

Synthesis and Characterization of Novel Oligomeric Poly(styrene-*co*-acrylonitrile)–Clay Complexes

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ABSTRACT: Oligomeric poly(styrene-*co*-acrylonitrile) quaternary ammonium salts were prepared through reactions of trimethylamine with corresponding poly(styrene-acrylonitrile-vinyl benzyl chloride)s, which were synthesized by the free-radical polymerization of a mixture of styrene, acrylonitrile, and vinyl benzyl chloride. Then, oligomeric poly(styrene-*co*-acrylonitrile)-modified clays were prepared through the cation exchange of the sodium ions in the clay with the corresponding poly(styrene-*co*-acrylonitrile) quaternary ammonium salts. The poly(styrene-acrylonitrile-vinyl benzyl chloride)s, poly(styrene-*co*-acrylonitrile) quaternary ammonium salts, and their clay complexes were characterized with infrared spectroscopy, gel permeation chromatography, thermogravimetric analysis, proton nuclear magnetic resonance, X-ray diffraction,

and transmission electron microscopy. X-ray diffraction and transmission electron microscopy studies showed that these novel clay complexes were well intercalated. Furthermore, thermogravimetric analysis data indicated that this series of polymerically modified clays had high enough thermal stability for nanocomposites by melt blending. The thermal treatment of one of these novel clays at 250°C under nitrogen was also conducted. Solubility and infrared studies of this thermally treated clay complex revealed that a novel polyimine/enamine structure clay complex had been formed in the gallery of the clay. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3355–3361, 2009

Key words: clay; oligomers; organoclay; polyimines

INTRODUCTION

Polymerically modified clays are among the most promising organically modified clays because their surface properties are easily tuned with a variety of functional polymers.¹ They have been widely used in many industrial fields and applications, such as catalysts,^{2,3} adsorbents,^{4–6} controlled-release systems,^{7–9} and the preparation of polymer–clay nanocomposites.^{10–15} In general, polymerically modified clays can be obtained through the absorption of polymers, surface chemical grafting, or ion exchange with polymers.¹⁶ The properties of these polymerically modified clays are affected by the properties of the polymers used as well as the preparation methods, and in most cases, their applications are limited by their properties. For polymerically modified clays prepared by physical absorption, their application fields are limited because of the weak force between the polymer and clay surface. Polymerically modi-

fied clays made by chemical grafting processes most often appear in scientific research and are not often used in industry, possibly because of their high costs. Ion exchange of the sodium ions in the gallery of the clays with the polymeric quaternary ammonium ions is the most industrially favorable method because of its lower costs.^{9,17}

Polyacrylonitrile and its copolymers have been studied extensively because of their commercial importance. They have been used as raw materials for textiles,¹⁸ rubbers,^{19–21} plastics,^{22,23} and fibers and as precursors in carbon fiber production.²⁴ Many studies of their applications as materials for nitric oxide release,²⁵ CO₂ absorption,^{26,27} and the synthesis of membranes containing reactive groups²⁸ have been reported. Recently, polyacrylonitrile–clay nanocomposites have attracted some interest because of their reinforced mechanical properties in comparison with the virgin polymer.^{29–33} However, there is no report on the preparation of poly(styrene-*co*-acrylonitrile)–clay complexes by an ion-exchange process.

In this study, oligomeric poly(styrene-*co*-acrylonitrile)-modified clays were prepared through the ion exchange of the sodium ions in the clays with the poly(styrene-*co*-acrylonitrile) quaternary ammonium salts. One of the objectives of this study was to

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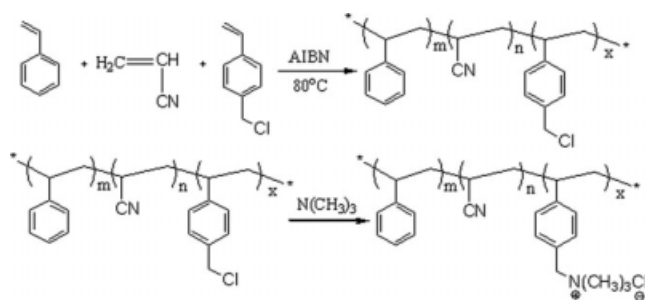


