Available online at www.sciencedirect.com
ScienceDirect
Applied Clay Science 38 (2007) 64 – 76
Applied Clay Science
www.elsevier.com/locate/clay

Polymer modified clay minerals: A review

Peng Liu *

Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

Received 17 August 2006; received in revised form 13 January 2007; accepted 15 January 2007
Available online 23 January 2007

Abstract

Recent progress in the surface modification of the clay minerals with polymers via physical adsorption and chemical grafting are reviewed. The surface modification of clay minerals especially with polymers could improve markedly their surface physical and chemical properties so the modified clay minerals could be applied as catalysts, adsorbents, in composite materials, and so on.

Keywords: Clay minerals; Polymer; Surface modification

1. Introduction

In the last decade, the natural clay minerals, such as montmorillonite (MMT), kaolinite (Murray, 2000), and palygorskite (attapulgite) (Galan, 1996), are widely used in catalysis (Cavani et al., 1991; Rosa-Brussin, 1995; Chitnis and Sharma, 1997; Harvey and Murray, 1997; Vaccari, 1999; Shichi and Takagi, 2000; Ding et al., 2001; Gournis et al., 2002; De Stefanis and Tomlinson, 2006), as adsorbents (Lee and Tank, 1985; Smith and Vengris, 1998; Huh et al., 2000; Cox et al., 2001; Pal and Vanjara, 2001; Adebajo et al., 2003; Li et al., 2004; Lin et al., 2004; Jaber et al., 2005; Dias Filho and Do Carmo, 2006), in nanocomposites (Giannelis, 1996; Gilman, 1999; LeBaron et al., 1999; Morgan and Dubois, 2000; Ray and Okamoto, 2003; Ahmadi et al., 2004), in sensors (Guth et al., 1996; Mousty, 2004; Darder et al., 2005), electrode (Zen, 2004; Tonle et al., 2005), as antibacterial materials (Williams et al., 2004), nuclear waste storage (Meunier et al., 1998), pesticide carriers (Taylor et al., 1998), and so on. Nowadays, surface modification of clay minerals has become increasingly important for improving the practical applications of clays and clay minerals (Kathleen, 2000; van Oss and Giese, 2003). Surface modification by polymers is found to be one of the most effective methods, as the surface properties can be widely changed by a variety of functional polymers.

There are two main approaches for the surface modification of clay minerals with polymers. One is physical adsorption, and the second is chemical grafting of functional polymers to the surfaces of the clay minerals.

The physical adsorption, controlled by thermodynamic criteria, can alter the nature of the clay mineral surfaces and improve their surface physical and chemical properties. The advantage of physical attachment is that the structure of the clay mineral is not altered. The main potential disadvantage is that the forces between the adsorbed molecules and the clay mineral might be weak.

Grafting of functional polymers to the surface of clay minerals can improve the interaction. It is an important

---

* Tel.: +86 931 8912516; fax: +86 931 8912582.
E-mail address: pliu@lzu.edu.cn.

0169-1317/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2007.01.004

field of research for its ability to control and tune the properties of clay mineral surfaces. The first approach used, named one-step grafting method (Fig. 1A), consists in the condensation of functionalized polymers with reactive groups of a solid substrate. This method does not give highly dense polymer brushes because chemisorption of the first fraction of chains hinders the diffusion of the following chains to the surface for further attachments. Another approach, named two-step grafting method (Fig. 1B), has been considered to obtain better densities. In this technique, a monolayer of polymerizable (macromonomer) or initiator (macroinitiator) molecules is covalently attached to a solid surface. After activation the chains grow from the interface then the only limit to propagation is the diffusion of monomers to the active species (Liu, 2006).

Here I present a preliminary review on the recent advances of the surface modification of natural clay minerals with polymers, including the modifying methods and mechanisms, characterizing and analytical techniques, and potential applications.

2. Physical adsorption

2.1. Nonionic polymers

Grandjean and Laszlo (1996) reported studies on montmorillonite dispersed in aqueous solutions of nonionic polymers. Proton self-diffusion coefficients and carbon-13 relaxation times were measured to describe the influence of the clay mineral on the polymer mobility. The influence of the polymer nature on these parameters was also investigated.

The adsorption of polyvinylpyrrolidone (PVP) with molecular weights from 5000 to 600000 on kaolinite has been studied (Hild et al., 1997). The effects of the adsorbent concentration, solution pH and PVP molecular weight on the isotherms were investigated. The varying affinity to the kaolinite was related to certain molecular weight fractioning of the synthetic polymer samples. An adsorption decrease of about 20% in the pH range 3.5–10.3 indicated that the protonation of kaolinite edge surfaces might also be involved in the adsorption process. The same group (Sequaris et al., 2000) reported the adsorption of PVP on Na-montmorillonite. The adsorption of PVP on kaolinite in presence of sodium dodecyl benzenesulfonate (SDBS) was also studied (Torn et al., 2003).

Volpert et al. (1998) described the solution properties and the adsorption behavior of hydrophobically modified polyacrylamides synthesized by micellar copolymerization on clay minerals. Different from homopolyacrylamide, in which a classical high affinity adsorption isotherm was found with a plateau at relatively low concentration, the hydrophobic modification of the polymer considerably enhanced its affinity to the silicate surface.

A new material based on the intercalation of poly(ethylene oxide) (PEO) into homoionic NH_4^+-smectites (montmorillonite and hectorite) has been synthesized and characterized (Aranda and Ruiz-Hitzky, 1999; Lin and Chen, 2004). Because of the strong interaction of PEO with the NH_4^+ ions, the ionic conductivity of PEO-NH_4^+-smectites is several orders of magnitude lower than similar nanocomposites prepared from smectite exchanged with alkali ions.

The adsorption of two commercial neutral cellulose derivatives: hydroxyethylcellulose (HEC) and hydrophobically modified hydroxyethylcellulose (HMHEC) on montmorillonite was studied in aqueous solution and in the presence of 2% NaCl (Simon et al., 2002). For both polymers, the adsorption onto clay is always larger in water than in salt solutions.

Small-angle neutron scattering (SANS) measurements (Nelson and Cosgrove, 2004a) and dynamic light scattering (Nelson and Cosgrove, 2004b) were used to characterize the distribution and adsorption of poly(ethylene oxide) (PEO) with different molecular weights on Laponite. These experiments showed not only that polymer was present on the face of the clay mineral particles but that also extended or “wrapped” over the edges. The edge layer was thicker than the face layer for all the molecular weights studied. The polymer layers were unusually thin, with a thickness and adsorbed amount that show little variation with molecular weight. SANS studies on the adsorption of selected poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) tri-block copolymers on Laponite (Nelson and Cosgrove, 2005) were also reported.

Adsorption, adsorption kinetics and electrokinetic properties of poly(vinylimidazole) perlite were investigated

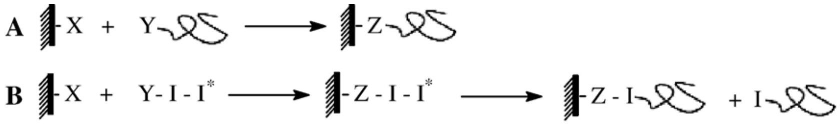


Fig. 1. General mechanism for one-step (A) and two-step(B) grafting reactions.

as a function of temperature, ionic strength and pH (Tekin et al., 2006). The zeta potential measurements had been performed to determine the isoelectric point (IEP) and potential determining ions (PDI). Experimental adsorption data were fitted by Langmuir and Freundlich models. The Langmuir model gave the best representation of the adsorption data. Pseudo-first-order kinetic equation provided the best fit to the experimental data.

2.2. Anionic polymers

The adsorption of two grades of sodium carboxymethyl cellulose (NaCMC) having a different degree of substitution (DS) on kaolinite with or without of the presence of sodium polyacrylate (NaPA) was reported (Husband, 1998). The greater rheological effect of high DS polymer on the kaolinite dispersion was most likely to be a result of its higher counterion density.

