syntheses were not reported before. They were prepared using protocols related to those reported by Gilman et al.¹⁷ Costache et al.³⁰ and Chigwada et al.³⁶ for ionic liquids bearing one or two long aliphatic alkyl chains C_n (n ≤ 16), and Stoeffler et al.^{4,5} for 2C₁₈ImBr, and different kinds of anions, except iodide.

A solution of sodium methoxide was prepared in a septum sealed 100-mL round-bottomed, three-necked flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer, by dissolving 1 equiv. of sodium (0.465 g, 20 × 10⁻³ mol) in dry freshly distilled methanol (10 mL). Imidazole (1 equiv., 1.37 g, 20.23 × 10⁻³ mol) diluted in acetonitrile (10 mL) was then added into the stirred mixture of sodium methoxide previously cooled at room temperature. After 15 min, a white precipitate was formed. The suspension was then concentrated under reduced pressure for 1 h. The dried white powder was dissolved in acetonitrile and a solution of alkyl iodide R¹I [1 equiv., 20 × 10⁻³ mol i.e., 5.12 mL, for dodecyl iodide (C₁₂H₂₅I) and 7.70 g for octadecyl iodide (C₁₈H₃₇I)] diluted in acetonitrile (10 mL) was then added under an inert atmosphere of nitrogen at room temperature. The mixture was stirred for 1 h, then heated under reflux at 100°C for about 24 h. A solution of alkyl iodide R²I (1 equiv., 20 × 10⁻³ mol i.e., 2.30 mL for butyl iodide (C₄H₉I), 5.12 mL for dodecyl iodide (C₁₂H₂₅I) and 7.70 g for octadecyl iodide (C₁₈H₃₇I)] diluted in acetonitrile (10 mL) was added to the mixture at room temperature. The stirred suspension was heated under reflux at 100°C for about 24 h leaving a brownish viscous oil in each case. After cooling to room temperature, the solvent was removed by evaporation under vacuum, the orange-coloured or beige solid was filtered, washed repeatedly with pentane and dried. Purification of the resulting imidazolium salts was accomplished by crystallization from a 75/25 ethyl acetate/acetonitrile: mixture. After drying, imidazolium iodides **1a-1e** were fully characterized by spectroscopy and TGA analysis [TGA curves and TGA derivative weight curves (DTG)] (Figures 1–3 and 5).

Butyldodecylimidazolium Iodide (C₄C₁₂Im) (1a). Orange-coloured powder, Yield = 83%. ¹H NMR (CDCl₃): δ 0.75–0.95 (2t, J = 7.3 Hz, 6H, 2 CH₃), 1.15–1.40 (m, 24H, 12 CH₂), 1.80–1.95 (m, 2H, NCH₂CH₂), 4.25–4.38 (m, 4H, NCH₂), 7.35 (s, 1H, H arom), 7.42 (s, 1H, H arom), 9.10 [s (b), 1H, H arom]. ¹³C NMR (CDCl₃): δ 13.37 (CH₃); 13.97 (CH₃); 19.28 (CH₂Me); 22.49 (CH₂Me); 26.04; 28.83; 29.14–29.41; 30.20; 30.50; 31.7; 32.05 (CH₂); 49.10; 49.70 (NCH₂CH₂); 49.99

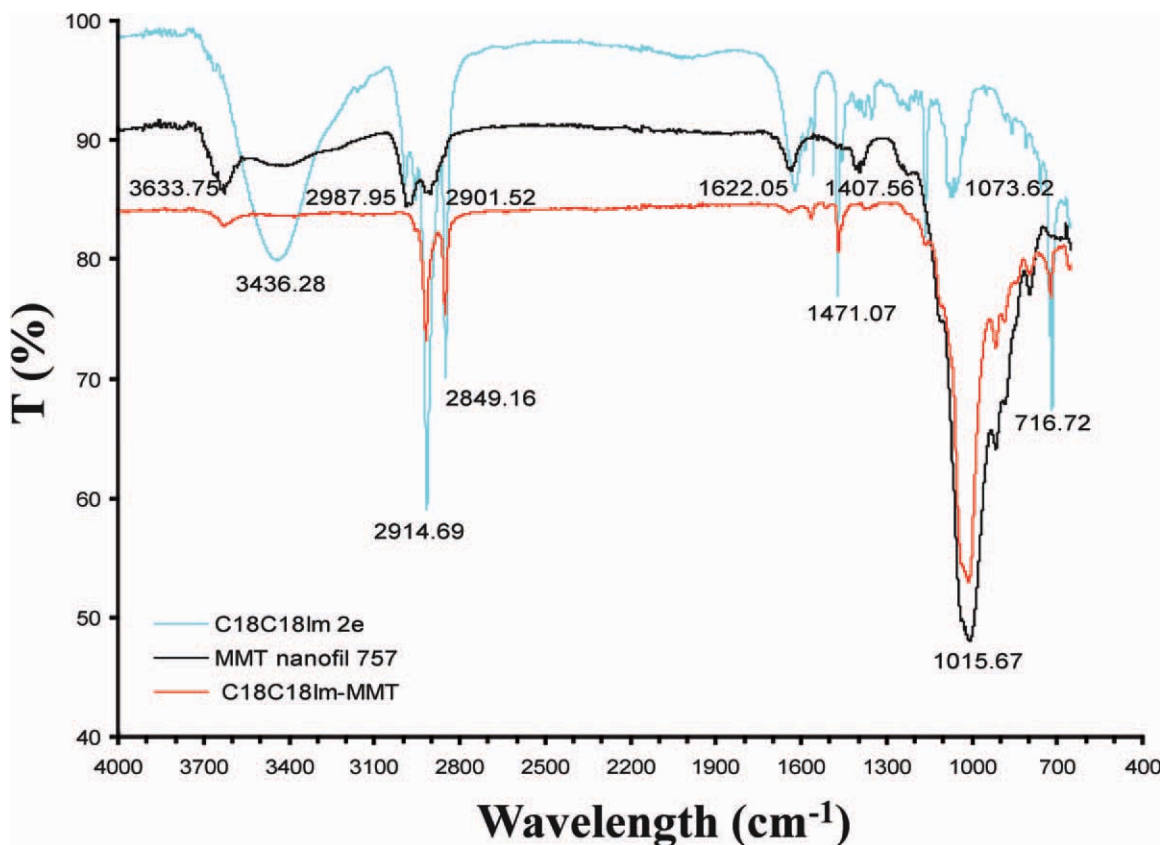


Figure 1. FTIR spectra of MMT *nanofil 757*, C18C18Imidazolium 1e and C18C18Im-MMT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