Figure 1 Scheme for preparing poly(styrene-*co*-acrylonitrile) quaternary ammonium salts.

prepare a series of oligomers with different monomer ratios of styrene to acrylonitrile to investigate the thermal stability of their corresponding clay complexes for possible applications in the preparation of clay nanocomposites by melt blending. The other objective was to thermally treat the obtained poly(styrene-*co*-acrylonitrile)-clay complexes under nitrogen to obtain novel polyimine/enamine clay complexes that could be applied as novel vesicles in nitric oxide release.

EXPERIMENTAL

Materials

Pristine sodium montmorillonite (Na-MMT; cation-exchange capacity = 90 mequiv/100 g) was kindly provided by Zhejiang Fenghong Clay Chemicals Co., Ltd. (Hongzhou, China). Acrylonitrile, styrene, vinyl benzyl chloride, trimethylamine (30% aqueous solution), *N,N*-dimethylformamide (DMF), and *N,N'*-azobisisobutyronitrile (AIBN) were purchased from Shanghai Shanpu Chemical Reagent Co., Ltd. (Shanghai, China), and used without further purification. Tetrahydrofuran (THF) was purchased from Yueyang Chemical Co., Ltd. (Yueyang, China), and distilled before use.

Preparation of the poly(styrene-*co*-acrylonitrile)-clay complexes

In general, the poly(styrene-*co*-acrylonitrile) quaternary ammonium salts were prepared through the reaction of trimethylamine with the corresponding poly(styrene-*co*-acrylonitrile-vinyl benzyl chloride)s [P(St-AN-VBC)s], which were synthesized by the free-radical copolymerization of styrene, acrylonitrile, and vinyl benzyl chloride. The scheme for preparing the poly(styrene-*co*-acrylonitrile) quaternary ammonium salts is shown in Figure 1. The oligomeric poly(styrene-*co*-acrylonitrile)-modified clays were prepared through the cation exchange of the sodium ions in the montmorillonites (MMTs) with the corresponding poly(styrene-*co*-acrylonitrile) quaternary ammonium ions.

Synthesis of P(St-AN-VBC)

A 500-mL, three-necked, round flask equipped with a condenser, a stirrer and a thermometer was charged with 78.4 g (754 mmol) of styrene, 22.4 g (423 mmol) of acrylonitrile, 5.6 g (36 mmol) of vinyl benzyl chloride, 5.6 g (34 mmol) of AIBN as an initiator, and 100 mL of THF as a solvent. The temperature was raised to 80°C and kept there for 2 h. After most of the solvent was removed on a rotary evaporator, 500 mL of methanol was added to the flask to precipitate the polymer. The precipitate was filtered and then redissolved and reprecipitated three times. In the end, the solvent was evaporated, and 84 g of a white solid remained with a yield of 84%.

¹H-NMR (CDCl₃, δ): 7.4–6.3 (br, 107H), 4.5–4.3 (br, 2H), 3.8–3.7 (br, 2H), 2.8–2.6 (br, 10H), 2.0–0.8 (br, 104H).

This process was used for the preparation of P(St-AN-VBC) with a weight ratio of styrene to acrylonitrile of 4 to 1. Other P(St-AN-VBC)s could be achieved through control of the weight ratio of styrene to acrylonitrile, whereas the total weight of these two monomers in the reaction system was kept unchanged.