The flow properties of natural Ca^{2+}-bentonite and Na^+-bentonite-water systems were studied after adding an anionic polyacrylamide (PAM) (Gungor and Karaoglan, 2001). The importance of the exchangeable cations, on the interaction of the clay mineral particles and PAM molecules was shown. Whereas PAM has a flocculation effect in Ca^{2+}-bentonite-water system, it has a deflocculation effect in Na^+-bentonite-water system. Ca^{2+} ions advance the formation of bridging flocculation. PAM molecules were adsorbed at the particle surfaces but not intercalated into Ca^+-montmorillonite. The shifts of the vibration frequencies of PAM added to Ca^{2+}- and Na^+-bentonites were an indicator of the interaction between the PAM molecules and clay mineral particles.

Systematic investigation of the interaction of alumina, silica, and kaolinite (Zaman et al., 2002) or hematite (Kirwan et al., 2003, 2004) with Na-polyacrylic acid (PAA) was performed by conducting adsorption experiments and employing attenuated total reflection infrared spectroscopy (FTIR-ATR) techniques. Adsorption studies indicated that the adsorption density of Na-PAA on the surface of kaolinite was considerably smaller than that on alumina particles and there was no indication of adsorption of PAA on the surface of silica particles. FTIR/ATR experiments confirmed that there were specific interactions between PAA and the surface of alumina and kaolinite particles as the absorption bands were shifted to higher wavenumbers.

The adsorption of poly (4-sodium styrene sulfonate) on three different Egyptian kaolinites saturated with sodium or calcium ions, was studied by Sadek et al. (2006). The polymer adsorption on calcium kaolinite was higher than that of sodium kaolinite at the same pH value.

The probable bonding mechanisms between polyacrylamide (PAM) and smectite using three kinds of PAMs (nonionic PAM 903N, cationic PAM 494C containing 20% cationic *N*, *N*, *N*-trimethyl aminoethyl acrylate units, and anionic PAM836A containing about 18% anionic acrylate units) were studied by Deng et al. (2006).The nonionic PAM 903N and the nonionic acrylamide units in charged copolymers (cationic PAM 494C and anionic PAM 836A) reacted similarly with smectite. The major bonding between the polymer and the smectite are: (1) ion–dipole interaction/coordination between exchangeable cations and the carbonyl (C=O) oxygens of amide groups ($CONH_2$), which is more likely important for the transition-metal cation exchanged smectite and (2) H-bonding between the amide groups and water molecules in the hydration shells of exchangeable cations. The amino group (NH_2) seems to be not as important as the carbonyl group (C=O) to the bonding between the polymers and the smectite. It is unlikely that protonation of amide groups occurred in the interlayer of smectite. Hydrophobic bonding did not appear to contribute substantially to the adsorption of PAMs.

3. Chemical bonding

3.1. One-step grafting methods

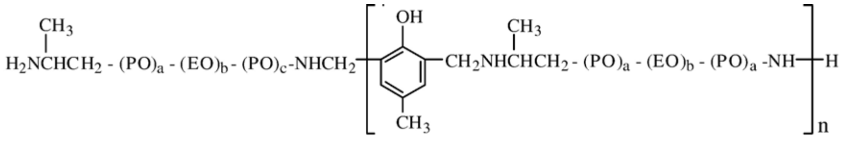
The polycation-exchanged bentonites were prepared by the adsorption of polycations of the type $[CH_2\text{-}CHOHCH_2N(CH_3)_2]_n^{n+}$ onto a low-iron Texas bentonite, Westone-L (WL) (Breen, 1999). The influence of clay mineral type, particle size and cation on the amount of adsorbed polycations was reported along with variable temperature X-ray diffraction patterns of the resulting complexes. The use of polycation-exchanged clay minerals as scavengers of *p*-nitrophenol from water and the significant activity of acid-treated polycation-exchanged clays for the catalytic isomersion of α-pinene to camphene and limonene were described.

Lin et al. (2001, 2004) reported the preparation of Na^+-montmorillonite with basal spacing as high as 58 or 92 Å by intercalating telechelic POP-diamines (poly (propylene glycol)-bis (2-aminopropyl ether)) with different molecular weights The use of telechelic POP-diamines as the intercalating agents allows us to tailor highly ordered montmorillonite with enlarged basal spacing. The expanded interlayer space encapsulating hydrophobic POP-amines rendered the silicates amphiphilic and self-assembling. The author had also prepared amine terminating Mannich oligomers (AMO) or polyamines (Fig. 2A) for the exfoliation of montmorillonite (Chu et al., 2005).

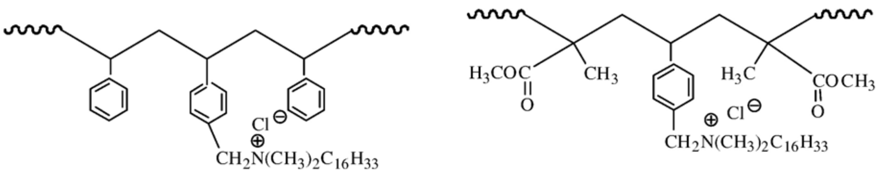
The adsorption of the cationic polymer, polyethyleneimine (PEI), on bentonite particles was investigated (Oztekin et al., 2002). The adsorption rates for the bentonite dispersions are very fast. The adsorbed polyelectrolyte affected the rheological properties of the bentonite dispersions and the adsorption capacity. The influence of the polyelectrolyte on the rheological behavior changed with the exchangeable ions, i.e. Na^+ and Ca^{2+} ions.

The ammonium group-terminated i-polypropylene ($PP\text{-}t\text{-}NH_3^+$) polymers (Dong et al., 2002) were prepared by the combination of rac-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2$-$ZrCl_2$/MAO catalyst and p-NSi_2-St/H_2 (p-NSi_2-St: 4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene) chain transfer agent. The results demonstrated that the advantage of chain-end-functionalized PP ($PP\text{-}t\text{-}NH_3^+$) that seemed to adopt a unique molecular structure atop of the clay surfaces and resulted in an exfoliated montmorillonite structure (Wang et al., 2003).

Su et al.described new organic treatments that may be applied to clay which would enable the formation of

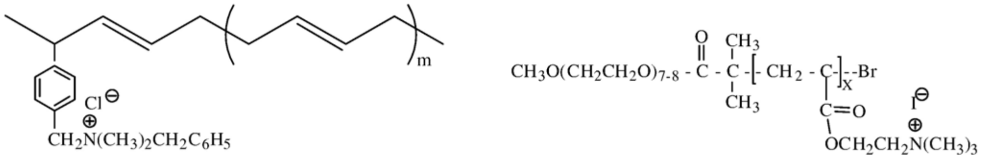


A Amine-terminating Mannich Oligomers (POP-AMO and POE-AMO)



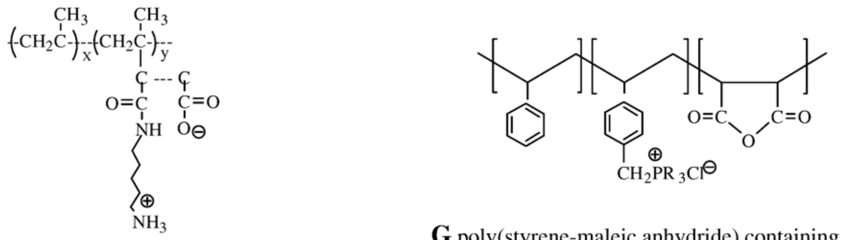
B ammonium salt of COPS

C MAPS surfactant



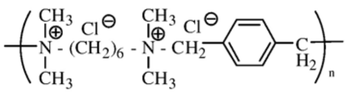
D the polybutadiene surfactant

E modified poly(ethylene glycol)



F modified PP-g-MA (PP-g-HMA)

G poly(styrene-maleic anhydride) containing quaternary phosphonium salt



H polymeric quaternary ammonium salts(PQAS)

Fig. 2. The structure of the polymer surfactants.

nanocomposites by melt blending of polystyrene, PS, high impact polystyrene, HIPS, and acrylonitrile-butadiene-styrene terpolymer, ABS. In their work, ammonium salts of the copolymer of styrene and vinylbenzyl chloride (COPS) (Fig. 2B) and the copolymer of methyl methacrylate and vinylbenzyl chloride (MAPS) (Fig. 2C) were prepared and used as modifiers. The intercalated nanocomposites of all of these polymers had been produced by melt blending in a Brabender mixer and, in some cases, exfoliated nanocomposites have been obtained. These novel new clays open new opportunities for melt blending of polymers with clays to obtain nanocomposites with important properties (Su et al., 2004a,b; Su and Wilkie, 2004). The authors had also prepared a butadiene surfactant (Fig. 2D), obtained from the reaction of vinylbenzyl chloride grafted polybutadiene with a tertiary amine, for the same aim (Su et al., 2004c).