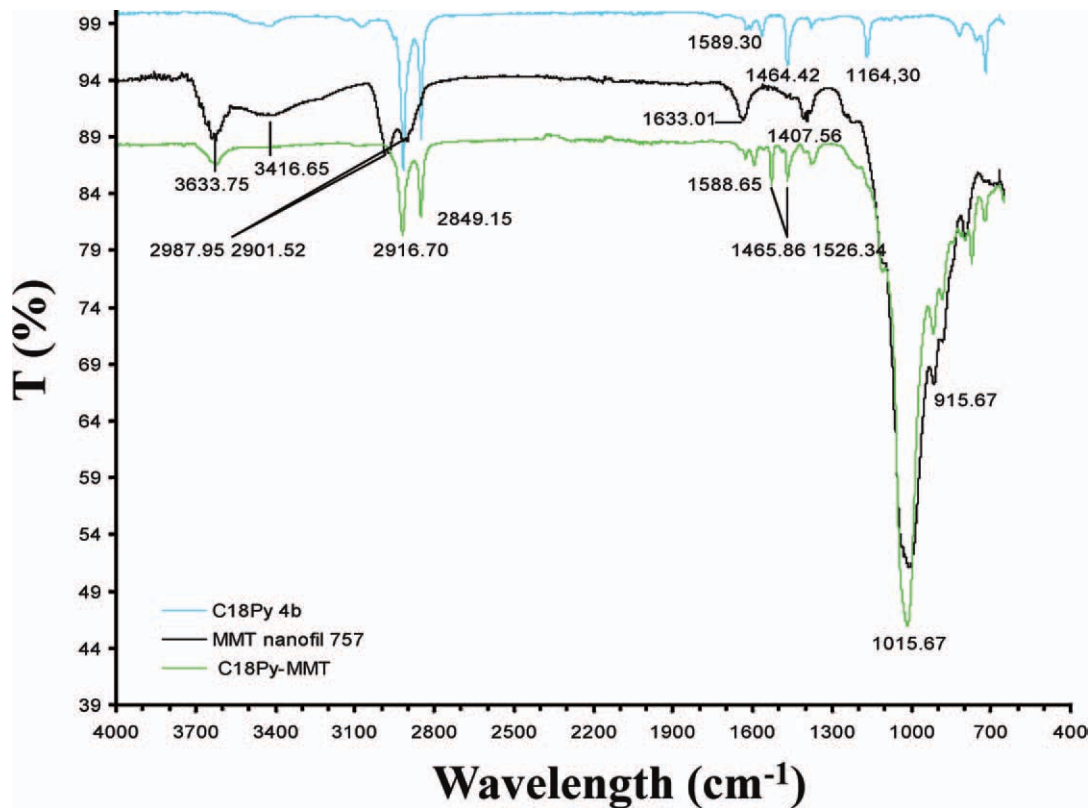


Figure 2. FTIR spectra of MMT *nanofil 757*, C18Pyridinium 2b and C18Py-MMT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

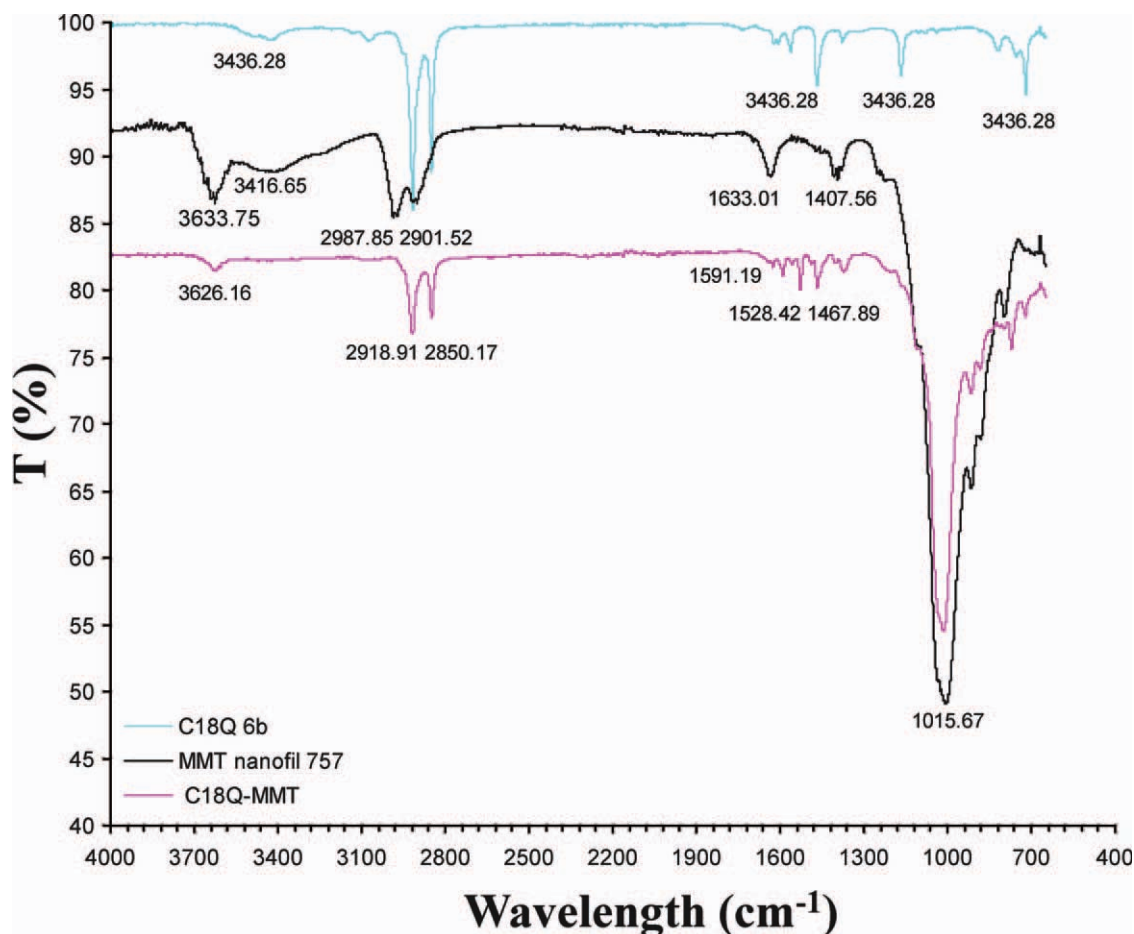


Figure 3. FTIR spectra of MMT *nanofil* 757, C18Q 3b and C18Q-MMT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(CH₂N=); 58.34 (CH₂N-); 120.89 (NC=); 122.56 (=CN); 135.78 (N-C=N). IR (KBr) ν (cm⁻¹): 1377 (C=N). HRMS (m/z): calcd for C₁₉H₃₇N₂I, 420.4134; found, 420.4118 [M + H]⁺.

Butyloctadecylimidazolium Iodide (C₄C₁₈Im) (1b). White powder, Yield = 97%. ¹H NMR (CDCl₃): δ 0.80–0.95 (m, 6H, 2 CH₃), 1.10–1.40 (m, 36H, 18 CH₂), 1.75–1.95 (m, 2H, NCH₂CH₂), 4.25–4.35 (m, 2H, CH₂N=), 7.25 (s, 1H, H arom), 7.35 (s, 1H, H arom), 9.15 [s (b), 1H arom]. ¹³C NMR (CDCl₃): δ 13.46 (CH₃); 14.07 (CH₃); 19.40 (CH₂Me); 22.61 (CH₂Me); 26.17; 28.46; 28.95; 29.29–29.63; 30.27; 30.43; 31.84; 32.13; 32.31; 33.49 (CH₂); 49.69 (NCH₂CH₂); 49.87 (CH₂N=); 50.15 (CH₂N-); 121.44; 122.48 (=CN); 136.06 (N-C=N). IR (KBr) ν (cm⁻¹): 1377 (C=N). HRMS (m/z): calcd for C₂₅H₄₉N₂I, 504.5724; found, 504.5706 [M + H]⁺.