Synthesis of poly(styrene-*co*-acrylonitrile) quaternary ammonium salts

A 1000-mL, three-necked, round flask equipped with a condenser, a stirrer, and a thermometer were charged with 80 g of P(St-AN-VBC) from the previous example and 300 mL of THF as a solvent. The mixture was stirred until all components were completely dissolved at 40°C. Then, 10.1 g (49.5 mmol; an excess amount) of trimethylamine (30% aqueous solution) was added to the system dropwise. This reaction was kept overnight. Then, the solvent was evaporated *in vacuo*, and a pale yellow solid remained.

¹H-NMR (CDCl₃, δ): 7.4–6.3 (br, 107H), 3.8–3.7 (br, 2H), 3.2–3.0 (br, 8H), 2.0–0.8 (br, 104H).

Preparation of the poly(styrene-*co*-acrylonitrile)-clay complexes

A suspension of 36 g of pristine Na-MMT in 900 mL of distilled water was stirred overnight at room temperature. Then, 1800 mL of THF was added dropwise, and the stirring was continued for 2 h. To this stirred MMT suspension, a solution of 100 g of poly(styrene-*co*-acrylonitrile) quaternary ammonium salt obtained from the previous example in 400 mL of THF was added dropwise. After the solution was stirred overnight, the white precipitate was filtered, washed with distilled water at least three times, then washed with 200 mL of a THF solution (THF/water = 70/30 v/v) twice, and washed with water

TABLE I
GPC Analysis Data for P(St-AN-VBC)s with Different Acrylonitrile Contents

No.	St (g)	VBC (g)	AN (g)	AN content (%)	AIBN (g)	Yield (%)	M_w	M_n	MWD
1	78.4	5.6	22.4	20	5.6	70	9240	3065	3.04
2	89.6	5.6	11.2	10	5.6	68	8282	3011	2.75
3	95.2	5.6	5.6	5	5.6	72	8663	2921	2.96

AN = acrylonitrile; M_n = number-average molecular weight; M_w = weight-average molecular weight; St = styrene; VBC = vinyl benzyl chloride.

again until no chloride ions could be detected with an acidic aqueous AgNO_3 solution. It was then dried *in vacuo* overnight at 90°C.

Thermal treatment of the poly(styrene-*co*-acrylonitrile)-clay complexes

A poly(styrene-*co*-acrylonitrile)-clay complex with a weight ratio of styrene to acrylonitrile of 1 to 4 was heated under N_2 at 250°C for 3 h. Then, the infrared (IR) analysis of the poly(styrene-*co*-acrylonitrile)-modified clay before and after the thermal treatment were taken. The dispersion testing experiments were also performed in DMF on these clays before and after the thermal treatment. In a typical experiment, 0.2 g of the sample was dispersed by ultrasonification in 5 mL of DMF in a vial; after 30 min, a picture of the dispersion in the vial was taken.

Instrumentation

The molecular weight and molecular weight distribution (MWD) of all oligomers were obtained with gel permeation chromatography (GPC). Analyses were performed on an Alltech (Illinois) instrument with THF as the eluting solvent at a flow of 1 mL/min through a Jordi GPC 10000 A column (300 × 7.8 mm) equipped with an Alltech ELSD 800 detector. This system was calibrated with standard polystyrenes. IR spectra were obtained with a Rayleigh WQF-200 instrument (Beijing, China) using conventional KBr pellets. A mixture of 1 mg of the sample powder with 100 mg of dried KBr crystals was pressed into a pellet 13 mm in diameter. $^1\text{H-NMR}$ spectra were collected with a Varian (Palo Alto, CA) Inova-300 FT-NMR spectrometer operating at 400 MHz with CDCl_3 as the solvent. Thermogravimetric analysis (TGA) scans were conducted from 30 to 600°C with a Netzsch (Bavaria, Germany) STA409PC instrument under a flowing nitrogen atmosphere at a scan rate of 10°C/min. All TGA results were averages of a minimum of three determinations; temperatures were reproducible to $\pm 3^\circ\text{C}$, whereas the error bars on the nonvolatile material were $\pm 3\%$. X-ray diffraction (XRD) patterns were collected from 1.1 to 10° with a scan time of 10 s/step with a Bruker