Alemdar et al. prepared a special type of cationic polymer [modified poly(ethylene glycol)] (Fig. 2E). The rheological and colloidal properties of sodium montmorillonite dispersions were investigated in the presence of the polymer were investigated (Alemdar and Butun, 2005; Alemdar et al., 2005). The rheology and zeta potential measurements showed that the cationic polymer was strongly adsorbed onto the sodium montmorillonite surface. The results indicated a gradual increase in gelation with the addition of the cationic polymer, which reached a maximum at a cationic polymer concentration of 0.4–0.8 g/L. This gel-like dispersion showed pronounced thixotropy. The basal spacing measurements indicated that the cationic polymer strongly adsorbed onto the sodium montmorillonite instead of entering the montmorillonite interlayer spaces.

The hexamethylenediamine(HMDA)-modified maleic-anhydride-grafted polypropylene was synthesized (Fig. 2F) for maleic-anhydride-grafted polypropylene/clay (PP-g-MA/montmorillonite) nanocomposites. Both X-ray diffraction data and transmission electron microscopy images of PP-g-HMA/montmorillonite nanocomposites indicated that most of the silicate layers were exfoliated and randomly dispersed within the PP-g-HMA matrix. The differential scanning calorimeter (DSC) studies revealed that introducing 5 wt.% of montmorillonite into PP-g-HMA caused strongly heterogeneous nucleation, which induced a change of the crystal growth process from a three-dimensional crystal growth to a two-dimensional spherulitic growth. Mechanical properties of PP-g-HMA/montmorillonite nanocomposites performed by dynamic mechanical analysis showed significant improvements in the storage modulus when compared to neat PP-g-HMA (Wu et al., 2005). The thermal stability and fire retardant performance of the nanocomposites were studied (Diagne et al., 2005).

Poly(styrene-maleic anhydride) quaternary phosphonium salt was prepared (Fig. 2G) and used for the intercalation into montmorillonite. WAXD appeared to reflect the packing of the polymers between the layers of MMT (Salahuddin and Akelah, 2002).

The surfactant containing quaternary ammonium ions in the main chain of the polymer, prepared by reaction between *p*-xylylenedichlorides and diamines (Burmistr et al., 2003), was reported for polymer–clay composites prepared by melt blending an organo-bentonite with linear polymers (polyamide, polystyrene and polypropylene) in a disk-screw extruder by Sukhyy's group (Burmistr et al., 2005). The organo-clay was prepared by surface treatment of Na^+-montmorillonite with polymeric quaternary ammonium salts (PQAS) (Fig. 2H). XRD indicated that organo-montmorillonite layers were exfoliated and dispersed into polyamide and PS. For PP-organo-montmorillonite composites we did not observe delamination, and as a result absence of reinforcements. TGA showed that the polyamide and PS nanocomposites have higher decomposition temperature in comparison with the original polymers.

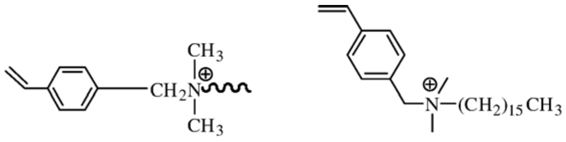
3.2. Two-step grafting methods

3.2.1. Macromonomers

The functional molecules containing carbon–carbon double bond and one or two reactive groups such as silanes or quaternary ammonium salts have been widely used for the pretreatment of clay minerals.

Polyvinylpyridinium salts were immobilized onto a clay matrix and were then tested for their antibacterial properties. The clay-polyvinylpyridinium matrix was prepared by the copolymerization of γ-methacryloxypropyltriethoxy silane bonded covalently to the clay mineral and 4-vinylpyridine and subsequent quaternization with benzyl halides. The antibacterial activity of the clay supported bactericides was tested by a suspension test with *Escherichia coli*, ATCC 35218, *Pseudomonas aeruginosa*, USDA B771, and *Staphylococcus aureus*, ATTC 25293 as the test organisms. About 99–100% removals of the test organisms occurred in 0.08 h (Seckin et al., 1997). The authors had also reported the preparation of the core-shell hybrid materials with covalent bonds between the montmorillonite and the polyacrylonitrile (PAN) shell (Seckin et al., 2002).

Vinyl benzyltrimethylammonium chloride was also used for the intercalation of montmorillonite via a cationic exchange. Styrene, was intercalated into the



A quarternary cocoamine **B** MMT-VB16

Fig. 3. The structures of the monomer surfactants.

organo-montmorillonite and the vinyl monomer-montmorillonite intercalates obtained were swollen and dispersed in an organic solvent. The free radical solution polymerization of the intercalated styrene of 5, 10, 25 and 50 wt.% vinyl monomer-montmorillonite had resulted in grafted polystyrene montmorillonite materials (Akelah and Moet, 1996). The effect of montmorillonite content on the polystyrene was determined by extraction with organic solvents, which showed an increase in the grafted polymer (0.84–2.94 g/g MMT), and a decrease in the external polystyrene with increasing amounts of montmorillonite.

γ-MPS-magadiite was prepared by reacting dodecyl trimethylammonium (C_{12}TMA) exchanged magadiite with γ-methacryloxypropyl trimethoxysilane (Isoda et al., 2000). Copolymerization of the grafted groups with methyl methacrylate yielded a novel type of intercalation compounds with covalently bound polymers in the interlayer space.

Polymer–clay nanocomposites of styrene and methyl methacrylate via various methods such as bulk, solution, suspension, and emulsion polymerization as well as by melt blending had been compared (Wang et al., 2002). Two different organic modifications of montmorillonite had been used: one contains a styryl monomer on the ammonium ion while the other had no double bonds. Exfoliation is more likely to occur if the ammonium ion contains a double bond which can participate in the polymerization reaction, but the presence of this double bond is not always sufficient to produce an exfoliated system. Solution polymerization always produced intercalated systems.

A novel process for the preparation of poly(propylene)/montmorillonite (PP/MMT) nanocomposites was developed via simultaneous solution grafting-intercalation in the presence of a reactive ammonium cation that can be grafted onto poly(propylene) (Xie et al., 2004). Introducing this reactive cation into long alkyl ammonium modified MMT interlayer spaces can transfer conventional microcomposites into intercalated/exfoliated nanocomposites, which was evidenced by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The PP chains were tethered onto the clay mineral surface through the reactive ammonium cations, which can be characterized by FTIR. This bonding also results in a good interface adhesion between PP and MMT, as confirmed by SEM investigation. The enhanced thermal properties of PP/MMT nanocomposites were indicated by thermogravimetric analysis.

Montmorillonite was modified with the quaternary salt of cocoamine, having a vinyl group, and a vinyl silane reagent, both separately and simultaneously (Fig. 3A). Therefore, the reactive double bonds in both modifiers can participate in the polymerization reaction independently, both between and outside of the clay mineral layers, which may lead to a completely exfoliated nanocomposite structure. Using these organically modified montmorillonites, P4VP nanocomposites have been prepared by in situ polymerization. The nanocomposites prepared from the MMT modified with the two reagents simultaneously were effectively exfoliated and showed the highest thermal stability and best dynamic mechanical properties (Sen et al., 2006).