Dodecyldodecylimidazolium Iodide (C₁₂C₁₂Im) (1c). Orange-coloured powder, Yield = 81%. ¹H NMR (CDCl₃): δ 0.75–0.90 (m, 6H, 2 CH₃), 1.10–1.35 (m, 40H, 20 CH₂), 1.75–1.95 (m, 2H, NCH₂CH₂), 4.30 (t, 2H, CH₂N=), 7.25 [s (b), 1H, H arom], 7.35 [s (b), 1H, H arom], 9.15 [s (b), 1H, H arom]. ¹³C NMR (CDCl₃): δ 14.04 (CH₃); 22.59 (2CH₂Me); 26.17; 28.46; 28.94; 29.25 – 29.53; 30.26; 30.42; 31.82; 33.50 (CH₂); 49.69 (NCH₂CH₂); 49.87 (CH₂N=); 50.18 (CH₂N-); 121.44; 122.36, (=CN); 136.10 (N-C=N). IR (KBr) ν (cm⁻¹):

1378 (C-N), 1662 (C=C). HRMS (m/z): calcd for C₂₇H₅₃N₂I, 532.6254; found, 532.6238 [M + H]⁺.

Dodecyloctadecylimidazolium Iodide (C₁₂C₁₈Im) (1d). Orange-coloured powder, Yield = 98%. ¹H NMR (CDCl₃): δ 0.75–0.90 (m, 6H, 2CH₃), 1.15–1.30 (m, 52H, 26 CH₂), 1.75–1.95 (m, 2H, NCH₂CH₂), 4.30 (t, 2H, CH₂N=), 7.45 (m, 1H, H arom), 7.65 (m, 1H, H arom), 9.15 [s (b), 1H, H arom]. ¹³C NMR (CDCl₃): δ 7.33 (CH₃); 14.04 (CH₃); 22.6 (2CH₂Me); 26.15; 28.45; 28.94; 29.26–29.63; 30.27; 30.42; 31.82; 33.48 (CH₂); 50.09 (CH₂N=); 50.18 (CH₂N-); 122.29; 122.42 (=CN); 136.02 (N-C=N). IR (KBr) ν (cm⁻¹): 1378 (C-N), 1659 (C=C). HRMS (m/z): calcd for C₃₃H₆₅N₂I, 616.7844; found, 616.7828 [M + H]⁺.

Diocetadecylimidazolium Iodide (C₁₈C₁₈Im) (1e). White powder, Yield = 97%. ¹H NMR (CDCl₃): δ 0.75–0.90 (m, 6H, 2CH₃), 1.15–1.30 (m, 64H, 32 CH₂), 1.80–1.90 (m, 2H, NCH₂CH₂), 4.30 (t, 2H, CH₂N=), 7.45 (m, 1H, H arom), 7.65 (m, 1H, H arom), 9.15 [s (b), 1H, H arom]. ¹³C NMR (CDCl₃): δ 14.10 (2CH₃); 22.67 (2CH₂Me); 26.23; 28.97; 29.35–29.69; 30.24; 31.91 (CH₂); 50.10; (CH₂N=); 50.32 (CH₂N-); 121.69; 122.48 (=CN); 136.88 (N-C=N). IR (KBr) ν (cm⁻¹): 1378 (C-N). HRMS (m/z): calcd for C₃₉H₇₇N₂I, 700.6065; found, 700.6076 [M + H]⁺.