(Karlsruhe, Germany) D8 instrument using a step size of 0.1°. $\text{Cu K}\alpha$ X-ray radiation and a random amount of the powder were used. Transmission electron microscopy (TEM) images were obtained with a JEOL (Tokyo, Japan) 1230 instrument under an accelerating voltage of 100 kV. To coat the clays on copper grids, a suspension of the organically modified clay sample in chloroform was mixed with a formvar/chloroform solution. A drop of this mixture was placed on top of the grid, and after it dried in the air, the sample for TEM was obtained.

RESULTS AND DISCUSSION

Molecular weight and MWD of P(St-AN-VBC)s

The molecular weight and MWD of P(St-AN-VBC)s were measured by GPC. The GPC analysis data are shown in Table I. The results indicate that the molecular weight and MWD of these copolymers can be tuned by adjustments of the weight ratio of the initiator to all monomers. The typical weight-average molecular weight and MWD for copolymers prepared according to Table I are 9000 and 2.8, respectively.

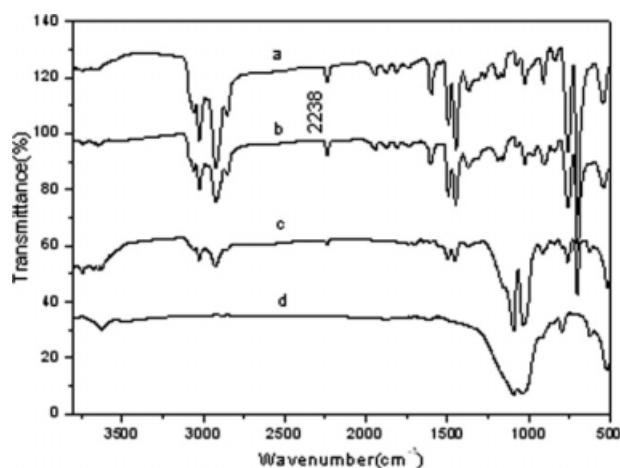


Figure 2 IR spectra obtained from (a) P(St-AN-VBC), (b) poly(styrene-*co*-acrylonitrile) quaternary ammonium salt, (c) poly(styrene-*co*-acrylonitrile)-clay complex, and (d) pure MMT.

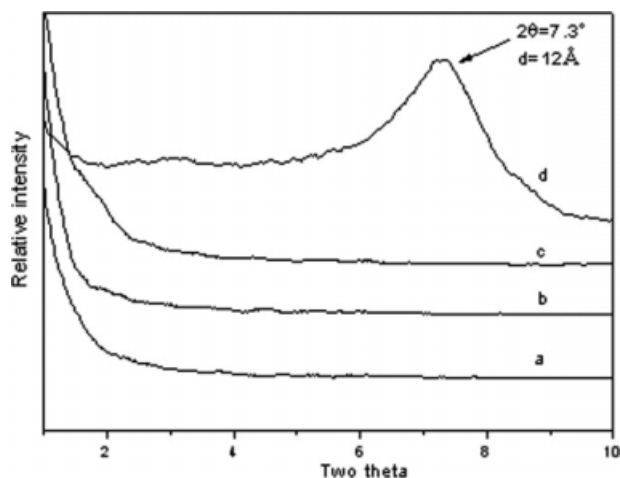


Figure 3 XRD traces in the reflection mode obtained from clays modified by poly(styrene-*co*-acrylonitrile) quaternary ammonium salts with different acrylonitrile contents (w/w): (a) 5% acrylonitrile, (b) 10% acrylonitrile, (c) 20% acrylonitrile, and (d) pure MMT.