3.2.2. Macro-initiators

Suter and coworkers reported about the grafting polymerization of styrene from high surface-area mica by ionically binding peroxide initiators (Fig. 4A) to the surface by ion exchange from aqueous solutions (Velten et al., 1999). This initiates classical free radical polymerization. Only a small fraction of the peroxide ions (perhaps 1%) had initiated polymerization of the bound chains.

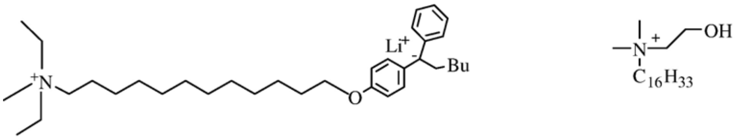
Surface-initiated polymerization (SIP) from clay nanoparticles was compared between surface-bound mono- and bicationic free radical initiators (Fan et al., 2003a). Distinct properties in molecular weight (MW), extent of exfoliation, and particle morphology were observed as a consequence of using two different initiator architectures. X-ray diffraction (XRD) results showed that the clay intercalated with a monocationic initiator had a larger basal spacing with a more highly and ordered structure. IR, X-ray photoelectron spectroscopy, and thermogravimetric analysis confirmed the attachment of both initiators. XRD further showed that the SIP product from the bicationic initiator retained some intercalated structure while a highly exfoliated structure was achieved. Consequently, the monocationic initiator gave a higher MW polymer. The degradation and relaxation kinetics of the polystyrene nanocomposites by the proposed method had been studied by the thermogravimetry, differential scanning calorimetry (DSC), and dynamic mechanical analysis (Vyazovkin et al., 2004). The investigation of polymer brushes grafted clay nanoparticles (Fan et al., 2005) and those adsorbed on flat surfaces (Fan et al., 2003b) has also been reported with the surface-bound monocationic free radical initiator by the group.

Exfoliated high-impact polystyrene (HIPS)/montmorillonite (MMT) nanocomposites were successfully prepared using anchored cationic radical initiator-MMT via in situ polymerization of styrene and dissolved PB in toluene. The uniform dispersion of PB rubber particles in micron sizes within the PS matrix was confirmed by particle size analysis, TEM and SEM micrographs. The thermal and mechanical properties of the resulting exfoliated HIPS/MMT nanocomposites were greatly enhanced compared to those of the pure HIPS, due to the good exfoliation and dispersion of the clay mineral platelets within the polymer matrix (Uthirakumar et al., 2005).

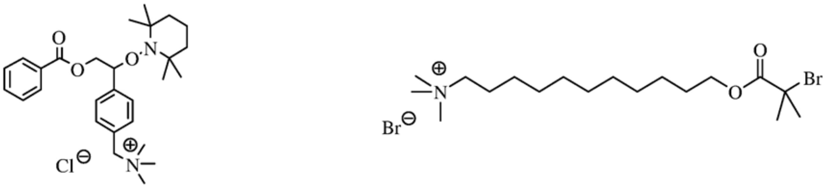
Hu et al. (2006) synthesized a novel perester silane, *t*-butyl peroxy-11-trichlorosilyl undecanoate, and bound it covalently to the surface of the silicate by self-assembling monolayer (SAM) techniques (Fig. 4B). Several hydrophilic and hydrophobic acrylate monomers were successfully grafted onto the silicate substrate by in situ polymerization from the surface-bound perester initiators.

The living anionic polymerization initiated directly from lamellar clay surfaces was successfully used for grafting reactions with montmorillonite (Zhou et al.,

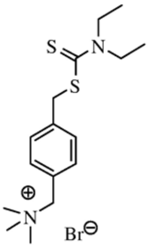
A peroxide quarternary ammonium salt for RP **B** peroxide silane for RP



C quarternary ammonium salt for AP **D** quarternary ammonium salt for ROP



E quaretrnary ammonium salt for SFRP **F** quaretrnary ammonium salt for ATRP



G cationic photo-iniferter

Fig. 4. The structures of the initiator surfactants.

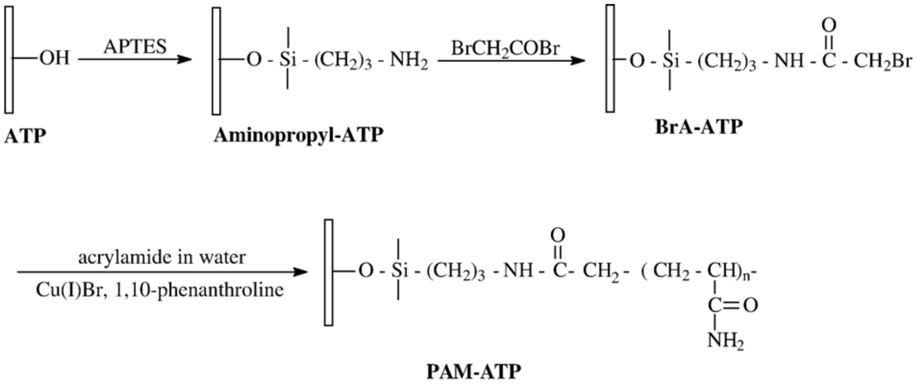


Fig. 5. The preparation procedure leading to PAM-ATP.

2001; Fan et al., 2002). A cationic 1,1-diphenylethylene (DPE) derivative, triethyl{12-[4-(1-phenylvinyl) phenoxy] dodecyl}ammonium bromide, was used as an initiator precursor in order to avoid self-polymerization. The polymerization of styrene was then surface-initiated when the ion-exchanged montmorillonite was reacted with *n*-BuLi (Fig. 4C). A living anionic polymerization mechanism was determined from molecular weight (MW) data and the molecular weight distribution. A comparison of FT-IR, TGA, XPS, XRD, and atomic force microscopy (AFM) data confirmed that polystyrene was indeed grafted on the clay mineral surfaces for these composite materials. The initiation efficiency was different between surface- and interlamellar bound initiators. The XRD analysis indicated that only a small number of initiator molecules were intercalated and most of the initiation took place at the outer surface (perimeter).

Poly(ε-caprolactone) (PCL) montmorillonite nanohybrids were synthesized by ring opening polymerization of ε-caprolactone according to a well-controlled coordination–insertion mechanism (Fig. 4D) (Lepoittevin et al., 2002; Kubies et al., 2002; Viville et al., 2004; Pollet et al., 2004). Montmorillonites were surface-modified by non-functional (trimethylhexadecylammonium) and hydroxy functional alkylammonium cations, i.e., (2-hydroxyethyl)dimethylhexadecylammonium. The hydroxy functions available at the clay mineral surface were activated with tin(II or IV) or Al(III) alkoxide initiators for lactone polymerization, thus yielding surface grafted PCL chains.

Sogah's group described the in situ polymerization using a silicate-anchored initiator of 2,2,6,6-tetramethylpiperidine N-oxide (TEMPO) type which initiates a so-called TEMPO-mediated, stable, free radical polymerization (SFRP) (Fig. 4E). They demonstrated that

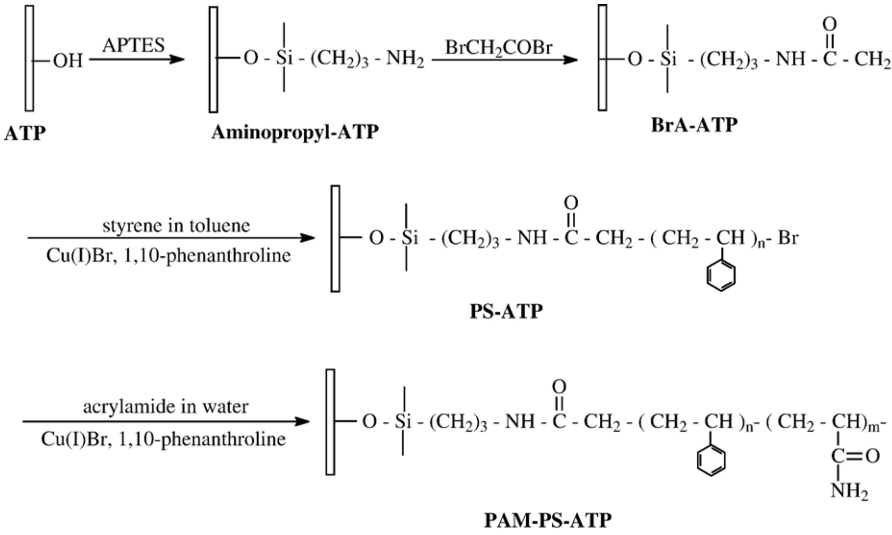


Fig. 6. Self-assembling process to PAM-PS-ATP.