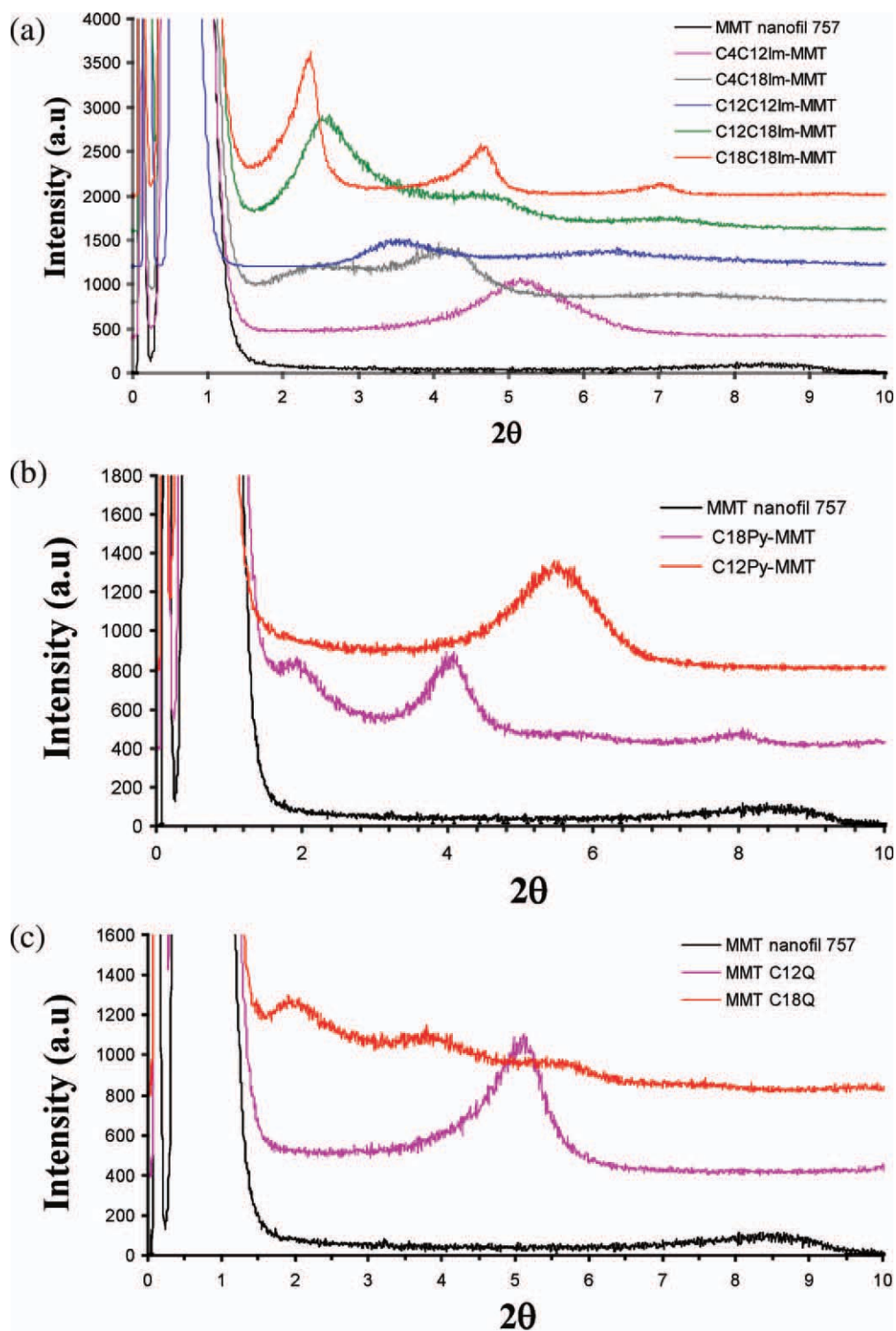


Figure 4. (a) XRD patterns of MMT modified by N-alkyl-N'-alkyl imidazolium iodide 1a-1e. (b) XRD patterns of MMT modified by dodecyl pyridinium iodide 2a, octadecyl pyridinium iodide 2b. (c) XRD patterns of MMT modified by dodecyl quinolinium iodide 3a and octadecyl quinolinium iodide 3b. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

General Procedure for the Synthesis of Pyridinium Iodides (2a–2b)

In a 100-mL flask were placed under a nitrogen pressure, 10×10^{-3} mol of alkyl iodide [dodecyl iodide ($C_{12}H_{25}I$) or octadecyl

iodide ($C_{18}H_{37}I$)] and distilled pyridine (1.5 equiv.). The stirred suspension was allowed to react for 24 h at room temperature. A yellow precipitate was formed. The reaction mixture was then filtered, washed repeatedly with pentane. Most of the solvent was

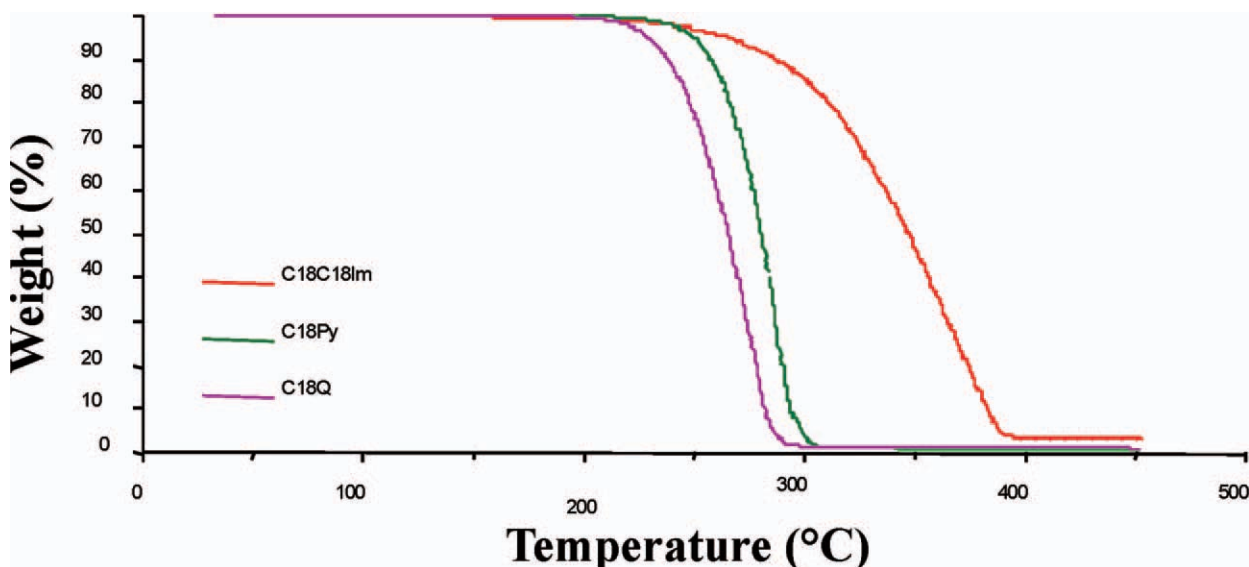


Figure 5. TGA curves for C18C18 imidazolium (C18C18Im), C18 pyridinium (C18Py) and C18 quinolinium (C18Q) salts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

removed under vacuum. Pyridinium iodides **4a-4b** were isolated after drying and fully characterized (Figures 1–3 and 5–7).

Dodecylpyridinium Iodides (C₁₂Py) (2a). Yellowish powder, Yield = 92%. ¹H NMR (CDCl₃) δ: 0.82 (t, *J* = 7.3 Hz, 3H, CH₃), 1.15–1.30 (m, 18H, 9 CH₂), 1.90–2.02 (m, 2H, NCH₂CH₂), 4.90 (t, *J* = 7.5 Hz, 2H, NCH₂), 8.05 (t, *J* = 7.2 Hz, 2H, H arom), 8.45 (t, *J* = 7.8 Hz, 1H, H arom), 9.35 (d, *J* = 5.4 Hz, 2H, H arom). ¹³C NMR (CDCl₃) δ: 13.84 (CH₃); 22.31 (CH₂Me); 25.65; 28.74; 28.96; 29.03; 29.23; 31.52; 31.62 (CH₂); 61.64 (CH₂N=); 128.39 (C=C); 144.56; 145.56 (=CN). IR (KBr) ν (cm⁻¹): 1328 (C–N), 1635 (C=C). HRMS (*m/z*): calcd for C₁₇H₃₀NI, 375.3201; found, 375.3190 [M + H]⁺.

Octadecylpyridinium Iodides (C₁₈Py) (2b). White powder, Yield = 90%. ¹H NMR (CDCl₃) δ: 0.84 (t, *J* = 7.3 Hz, 3H, CH₃), 1.15–1.30 (m, 30H, 15 CH₂), 1.90–2.02 (m, 2H,

NCH₂CH₂), 4.90 (t, *J* = 7.5 Hz, 2H, NCH₂), 8.05 (t, *J* = 7.2 Hz, 2H arom), 8.45 (t, *J* = 7.8 Hz, 1H, H arom), 9.35 (d, *J* = 5.4 Hz, 2H, H arom). ¹³C NMR (CDCl₃) δ: 14.04 (CH₃); 22.58; 25.91; 28.99; 29.25–29.60; 31.81–31.84 (CH₂); 62.02 (CH₂N=); 128.57 (C=C); 144.82; 145.50 (=CN). IR (KBr) ν (cm⁻¹): 1377 (C–N), 1620 (C=C). HRMS (*m/z*): calcd for C₂₃H₄₂NI, 459.2118; found, 459.2108 [M + H]⁺.