FTIR spectra

FTIR spectra of P(St-AN-VBC), poly(styrene-*co*-acrylonitrile) quaternary ammonium salt, poly(styrene-*co*-acrylonitrile)-modified clay, and pure clay are shown in Figure 2. In Figure 2(a), the absorption bands at 3103–3000 (aromatic C–H stretching region), 2238 (C≡N stretching), and 1264 cm^{-1} (CH₂–Cl wagging band) are attributed to the typical absorption bands of the P(St-AN-VBC) copolymer. The disappearance of the absorption band at 1264 cm^{-1} in Figure 2(b) indicates the rupture of the CH₂–Cl bond, which leads to the formation of the poly(styrene-*co*-acrylonitrile) quaternary ammonium salt. The absorption bands at 3627, 1043, and 620–513 cm^{-1} are attributed to the typical absorption bands of the pristine MMT in Figure 2(d). In Figure

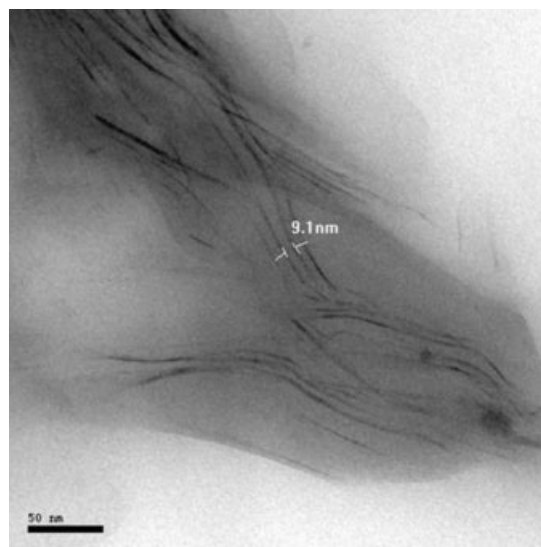


Figure 4 TEM image of a typical poly(styrene-*co*-acrylonitrile)-clay complex with a weight ratio of styrene to acrylonitrile of 4/1.

2(c), both the characteristic absorption bands of poly(styrene-*co*-acrylonitrile) quaternary ammonium and pure MMT can be observed, and they indicate that a novel poly(styrene-*co*-acrylonitrile)-modified MMT was obtained.

XRD and TEM results

XRD traces of the pristine MMT and poly(styrene-*co*-acrylonitrile)-clay complexes are presented in Figure 3. There is an apparent peak at $2\theta = 7.3^\circ$ for the pristine MMT, which corresponds to a basal spacing of 1.2 nm. For poly(styrene-*co*-acrylonitrile)-modified clays [Fig. 3(a–c)], there are no obvious peaks in the X-ray traces, and this indicates that the silicate layers in the poly(styrene-*co*-acrylonitrile)-clay complexes