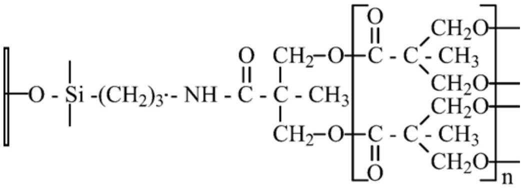


Fig. 7. The ideal structure of HAPE-ATP.

intergallery polymerization via a silicate-anchored initiator was a viable approach to direct synthesis of dispersed silicate nanocomposites. In addition, critical polymer properties such as MW and polydispersity were controlled, and block copolymer formation appears possible. These results constituted the first example of a dispersed PS-montmorillonite nanocomposite (Weimer et al., 1999).

Hallensleben's group demonstrated that 'living'/controlled graft polymerization via the atom transfer radical polymerization (ATRP) from initiator-modified montmorillonite was possible (Bottcher et al., 2002). A new cationic initiating molecule, 11′-(*N*, *N*, *N*-trimethylammonium bromide) undecanyl-2-bromoisobutyrate had been immobilized by intercalation into and applied for the surface-initiated ATRP of styrene (Fig. 4F). The grafted polymer chains were detached from the solid in order to prove the well-known ATRP features. The method had also been applied for the fabrication of poly(styrene-*b*-butyl acrylate) copolymer brushes on the surfaces of exfoliated and intercalated clay layers (Zhao et al., 2004).

Li et al. and Wheeler et al. used 3-aminopropyl dimethylethoxysilane to modify H-magadiite. 2-Bromopropionyl bromide, an initiator of ATRP, was added to the mixture to react with the NH_2 groups of the surfactant. The initiator immobilized on magadiite was used for the surface-initiated ATRP of styrene (Wheeler et al., 2005, 2006). The resulting nanocomposites had an intercalated and partially exfoliated structure, and a maximum increase of 35.5 °C in the degradation temperature was displayed. In particular, the surface elastic modulus and hardness of these nanocomposites were more than twice of those of pure polystyrene (Li et al., 2005).

Shipp's group reported preparation of PS-, PBA- and PMMA-montmorillonite nanocomposites that have well controlled molecular weights and narrow polydispersities using reversible addition-fragmentation chain transfer (RAFT) polymerization in bulk (Fig. 3B). The morphology of polystyrene-, and poly(*n*-butyl acrylate)-nanocomposites were found to be exfoliated using montmorillonite modified with *N*,*N*-dimethyl-nhexadecyl-(4-vinylbenzyl) ammonium (MMT-VB16) (Salem and Shipp, 2005).

Di and Sogah (2006) reported the preparation of exfoliated polymer/montmorillonite nanocomposites by in situ polymerization from a montmorillonite-anchored photoiniferter, 4-(*N*,*N*-diethyldithiocarbamylmethyl)

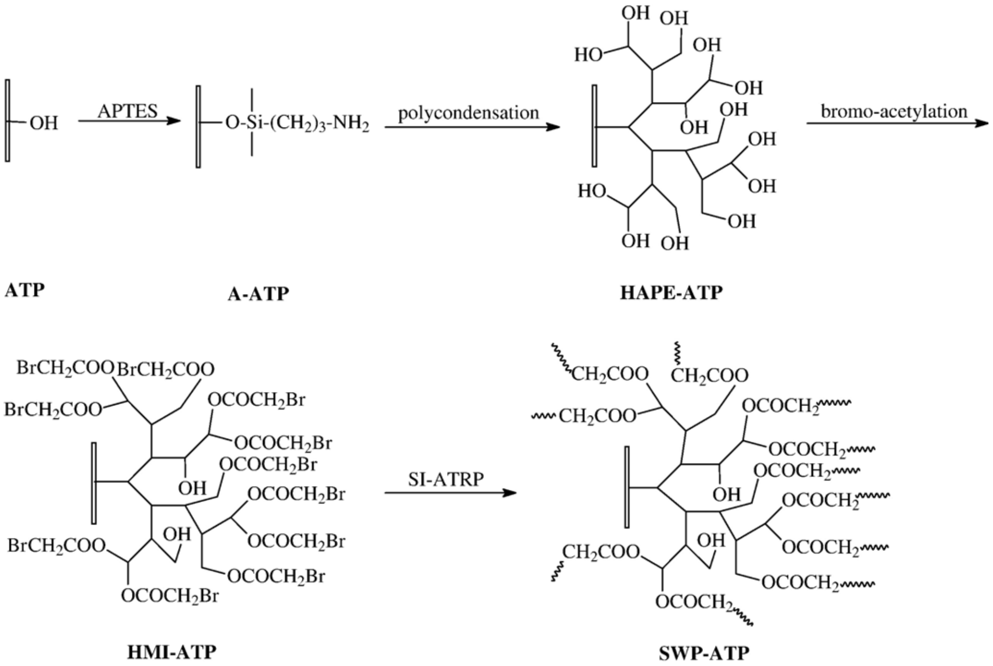


Fig. 8. The preparation procedure to the well-defined star polymer-grafted attapulgite.

benzyltrimethylammonium bromide (Fig. 4G) (Di and Sogah, 2006). The structure and dynamics of polymer-grafted montmorillonite in solution were investigated using static and dynamic light scattering techniques (Shah et al., 2005).

A well-defined polyacrylamide grafted on attapulgite was prepared by surface-initiated ATRP technique (Fig. 5) and the products were characterized by elemental analysis, FT-IR, TGA, and TEM (Liu and Guo, 2006). Compared with the bare attapulgite, the products had a better dispersibility in water. The PAM-ATP nanofibrils also had higher adsorption capacities towards Hg(II) ion and methylene blue (MB).

Polyacrylamide–polystyrene copolymers were grafted on attapulgite by a four-step self-assembling process (Fig. 6): i) the γ-aminopropyltriethoxyl silane was self-assembled onto the surfaces of the attapulgite; ii) the surface amino groups were amidated with bromoacetylbromide; iii) the bromo-acetamide modified attapulgite was used as macro-initiator for the surface-initiated atom transfer radical polymerization of styrene with the catalyst of the complex of 1,10-phenanthroline and Cu(I)Br; iv) the polystyrene grafted attapulgite was then used as macro-initiator for the polymerization of acrylamide. The two steps of the surface-initiated atom transfer radical polymerizations were conducted under ultrasonic irradiation at room temperature (Liu et al., 2006).

3.2.3. Hyperbranched polymers

The AB_2 type monomer, 2, 2-bis(hydroxymethyl) propionic acid (bis-MPA), was grafted to attapulgite modified with amino groups (Amino-ATP) via a melt polycondensation with *p*-toluenesulfonic acid as catalyst (Fig. 7) (Liu, 2007). Higher degree of grafting was achieved in shorter polymerizing time, compared with the solution polycondensation. The competitive adsorption capacities of the three adsorbents, bare ATP, aminopropyl attapulgite, and hyperbranched aliphatic polyester grafted attapulgite, towards Cu(II), Hg(II), Zn(II), and Cd(II) ions were also compared (Liu, submitted for publication).

Well-defined star polymer-grafted attapulgite with a hydrophilic core and hydrophobic shell and higher degree of grafting was prepared by postgraft-polymerization of a vinyl polymer on attapulgite modified with a hyperbranched macroinitiator (HMI-ATP) via surface-initiated atom transfer radical polymerization (SI-ATRP) (Fig. 8) (Liu and Wang, 2007). HMI-ATP, with bromoacetic ester surface groups, was prepared by bromoacetylation of the surface hydroxyl groups of HAPE-ATP. SI-ATRP of methyl methacrylate (MMA) was conducted using HMI-ATP prepared in presence of 1, 10-phenanthroline and Cu(I)Br as catalyst in toluene. The postgraft-polymerization exhibited the characteristics of a controlled/“living” polymerization.