General Procedure for the Synthesis of Quinolinium Iodides (3a–3b)

In a 100-mL flask, quinoline (13.5 mmol) and 1 equiv. of alkyl iodide [dodecyl iodide (C₁₂H₂₅I) or octadecyl iodide (C₁₈H₃₇I)] was placed at room temperature and under nitrogen pressure. The mixture was refluxed at 100°C for 3 h, followed by cooling to room temperature leading to a yellow oil, which was crystallized from a 1/1 mixture of ethyl acetate/acetonitrile. The

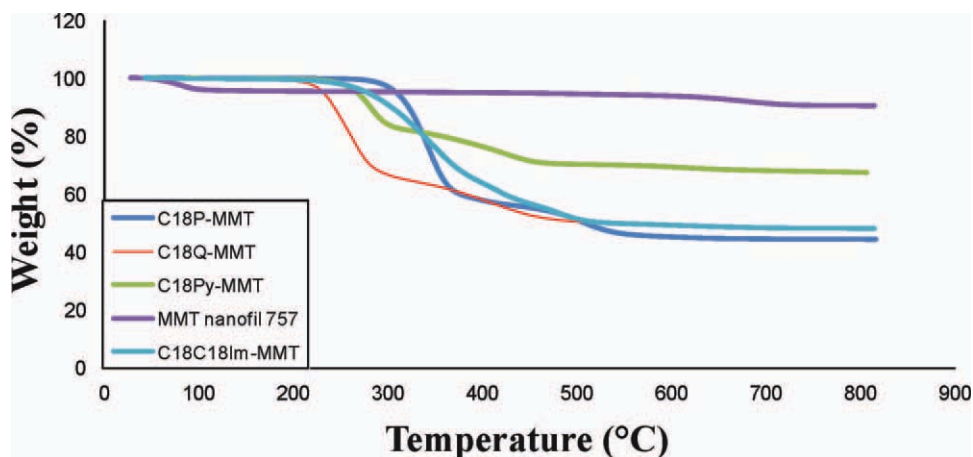


Figure 6. TGA curves for MMT *nanofil* 757, C18C18 imidazolium-MMT (C18C18Im-MMT), C18 pyridinium-MMT (C18Py-MMT), C18 quinolinium-MMT (C18Q-MMT), DMBT-MMT, and C18 phosphonium-MMT (C18P-MMT). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

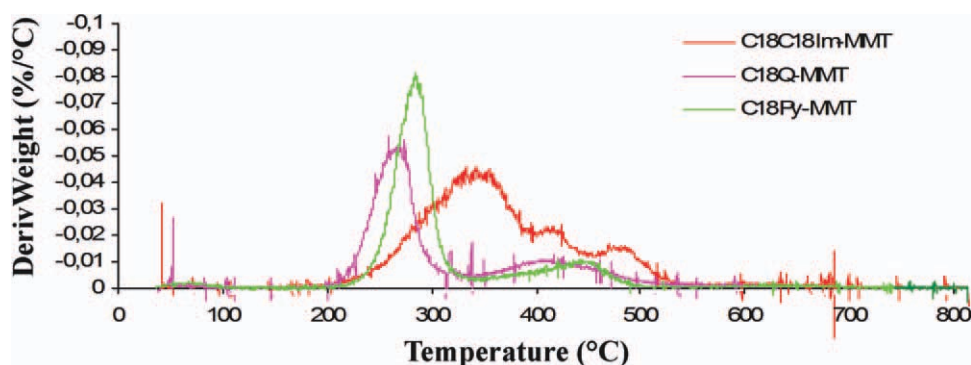


Figure 7. TGA derivative weight curves for C18C18 imidazolium-MMT (C18C18Im-MMT), C18 pyridinium-MMT (C18Py-MMT) and C18 quinolinium-MMT (C18Q-MMT). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solvents were removed under vacuum. The solid was then filtered, washed with pentane, dried under vacuum. The purified quinolinium iodides **6a–6b** were characterized by ^1H , ^{13}C NMR, FTIR spectroscopy and TGA analysis (Figures 1–3 and 5–7).

Dodecylquinolinium iodides (C₁₂Q) (3a). Yellowish powder, Yield = 70%. ^1H NMR (CDCl_3) δ : 0.80 (t, $J = 7.3$ Hz, 3H, CH_3), 1.15–1.39 (m, 18H, 9 CH_2), 1.95–2.10 (m, 2H, NCH_2CH_2), 5.29 (t, $J = 7.5$ Hz, 2H, NCH_2), 7.93 (t, $J = 7.2$ Hz, 1H, H arom), 8.15 (m, 3H, H arom), 8.26 (t, $J = 8.4$ Hz, 2H, H arom), 9.00 (d, $J = 8.4$ Hz, 1H, H arom). ^{13}C NMR (CDCl_3) δ : 13.98 (CH_3); 22.48; 26.33; 28.99; 29.12–29.38; 30.15; 31.68 (CH_2); 58.38 ($\text{CH}_2\text{N}=\text{}$); 118.53; 122.2; 129.85; 130.29; 131.16; 136.35; 137.48 (C=C); 147.61; 149.18 (=CN). IR (KBr) ν (cm^{-1}): 1375 (C–N), 1623 (C=C). HRMS (m/z): calcd for $\text{C}_{21}\text{H}_{32}\text{NI}$, 425.3886; found, 425.3868 [$\text{M} + \text{H}$] $^+$.

Octadecylquinolinium Iodides (C₁₈Q) (3b). Yellowish powder, Yield = 53%. ^1H NMR (CDCl_3) δ : 0.80 (t, $J = 7.3$ Hz, 3H, CH_3), 1.15–1.49 (m, 30H, 15 CH_2), 2.00–2.15 (m, 2H, NCH_2CH_2), 5.28 (t, $J = 7.5$ Hz, 2H, NCH_2), 7.90 (t, $J = 7.2$ Hz, 1H, H arom), 8.15 (m, 3H, H arom), 8.27 (t, $J = 8.4$ Hz, 2H, H arom), 8.90 (d, $J = 8.4$ Hz, 1H, H arom). ^{13}C NMR (CDCl_3) δ (ppm): 14.02 (CH_3); 22.54; 26.39; 29.05; 29.22–29.56; 30.19; 31.77 (CH_2); 58.43 ($\text{CH}_2\text{N}=\text{}$); 118.54; 122.28; 129.88; 130.29; 131.18; 136.32; 137.52 (C=C); 147.60; 149.28 (=CN). IR (KBr) ν (cm^{-1}): 1375 (C–N), 1623 (C=C). HRMS (m/z): calcd for $\text{C}_{27}\text{H}_{44}\text{NI}$, 509.5476; found, 509.5450 [$\text{M} + \text{H}$] $^+$.

Organic Modification of MMT Nanofil 757

MMT modification is achieved by performing ion exchange reaction with imidazolium (**1a–1e**), pyridinium (**2a–2b**) and quinolinium (**3a–3b**) salts prepared above, according to methods reported previously.^{8,9,31,36,40–45}

An excess of the salts **1a–1e**, **2a–2b**, and **3a–3b** (2 equiv.) based on the cation exchanged capacity (CEC = 95 meq/100 g) of the sodium MMT Nanofil 757, purchased from Sud Chemie was used.⁴⁰ MMT was dried at 110°C for 48 h and washed with distilled water (10 wt %) with vigorous stirring for 24 h to cause the delamination of the MMT. The determined amount of the obtained imidazolium **1a–1e** (2.66 g), pyridinium **2a–2b** (1.74 g), quinolinium **3a–3b** salts (1.93 g) and the MMT Nanofil

757 (2 g, 1.9×10^{-3} equiv.) were dispersed in 400 mL of deionized water. This dispersion was mixed and stirred vigorously at 80°C for 17 h, followed by filtration and repeated washing with organic solvent (acetonitrile at room temperature or hot ethanol) to remove some eventually remaining traces of imidazolium, pyridinium, or quinolinium salts. Washing was then performed with deionized water until no iodide ions could be detected using an aqueous silver nitrate (AgNO_3) solution. The solvent was removed by evaporation under vacuum. Modified MMT was then dried for 1 night, at a suitable temperature (not higher than 80°C) to prevent from any degradation of alkyl ammonium MMT by Hofmann elimination mechanism.^{12,14,17,23} The product was stored in a dessicator before analysis.

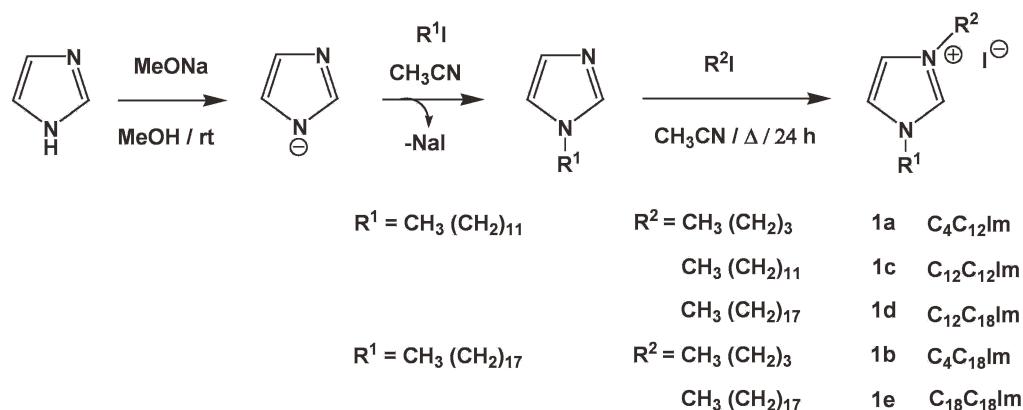
RESULTS AND DISCUSSION

Synthesis of Imidazolium (1a–1e), Pyridinium (2a–2b), and Quinolinium (3a–3b) Salts

We report herein, a general and simple method for the synthesis of a series of ammonium salts containing imidazole, pyridine and quinoline moieties (Schemes 1–3). Dialkylimidazolium, alkylpyridinium, and alkylquinolinium cation-based ionic liquids were easily prepared by alkylation of the commercially available imidazole, pyridine or quinoline with an alkyl iodide to give respectively the corresponding 1-alkyl-3-alkylimidazolium, 1-alkylpyridinium iodide and alkylquinolinium iodide. The length of the alkyl chain attached to the cation has been varied, to cover a range of conformational variability, while retaining the same basic chemical structure (quaternary ammonium). The FTIR, ^1H and ^{13}C -NMR spectra and the characterization data for these salts are reported in the experimental part. These original salts were used to modify the MMT. This approach was used to estimate the influence of the imidazole, pyridine and quinoline salts on the properties and the molecular geometry of the resulting modified MMT.

Preparation of Modified MMT (CnCnIm-MMT, CnPy-MMT, CnQ-MMT)

The imidazolium (**1a–1e**), pyridinium (**2a–2b**), and quinolinium (**3a–3b**) salts shown in Schemes 1–3 were used to treat MMT, via standard literature ion-exchange methods^{8,9,31,36,40–45} to give a series of imidazolium (**1a–1e**)-MMT, pyridinium (**2a–2b**)-MMT and quinolinium (**3a–3b**)-MMT materials. The following

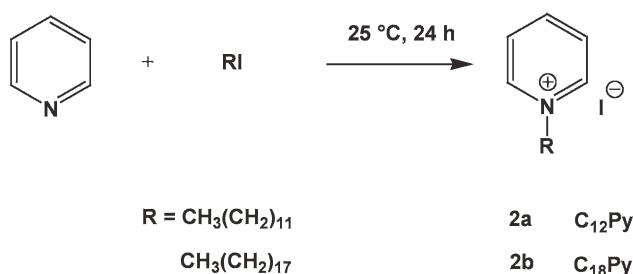


Scheme 1. Synthesis of 1-alkyl-3-alkyl imidazolium iodides 1a-1e.

abbreviations were used to design the different MMTs: MMT- Na^+ means the pristine MMT. An imidazolium MMT denoted $\text{C}_n\text{C}_n'\text{Im}$ -MMT was obtained when the N-alkyl-N'-alkylimidazolium iodide was used as an intercalation agent. A pyridinium MMT denoted C_nPy -MMT was obtained when alkyl pyridinium iodide was used like surfactant and C_nQ -MMT was employed for the MMT modified by an alkyl quinolinium iodide. The modified MMT were analysed by FTIR, TGA and XRD to determine whether the spacing between the layers (d spacing) had changed. In the following subsections, we attempt to show how each structural feature of these organic salts affects the molecular geometry and the properties of the organo modified-MMT.

FTIR Spectroscopy

FTIR spectra of pristine MMT *nanofil 757*, $\text{C}_{18}\text{C}_{18}$ Imidazolium **1e** and $\text{C}_{18}\text{C}_{18}$ Imidazolium modified MMT ($\text{C}_{18}\text{C}_{18}\text{Im}$ -MMT); C_{18} Pyridinium **2b** and C_{18} Pyridinium modified MMT (C_{18}Py -MMT); C_{18} Quinolinium modified **3b** and C_{18} Quinolinium modified (C_{18}Q -MMT) are reported in Figures 1–3, respectively. In the FTIR spectrum of MMT, the bands between 3500 , 3700 cm^{-1} and near 3400 cm^{-1} are indicative of MMT. According to Sibold et al.,²³ [Madejova et al.⁴⁶ and Tyaji et al.,⁴⁷ we have observed the characteristic bands near 3400 cm^{-1} ($-\text{OH}$ stretching mode of interlayer water); at ~ 3630 and $\sim 3698 \text{ cm}^{-1}$ ($-\text{OH}$ stretching mode of $\text{Al}-\text{OH}$ and $\text{Si}-\text{OH}$ of MMT structure), the overlap absorption bands in the 1640 cm^{-1} region ($-\text{OH}$ bending mode of adsorbed water) and the characteristic bands at 1110 – 1030 cm^{-1} due to $\text{Si}-\text{O}$ stretching.

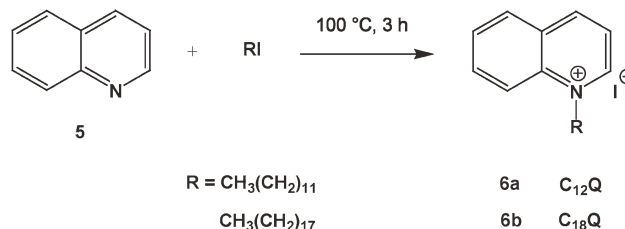


Scheme 2. Synthesis of dodecyl pyridinium iodide 2a and octadecyl pyridinium iodide 2b.