4. Summary and prospect

The preparation of organic polymer/inorganic clay mineral nanocomposites offers a route to new materials with predefined structure and performance. Variations and combinations of these methods will need to be explored to prepare truly advanced materials possessing novel properties. Future developments in this field may include synthesis of novel functional organic polymer/inorganic clay mineral nanocomposites, including interpenetrating polymer networks, nano-objects, and biomimetic materials.

Acknowledgements

This work was supported by the Natural Science Foundation of Gansu Province (3ZS041-A25-002) and the Interdisciplinary Innovation Research Fund For Young Scholars, Lanzhou University (LZU200302).

References

Adebajo, M.O., Frost, R.L., Kloprogge, J.T., Carmody, O., Kokot, S., 2003. Porous materials for oil spill cleanup: a review of synthesis and adsorbing properties. J. Porous Mater. 10, 159–170.

Ahmadi, S.J., Huang, Y.D., Li, W., 2004. Synthetic routes, properties and future applications of polymer-layered silicate nanocomposites. J. Mater. Sci. 39, 1919–1925.

Akelah, A., Moet, A., 1996. Polymer–clay nanocomposites: free-radical grafting of polystyrene on to organophilic montmorillonite interlayers. J. Mater. Sci. 31, 3589–3596.

Alemdar, A., Butun, V., 2005. Interaction between a tertiary amine methacrylate based polyelectrolyte and a sodium momtmorillonite dispersion and its rheological and colloidal properties. J. Appl. Polym. Sci. 95, 300–306.

Alemdar, A., Oztekin, N., Gungor, N., Ece, O.I., Erim, F.B., 2005. Effects of polypropyleneimine adsorption on the rheological properties of purified bentonite suspensions. Colloids Surf., A Physicochem. Eng. Asp. 252, 95–98.

Aranda, P., Ruiz-Hitzky, E., 1999. Poly(ethylene oxide)/NH_4^+-smectite nanocomposites. Appl. Clay Sci. 15, 119–135.

Bottcher, H., Hallensleben, M.L., Nub, S., Wurm, H., Bauer, J., Behrens, P., 2002. Organic/inorganic hybrids by “living”/controlled ATRP grafting from layered silicates. J. Mater. Chem. 12, 1351–1354.

Breen, C., 1999. The characterization and use of polycation-exchanged bentonites. Appl. Clay Sci. 15, 187–219.

Burmistr, M.V., Shilov, V.V., Sukhyy, K.M., Pissis, P., Polizos, G., 2003. Dielectric relaxation and ionic conductivity of oxyethylene-alkylaromatic polyionenes. Polym. Sci., Ser. A 45, 785–794.

Burmistr, M.V., Sukhyy, K.M., Shilov, V.V., Pissis, P., Spanoudaki, A., Sukha, I.V., Tomilo, V.I., Gomza, Y.P., 2005. Synthesis, structure, thermal and mechanical properties of nanocomposites based on linear polymers and layered silicates modified by polymeric quaternary ammonium salts (ionenes). Polymer 46, 12226–12232.

Cavani, F., Trifiro, F., Vaccari, A., 1991. Hydrotalcite-type anionic clays. Preparation, properties and applications. Catal. Today 11, 173–301.

Chitnis, S.R., Sharma, M.M., 1997. Industrial applications of acid-treated clays as catalysts. React. Funct. Polym. 32, 93–115.

Chu, C.C., Chiang, L.M., Tsai, C.M., Lin, J.J., 2005. Exfoliation of montmorillonite clay by Mannich polyamines with multiple quaternary salts. Macromolecules 38, 6240–6243.

Cox, M., Rus-Romero, J.R., Sheriff, T.S., 2001. The application of montmorillonite clays impregnated with organic extractants for the removal of metals from aqueous solution Part I. The preparation of clays impregnated with di-(2-ethylhexyl) phosphoric acid and their use for the removal of copper(II). Chem. Eng. J. 84, 107–113.

Darder, M., Colilla, M., Ruiz-Hitzky, E., 2005. Chitosan–clay nanocomposites: application as electrochemical sensors. Appl. Clay Sci. 28, 199–208.

De Stefanis, A., Tomlinson, A.A.G., 2006. Towards designing pillared clays for catalysis. Catal. Today 114, 126–141.

Deng, Y.J., Dixon, J.B., White, G.N., Loeppert, R.H., Juo, A.S.R., 2006. Bonding between polyacrylamide and smectite. Colloids Surf., A Physicochem. Eng. Asp. 281, 82–91.

Di, J.B., Sogah, D.Y., 2006. Intergallery living polymerization using silicate-anchored photoiniferter. A versatile preparatory method for exfoliated silicate nanocomposites. Macromolecules 39, 1020–1028.

Diagne, M., Gueye, M., Vidal, L., Tidjani, A., 2005. Thermal stability and fire retardant performance of photo-oxidized nanocomposites of polypropylene-graft-maleic anhydride/clay. Polym. Degrad. Stab. 89, 418–426.

Dias Filho, N.L., Do Carmo, D.R., 2006. Study of an organically modified clay: selective adsorption of heavy metal ions and voltammetric determination of mercury (II). Talanta 68, 919–927.

Ding, Z., Kloprogge, J.T., Frost, R.L., Lu, G.Q., Zhu, H.Y., 2001. Porous clays and pillared clays-based catalysts. Part 2: a review of the catalytic and molecular sieve applications. J. Porous Mater. 8, 273–293.

Dong, J.Y., Wang, Z.M., Han, H., Chung, T.C., 2002. Synthesis of isotactic polypropylene containing a terminal Cl, OH, or NH_2 group via metallocene-mediated polymerization/chain transfer reaction. Macromolecules 35, 9352–9359.

Fan, X.W., Zhou, Q.Y., Xia, C.J., Cristofoli, W., Mays, J., Advincula, R.C., 2002. Living anionic polymerization (LASIP) of styrene from clay nanoparticles using surface bound 1,1-diphenylethylene (DPE) initiators. Langmuir 18, 4511–4518.

Fan, X.W., Xia, C.J., Advincula, R.C., 2003a. Grafting of polymers from clay nanoparticles via in situ free radical surface-initiated polymerization: monocationic versus bicationic initiators. Langmuir 19, 4381–4389.

Fan, X.W., Xia, C.J., Fulghum, T., Park, M.K., Locklin, J., Advincula, R.C., 2003b. Polymer brushes grafted from clay nanoparticles adsorbed on a planar substrate by free radical surface-initiated polymerization. Langmuir 19, 916–923.

Fan, X.W., Xia, C.J., Advincula, R.C., 2005. On the formation of narrowly polydispersed PMMA by surface initiated polymerization (SIP) from AIBN-coated/intercalated clay nanoparticle platelets. Langmuir 21, 2537–2544.

Galan, E., 1996. Properties and applications of palygorskite–sepiolite clays. Clay Miner. 31, 443–453.

Giannelis, E.P., 1996. Polymer layered silicate nanocomposites. Adv. Mater. 8, 29–35.

Gilman, J.W., 1999. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. Appl. Clay Sci. 15, 31–49.

Gournis, D., Karakassides, M.A., Bakes, T., Boukos, N., Petridis, D., 2002. Catalytic synthesis of carbon nanotubes on clay minerals. Carbon 40, 2641–2646.

Grandjean, J., Laszlo, P., 1996. Interaction of nonionic polymers at a clay interface. Magn. Reson. Imaging 14, 983–984.

Gungor, N., Karaoglan, S., 2001. Interaction of polyacrylamide polymer with bentonite in aqueous system. Mater. Lett. 48, 168–175.

Guth, U., Brosda, S., Schomburg, J., 1996. Application of clay minerals in sensor techniques. Appl. Clay Sci. 11, 229–236.