The FTIR spectra of the modified MMTs are very different from those of the pure salts. In the FTIR of imidazolium (**1a-1e**)-MMT, pyridinium (**2a-2b**)-MMT and quinolinium (**3a, 3b**)-MMT, the bands at ~ 2940 and $\sim 2850 \text{ cm}^{-1}$ were ascribed respectively to the asymmetric and symmetric vibrations of the methylene groups $(\text{CH}_2)_n$ of the aliphatic chain according to literature data.^{44,48} Modified MMT showed a weak intensity of the $-\text{OH}$ bending vibration at $\sim 1639 \text{ cm}^{-1}$ due to adsorbed water. The $\text{C}=\text{C}$ aromatic displayed an unusually sharp and relatively strong vibration band at ~ 1468 – 1430 cm^{-1} as shown in the FTIR spectrum of modified MMT. In addition to this, the HCH stretching vibration band at ~ 1487 – 1465 cm^{-1} and the $\text{C}-\text{N}$ vibration at $\sim 1375 \text{ cm}^{-1}$ were observed in the FTIR spectrum of all modified MMT. The FTIR absorption bands in the low frequency region of the upgraded MMT and the modified MMT analogues were largely comparable indicating that the clay mineral has not changed upon exchange of the interlayer sodium ions by the quaternary ammonium ions of imidazolium, pyridinium and quinolinium salts.

XRD

XRD diffraction has been used to characterize the layered structures of the modified clays, since changes in 2θ indicate changes in the d -spacing of the MMT. Properties of a few organoclays used in this study have already been described elsewhere.^{4,5} However, to facilitate the comprehension, it is necessary to summarize them in the present article. Table I gives a summary of the d -spacing of the modified clays while Figure 4(a,b,c) show the XRD curves for the different imidazolium-, pyridinium- and quinolinium-MMT. The characteristic reflection for



Scheme 3. Synthesis of dodecyl quinolinium iodide 3a and octadecyl quinolinium iodide 3b.

Table I. XRD Data of 1-Alkyl-3-alkyl Imidazolium Iodide 1a-1e; Dodecyl Pyridinium Iodide 2a, Octadecyl Pyridinium Iodide 2b, Dodecyl Quinolinium Iodide 3a, and Octadecyl Quinolinium Iodide 3b Modified Montmorillonites

Sample	2θ (°)	d spacing (Å)
MMT nanofil 757	8.56	10.3
C4C12Im-MMT	5.23	16.9
C12C12Im-MMT	3.61	24.5
C4C18Im-MMT	2.53	34.9
C12C18Im-MMT	2.62	33.7
C18C18Im-MMT	2.33	37.9
C12Py-MMT	5.55	15.9
C18Py-MMT	1.96	45.1
C12Q-MMT	5.10	17.3
C18Q-MMT	2.03	43.5

pristine clay, MMT-Na⁺ appears at 2θ = 8.56° (d = 10.3 Å).²³ For the C18C18Im-MMT, this reflection is broadened and shifted to 2θ = 2.33° (d = 37.9 Å) in agreement with a larger interlayer spacing indicative of the intercalation of the C18C18 imidazolium in the d-spacing. The spectra XRD of C4C12, C4C18, C12C12Im-MMT, C12Py-MMT, and C12Q-MMT [Figure 4(a,b,c)] show two intense and regular diffraction peaks that suggest a high degree of coherence possibly resulting from uniform intercalation and a long-range order according to Stoeffler et al.^{4,5} and Livi et al.³⁹ For the C18C18Im-MMT, C18Py-MMT and C18Q-MMT, the cationic exchange leads to a part of organic cations that is really intercalated between the sheets inducing about a 2.0 nm gallery height, while another part of organic cations causes the clay swelling only due to steric volume of the organic ligands, as a result the spectra show three peaks.

The XRD data for imidazolium-MMT show that the basal spacing increased with the alkyl chain length (Table I). The same results were observed with C18 quinolinium and C18 pyridin-

ium modified MMT, with an even larger basal spacing: C18Q-MMT has a d-spacing of 43.5 Å, while the C18Py-MMT modified clay has an even greater d-spacing (45.1 Å). The comparison of the basal spacing of these materials suggests that, even though only a single long chain is present, the d-spacing of C18Py-MMT and C18Q-MMT is larger than the interlayer of C4C18 and C18C18Im-MMT. Furthermore, the XRD curves confirm that the largest basal spacing is connected to the C18Py-MMT, with a slightly higher d-spacing (1.6 Å) than that of the C18Q-MMT. These data are in good agreement with the observation of Chigwada et al.³⁶ and Stoeffler et al.^{4,5} in the case of alkyl chain containing 16 carbon atoms. Indeed, they have reported that Cloisite Na⁺ presents the lowest basal spacing (9.7 Å), the presence of three butyl groups in addition to the long alkyl chain in 3C4C16PBr-MMT increases the basal spacing to 21.9 Å. Finally, MMTs intercalated with onium cations having two long alkyl chains (Cloisite 20A, purified Cloisite 20A and 2C18ImBr-MMT) show the largest gallery expansion, with respective basal spacings of 25.7 Å, 25.9 Å and 25.2 Å.

In summary, quinoline is more bulky and might have more difficulty in penetrating the clay interlayer than pyridine and this might be why more complete exchange was achieved with pyridinium salt.

Thermogravimetric Analysis

The TGA data, recorded in a nitrogen atmosphere from room temperature for imidazolium, pyridinium, quinolinium salts and for all the modified clays are summarized in Table II. The enhancement in thermal stability that occurs when the imidazolium, pyridinium and quinolinium salts are intercalated into the MMT is probed by TGA curves (Figures 5–7).

According to Ngo et al.,³⁷ the decomposition temperature of imidazolium salts is not sensitive to the presence of oxygen, as similar thermal decomposition behavior is observed in both O₂ and N₂ analysis environments. For an easier lecture, analyses of all compounds are not represented. Thermal decomposition is strongly dependent on the salt structure as can be seen in

Table II. TGA Data of 1-Alkyl-3-alkyl imidazolium Iodide 1a-1e; Dodecyl Pyridinium Iodide 2a, Octadecyl Pyridinium Iodide 2b, Dodecyl Quinolinium Iodide 3a, Octadecyl Quinolinium Iodide 3b and Modified Montmorillonite

Salts	TGA T ₁₀ (°C)	Modified MMT	TGA T ₁₀ (°C)
C4C12Im	272	C4C12Im-MMT	320
C12C12Im	275	C12C12Im-MMT	307
C4C18Im	286	C4C18Im-MMT	324
C12C18Im	279	C12C18Im-MMT	331
C18C18Im	290	C18C18Im-MMT	340
C12Py	250	C12Py-MMT	270
C18Py	256	C18Py-MMT	280
C12Q	237	C12Q-MMT	287
C18Q	258	C18Q-MMT	302
C18P	301	C18P-MMT	330
		DMBT-MMT	220

Figures 5–7, and Table II. However, the TGA data clearly show the improvement in thermal stability for all the organically modified MMT compared to sodium containing natural MMT. Indeed, MMT clays modified with the delocalized imidazolium salts showed valuable thermal properties (10% weight loss at $\sim 320^\circ\text{C}$ for C18C18Im-MMT compared to 10% weight loss at $\sim 280^\circ\text{C}$ for C18Py-MMT and 10% weight loss at $\sim 287^\circ\text{C}$ for C18Q-MMT). According to the TGA curves, all surfactants are completely degraded at 700°C . The modified MMTs reported here also compete favorably with the classical alkyl quaternary ammonium-modified MMT. As an example Xie et al.^{12,13} have demonstrated that the onset temperature of decomposition of long-chain alkyl quaternary ammonium MMT was approximately 155°C via TGA and 180°C via TGA-MS. Our results obtained are in good agreement with recent studies concerning the thermal properties of imidazolium,^{4,5,15,24,32,37,49} pyridinium,^{4,5,36} quinolinium,³⁶ alkyl ammonium and their modified MMT.^{7,8,9,18,19,21,25–27,32,37,49} For example, the temperature at 10 wt % degradation (T_{10}) of C18C18ImBr-MMT *Cloisite Na⁺*, C16PyBr-MMT *Cloisite Na⁺* and C16Q-MMT *Cloisite Na⁺* was reported to start at 386°C , 371°C and 367°C as shown by TGA studies carried out by Stoeffler et al.^{4,5} and Chigwada et al.³⁶ In the present article T_{10} of C18C18ImI-MMT *Nanofil 757*, C18PyI-MMT *Nanofil 757*, and C18Q-MMT *Nanofil 757*, is respectively, about 320°C , 280°C and 287°C .

TGA also allowed us to complete the modified clay characterizations by investigating the degradation mechanisms and the effects of functionalization on the thermal stability. As reported in the literature,⁴² the first weight loss on the curve of weight loss as a function of temperature typically indicates the presence of organics that must be simply physisorbed.^{6,8,9,12–14,17,28,30,31,42,43} Such organic fraction either did not undergo the cation exchange process or stayed unconfined. The second weight loss corresponds to organics intercalated into clay *d*-spacing. Indeed, it is known that organics inside clay *d*-spacing display higher temperatures of degradation. In this study, the MMTs modified with distinct cations (ammonium versus imidazolium, pyridinium, quinolinium and phosphonium) were compared. First, the MMT (*Nanofil 919*) modified with the dimethyl (benzylmethyl) tallow quaternary ammonium (DMBT-MMT) was compared to those treated with the imidazolium, pyridinium, quinolinium and phosphonium salt since all these salts display C18 alkyl chains and a benzyl substituent. Figure 6 summarizes the data extracted from these thermogravimetric (TGA) curves and Figure 7 summarizes TGA derivative weight curves (DTG). Regarding the TGA curves of DMBT-MMT (Figure 6), the first weight loss corresponding to the degradation of the species physically adsorbed on the external surface of the platelets starts at 220°C , whereas the imidazolium, pyridinium, quinolinium, and phosphonium-modified MMT is still thermally stable at this temperature. Indeed, in Figure 6, for C18P-MMT the first degradation of the physisorbed species is at 340°C , a temperature corresponding to the evaporation of neat ionic liquid. In this case, a dramatic difference of 120°C is observed. For the species intercalated in the MMT *d*-spacing, the same trend is observed. In Figure 6, TGA curves of C18C18Im-MMT present three discrete events, located at 320 , 420 , and 470°C ; the first

peak of degradation of the physisorbed species is at 320°C . Whereas the degradation takes place at about 470°C for C18C18Im-MMT, $\sim 450^\circ\text{C}$ for C18Py-MMT, C18Q-MMT, and $\sim 500^\circ\text{C}$ for C18P-MMT, the degradation of intercalated species is extended between 300 and 400°C for MMT-DMBT. At 700°C , the weight residue is different for the modified clays. The difference might be an indication of incomplete exchange during the organic modification according to Chigwada et al.³⁶ Moreover, the amount of organic salts intercalated between the clay sheets depend on the nature, the hindrance steric, the molecular weight of the surfactant used.

These results clearly show the beneficial effects of the intercalation of ionic liquids in the MMT compared to DMBT ammonium-MMT, which leads to a better intrinsic thermal stability of the modified MMT. This higher thermal stability can be attributed to the aromatic character of the cations used, aromatic cations being known to have a better thermal stability than classical ammonium cations.^{32,37,49}

To sum up, the intercalation of imidazolium, pyridinium, or quinolinium salts in MMT through exchange with interlamellar Na^\oplus ions was confirmed leading to an expansion of the *d*-spacing (27 \AA – 35 \AA as compared to pristine clay, MMT- Na^\oplus). The thermal stability of the commercial alkyl quaternary ammonium-modified MMT was found to be lower than that of our modified clays (120 – 155°C). The imidazolium-MMT were shown to have higher thermal stability than the quinolinium-MMT and the later ones have higher thermal stability than the pyridinium-MMT. This excellent thermal stability of ionic liquids synthesized is a huge advantage for the processing of polymer/clay nanocomposites at higher temperature.

CONCLUSIONS

In this contribution, ionic liquids based on long alkyl chain imidazoline, pyridine, and quinoline containing iodide salts have been synthesized and used as surfactants to modify a lamellar silicate surface. The intercalation of these compounds into MMT has been confirmed by FTIR spectral data according to literature,^{23,46,47} TGA and XRD^{39,50} of onion iodide salts before and after intercalation in MMT. No band displacement is observed in the FTIR spectrum for imidazolium, pyridinium and quinolinium before and after blending with *Nanofil 757*. The characteristic absorption bands of the organoclay remain unaffected by intercalation as well. The XRD data of the modified clay showed that the organoclay has been swelled by the ammonium ion of these salts and has a larger interlayer spacing than the original Na^\oplus MMT. The results showed that as the alkyl group increased in length, the *d*-spacing increased. For alkyl chains with 18 carbon atoms, the pyridinium salts lead to the largest basal spacing. The thermal stability of several alkyl-imidazolium, pyridinium, and quinolinium molten salts as well as those of imidazolium, pyridinium and quinolinium-treated MMT-layered silicates was discussed. MMT clay modified with these salts showed superior thermal properties compared to the classical quaternary alkylammonium modified MMT. In fact, the use of imidazolium, pyridinium, quinolinium, and phosphonium salts as surfactant agents delay the degradation of modified layered silicates (280°C compared to 180°C for

ammonium-treated MMTs).^{13,14,23,39} Moreover, TGA analysis indicated that the imidazolium modified clays have higher thermal stability than the quinolinium modified clays and the later ones have higher thermal stability than the pyridinium modified clays.

These results seem to be promising in terms of the potential application of these alkyl imidazolium, pyridinium and quinolinium salts modified MMT for the preparation of high temperature polymer-layered silicates.

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