Harvey, C.C., Murray, H.H., 1997. Industrial clays in the 21st century: a perspective of exploration, technology and utilization. Appl. Clay Sci. 11, 285–310.

Hild, A., Sequaris, J.M., Narres, H.D., Schwuger, M., 1997. Adsorption of polyvinylpreeolidone on kaolinite. Colloids Surf., A Physicochem. Eng. Asp. 123–124, 515–522.

Hu, S.W., Wang, Y., McGinty, K., Brittain, W.J., 2006. Surface modification of a silicate substrate by a “grafting from” methodology utilizing a perester initiator. Eur. Polym. J. 42, 2053–2058.

Huh, J.K., Song, D.I., Jeon, Y.W., 2000. Sorption of phenol and alkylphenols from aqueous solution onto organically modified montmorillonite and applications of dual-mode sorption model. Sep. Purif. Technol. 35, 243–259.

Husband, J.C., 1998. Adsorption and rheological studies of sodium carboxymethyl cellulose onto kaolin: effect of degree of substitution. Colloids Surf., A Physicochem. Eng. Asp. 134, 349–358.

Isoda, K., Kuroda, K., Ogawa, M., 2000. Interlamellar grafting of γ-methacryloxypropylsilyl groups on magadiite and copolymerization with methyl methacrylate. Chem. Mater. 12, 1702–1707.

Jaber, M., Miehe-Brendle, J., Michelin, L., Delmotte, L., 2005. Heavy metal retention by organoclays: synthesis, applications, and retention mechanism. Chem. Mater. 17, 5275–5281.

Kathleen, A.C., 2000. Synthetic organo- and polymer-clays: preparation, characterization, and materials applications. Appl. Clay Sci. 17, 1–23.

Kirwan, L.J., Fawell, P.D., van Bronswijk, W., 2003. In situ FTIR-ATR examination of poly(acrylic acid) adsorbed onto hematite at low pH. Langmuir 19, 5802–5807.

Kirwan, L.J., Fawell, P.D., van Bronswijk, W., 2004. An in situ FTIR-ATR study of polyacrylate adsorbed onto hematite at high pH and high ionic strength. Langmuir 20, 4093–4100.

Kubies, D., Pantoustier, N., Dubois, P., Rulmont, A., Jerome, R., 2002. Controlled ring-opening polymerization of ε-caprolactone in the presence of layered silicates and formation of nanocomposites. Macromolecules 35, 3318–3320.

LeBaron, P.C., Wang, Z., Pinnavaia, T.J., 1999. Polymer-layered silicate nanocomposites: an overview. Appl. Clay Sci. 15, 11–29.

Lee, S.Y., Tank, R.W., 1985. Role of clays in the disposal of nuclear waste: a review. Appl. Clay Sci. 1, 145–162.

Lepoittevin, B., Pantoustier, N., Alexandre, M., Calberg, C., Jerome, R., Dubois, P., 2002. Polyester layered silicate nanohybrids by controlled grafting polymerization. J. Mater. Chem. 12, 3528–3532.

Li, H., Teppen, B.J., Laird, D.A., Johnston, C.T., Boyd, S.A., 2004. Geochemical modulation of pesticide sorption on smectite clay. Environ. Sci. Technol. 38, 5393–5399.

Li, C.P., Huang, C.M., Hsieh, M.T., Wei, K.H., 2005. Properties of covalently bonded layered-silicate/polystyrene nanocomposites synthesized via atom transfer radical polymerization. J. Polym. Sci., A, Polym. Chem. 43, 534–542.

Lin, J.J., Chen, Y.M., 2004. Amphiphilic properties of poly(oxylalkylene)amine-intercalated smectite aluminosilicates. Langmuir 20, 4261–4264.

Lin, J.J., Cheng, I.J., Wang, R., Lee, R.J., 2001. Tailoring basal spacings of montmorillonite by poly(oxyalkylene) diamines intercalation. Macromolecules 34, 8832–8834.

Lin, S.H., Juang, R.S., Wang, Y.H., 2004. Adsorption of acid dye from water onto pristine and acid-activated clays in fixed beds. J. Hazard. Mater. 113, 195–200.

Liu, P., 2006. Nanosurface-initiated living radical polymerization. In: Nalwa, H.S. (Ed.), Polymeric Nanostructures and Their Applications. American Scientific Publishers.

Liu, P., submitted for publication. Hyperbranched aliphatic polyester grafted attapulgite: preparation, characterization, and adsorption properties for heavy metal ions. J. Hazard. Mater.

Liu, P., 2007. Hyperbranched aliphatic polyester grafted attapulgite via a melt polycondensation process. Appl. Clay Sci. 35, 11–16.

Liu, P., Guo, J.S., 2006. Polyacrylamide grafted attapulgite (PAM-ATP) via surface-initiated atom transfer radical polymerization (SI-ATRP) for removal of Hg(II) ion and dyes. Colloids Surf., A Physicochem. Eng. Asp. 282–283, 498–503.

Liu, P., Wang, T.M., 2007. Preparation of well-defined star polymer from hyperbranched macroinitiator based attapulgite by surface-initiated atom transfer radical polymerization (SI-ATRP) technique. Ind. Eng. Chem. Res. 46, 97–102.

Liu, P., Wang, T.M., Su, Z.X., 2006. Self-assembly of well-defined polyacrylamide-polystyrene copolymer on fibrillar clays via ultrasonic-assisted surface-initiated atom transfer radical polymerization. J. Nanosci. Nanotechnol. 6, 1684–1688.

Meunier, A., Velde, B., Griffault, L., 1998. Reactivity of bentonites: a review. An application to clay barrier stability for nuclear waste storage. Clay Miner. 33, 187–196.

Morgan, A.B., Dubois, P., 2000. Polymer-layered silicate nanocomposites: Preparation, properties and use of new class of materials. Mater. Sci. Eng., R Rep. 28, 1–63.

Mousty, M., 2004. Sensors and biosensors based on clay-modified electrodes-new trends. Appl. Clay Sci. 27, 159–177.

Murray, H.H., 2000. Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. Appl. Clay Sci. 17, 207–221.

Nelson, A., Cosgrove, T., 2004a. A small-angle neutron scattering study of adsorbed poly(ethylene oxide) on laponite. Langmuir 20, 2298–2304.

Nelson, A., Cosgrove, T., 2004b. Dynamic light scattering studies of poly(ethylene oxide) adsorbed on laponite: Layer conformation and its effect on particle stability. Langmuir 20, 10382–10388.

Nelson, A., Cosgrove, T., 2005. Small-angle neutron scattering study of adsorbed pluronic tri-block copolymers on laponite. Langmuir 21, 9176–9182.

Oztekin, N., Alemdar, A., Gungor, N., Erim, F.B., 2002. Adsorption of polyethyleneimine from aqueous solution on bentonite clays. Mater. Lett. 55, 73–76.

Pal, O.R., Vanjara, A.K., 2001. Removal of malathion and butachlor from aqueous solution by clays and organoclays. Sep. Purif. Technol. 24, 167–172.

Pollet, E., Delcourt, C., Alexandre, M., Dubois, P., 2004. Organic–inorganic nanohybrids obtained by sequential copolymerization of ε-caprolactone and L,L-lactide from activated clay surface. Macromol. Chem. Phys. 205, 2235–2244.

Ray, S.S., Okamoto, M., 2003. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog. Polym. Sci. 28, 1539–1641.

Rosa-Brussin, Marcos F.D., 1995. Use of clays for the hydrotreatment of heavy crude oils. Catal. Rev., Sci. Eng. 37, 1–100.

Sadek, O.M., Mekhemer, W.K., Assaad, F.F., Mostafa, B.A., 2006. Adsorption of poly(4-sodium styrene sulfonate) on kaolinite clays. J. Appl. Polym. Sci. 100, 1712–1719.

Salahuddin, N., Akelah, A., 2002. Synthesis and characterization of poly(styrene-maleic anhydride)-montmorillonite nanocomposite. Polym. Adv. Technol. 13, 339–345.

Salem, N., Shipp, D.A., 2005. Polymer-layered silicate nanocomposites prepared through in situ reversible addition-fragmentation chain transfer (PART) polymerization. Polymer 46, 8573–8581.

Seckin, T., Onal, Y., Yesilada, O., Gultek, A., 1997. Preparation and characterization of a clay-polyvinylpyridinium matrix for the removal of bacterial cells from water. J. Mater. Sci. 32, 5993–5999.

Seckin, T., Gultek, A., Icduygu, M.G., Onal, Y., 2002. Polymerization and characterization of acrylonitrile with γ-methacryloxypropyltrimethoxy-silane grafted bentonite clay. J. Appl. Polym. Sci. 84, 164–171.

Sen, S., Memesa, M., Nugay, N., Nugay, T., 2006. Synthesis of effective poly(4-vinylpyridine) nanocomposites: in situ polymerization from edges/surfaces and interlayer galleries of clay. Polym. Int. 55, 216–221.

Sequaris, J.M., Hild, A., Narres, H.D., Schwuger, M.J., 2000. Polyvinylpyrrolidone adsorption on Na-montmorillonite. Effect of the polymer interfacial conformation on the colloidal behavior and binding of chemicals. J. Colloid Interface Sci. 230, 73–83.

Shah, D., Fytas, G., Vlassopoulos, D., Di, J., Sogah, D., Giannelis, E.P., 2005. Structure and dynamics of polymer-grafted clay suspensions. Langmuir 21, 19–25.

Shichi, T., Takagi, K., 2000. Clay minerals as photochemical reaction fields. J. Photochem. Photobiol., C Photochem. Rev. 1, 113–130.

Simon, S., Cerf, D.L., Picton, L., Muller, G., 2002. Adsorption of cellulose derivatives onto montmorillonite: a SEC-MALLS study of molar masses influence. Colloids Surf., A Physicochem. Eng. Asp. 203, 77–86.

Smith, E.H., Vengris, T., 1998. Clay minerals and heavy metals. Crit. Rev. Anal. Chem. 28, 13–18.

Su, S.P., Wilkie, C.A., 2004. The thermal degradation of nanocomposites that contain an oligeric ammonium cation on the clay. Polym. Degrad. Stab. 84, 347–362.

Su, S.P., Jiang, D.D., Wilkie, C.A., 2004a. Novel polymerically-modified clays permit the preparation of intercalated and exfoliated nanocomposites of styrene and its copolymers by melt blending. Polym. Degrad. Stab. 83, 333–346.

Su, S.P., Jiang, D.D., Wilkie, C.A., 2004b. Study on the thermal stability of polystyryl surfactants and their modified clay nanocomposites. Polym. Degrad. Stab. 84, 269–277.

Su, S.P., Jiang, D.D., Wilkie, C.A., 2004c. Polybutadiene-modified clay and its nanocomposites. Polym. Degrad. Stab. 84, 279–288.

Taylor, D.R., Stein, J., Svidovsky, N., 1998. Pesticide stability versus clay carrier surface acidity. ASTM Spec. Tech. Pub. 1347, 215–227.

Tekin, N., Kadinci, E., Demirbas, O., Alkan, M., Kara, A., Dogan, M., 2006. Surface properties of poly(vinylimidazole)-adsorbed expanded perlite. Microporous Mesoporous Mater. 83, 163–169.

Tonle, I.K., Ngameni, E., Walcarius, A., 2005. Preconcentration and voltammetric analysis of mercury (II) at a carbon paste electrode modified with natural smectite-type clays grafted with organic chelating groups. Sens. Actuators, B, Chem. 110, 195–203.

Torn, L.H., de Keizer, A., Koopal, L.K., Lyklema, J., 2003. Mixed adsorption of poly(vinylpyrrolidone) and sodium dodecylbenzenesulfonate on kaolinite. J. Colloid Interface Sci. 260, 1–8.

Uthirakumar, P., Hahn, Y.B., Nahm, K.S., Lee, Y.S., 2005. Exfoliated high-impact polystyrene/MMT nanocomposites prepared using anchored cationic radical initiator-MMT hybrid. Eur. Polym. J. 41, 1582–1588.

Vaccari, A., 1999. Clays and catalysis: a promising future. Appl. Clay Sci. 14, 161–198.

van Oss, C.J., Giese, R.F., 2003. Surface modification of clays and related materials. J. Dispers. Sci. Technol. 24, 363–376.

Velten, U., Ronald, A.S., Caseri, W.R., Suter, U.W., Li, Y.Z., 1999. Polymerization of styrene with peroxide initiator ionically bound to high surface area mica. Macromolecules 32, 3590–3597.

Viville, C., Lazzaroni, R., Pollet, E., Alexandre, M., Dubois, P., 2004. Controlled polymer grafting on single clay nanoplatelets. J. Am. Chem. Soc. 126, 9007–9012.

Volpert, E., Selb, J., Candau, F., Green, N., Argillier, J.F., Audibert, A., 1998. Adsorption of hydrophobically associating polyacrylamides on clay. Langmuir 14, 1870–1879.

Vyazovkin, S., Dranca, I., Fan, X.W., Advincula, R., 2004. Degradation and relaxation kinetics of polystyrene-clay nanocomposite prepared by surface initiated polymerization. J. Phys. Chem. B 108, 11672–11679.

Wang, D.Y., Zhu, J., Yao, Q., Wilkie, C.A., 2002. A comparison of various methods for the preparation of polystyrene and poly(methyl methacrylate) clay nanocomposites. Chem. Mater. 14, 3837–3843.

Wang, Z.M., Nakajima, H., Manias, E., Chung, T.C., 2003. Exfoliated PP/clay nanocomposites using ammonium-terminated PP as the organic modification for montmorillonite. Macromolecules 36, 8919–8922.

Weimer, M.W., Chen, H., Giannelis, E.P., Sogah, D.Y., 1999. Direct synthesis of dispersed nanocomposites by in situ living free radical polymerization using a silicate-anchored initiator. J. Am. Chem. Soc. 121, 1615.

Wheeler, P.A., Wang, J.Z., Baker, J., Mathias, L.J., 2005. Synthesis and characterization of covalently functionalized laponite clay. Chem. Mater. 17, 3012–3018.

Wheeler, P.A., Wang, J., Mathias, L.J., 2006. Poly(methyl methacrylate)/laponite nanocomposites: exploring covalent and ionic clay modifications. Chem. Mater. 18, 3937–3945.

Williams, L.B., Holland, M., Eberl, D.D., Brunet, T., De Courrsou, L.B., 2004. Killer clays! Natural antibacterial clay minerals. Mineral. Soc. Bull. 139, 3–8.

Wu, J.Y., Wu, T.M., Chen, W.Y., Tsai, S.J., Kuo, W.F., Chang, G.Y., 2005. Preparation and characterization of PP/clay nanocomposites based on modified polypropylene and clay. J. Polym. Sci., Polym. Phys. 43, 3242–3254.

Xie, S.B., Zhang, S.M., Wang, F.S., 2004. Synthesis and characterization of poly(propylene)/montmorillonite nanocomposites by simultaneous grafting-intercalation. J. Appl. Polym. Sci. 94, 1018–1023.

Zaman, A.A., Tsuchiya, R., Moudgil, B.M., 2002. Adsorption of a low-molecular-weight polyacrylic acid on silica, alumina, and kaolin. J. Colloid Interface Sci. 256, 73–78.

Zen, J.M., 2004. The prospects of clay mineral electrodes. Anal. Chem. 76, 205A–211A.

Zhao, H.Y., Farrell, B.P., Shipp, D.A., 2004. Nanopatterns of poly (styrene-block-butyl acrylate) block copolymer brushes on the surfaces of exfoliated and intercalated clay layers. Polymer 45, 4473–4481.

Zhou, Q.Y., Fan, X.W., Xia, C.J., Mays, J., Advincula, R., 2001. Living anionic surface initiated polymerization (SIP) of styrene from clay surfaces. Chem. Mater. 13, 2465–2467.