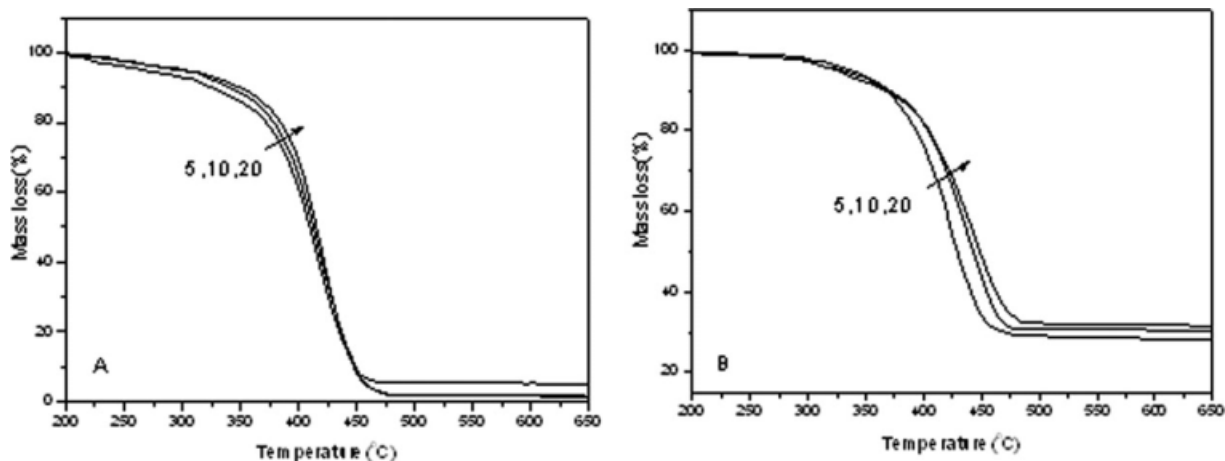


Figure 5 TGA traces obtained from (A) poly(styrene-*co*-acrylonitrile) quaternary ammonium salts and (B) poly(styrene-*co*-acrylonitrile)-clay complexes. The numbers are the weight percentages of acrylonitrile units in the polymers.

TABLE II
Characteristic Temperatures Obtained by TGA for PSANQAS and PSANQAS-Clay Complexes

	Temperature (°C)					
	AN in PSANQAS			AN in PSANQAS/MMT		
	5%	10%	20%	5%	10%	20%
Mass loss						
5%	266	300	300	311	326	335
10%	325	342	348	353	366	370
50%	410	414	415	418	421	426
Residual mass (%)	1.7	1.7	4.9	29.9	31.2	27.7

AN = acrylonitrile; PSANQAS = poly(styrene-acrylonitrile-vinyl benzyl chloride) quaternary ammonium salt.

were disordered or exfoliated. To confirm the structures of these poly(styrene-*co*-acrylonitrile)-clay complexes, TEM studies were performed. Figure 4 presents typical TEM images of these clay complexes. The images of the samples show a well-intercalated structure for the typical clay complex and indicate a *d*-spacing of 9.1 nm. It is well known that this great enlargement in *d*-spacing between the clay layers endows these novel clays with the possibility of preparing exfoliated clay-polymer nanocomposites.

TGA characterization

TGA traces obtained from poly(styrene-*co*-acrylonitrile) quaternary ammonium salts and their clay complexes are shown in Figure 5. From Figure 5(A), it is obvious that the initial degradation of these quaternary ammoniums starts at 215°C, and it is dependent on the number of acrylonitrile units in the copolymers. The greater the number is of acrylonitrile units in the copolymer, the higher the initial degradation temperature is. As previously reported, the initial weight loss of polyacrylonitrile in its thermal degradation process occurs at 320°C;³⁴ the temperature for the loss of ammonium groups in polystyryl ammonium salts is between 195 and 260°C.³⁵ The thermal degradation of poly(styrene-*co*-acrylonitrile) ammonium salts is a process including the degradation of polyacrylonitrile and polystyryl ammonium salt chains. Because polyacrylonitrile is much more thermally stable than polystyryl ammonium salt, this can well explain the previously

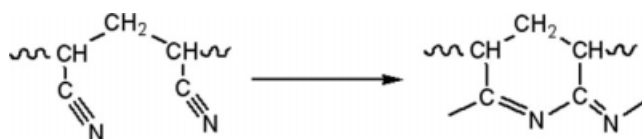


Figure 6 Cyclization process of the repetitive nitrile units by the thermal treatment.

observed degradation behavior of the poly(styrene-*co*-acrylonitrile) ammonium salt.

The TGA data analysis for both the poly(styrene-*co*-acrylonitrile) quaternary ammonium salts and their corresponding clay complexes is shown in Table II. The ammonium salt has the best thermal stability when the acrylonitrile content is 20% in the polymer, and the same results have been obtained with the clay complexes. The typical 10% weight loss degradation temperature of these novel polymeric quaternary ammonium salts is about 50°C higher than that of the long chain alkyl quaternary ammonium salts, as previously reported.^{36,37} The high thermal stability could offer these polymer-clay complexes the possibility of applications in preparing nanocomposites for which a high melt-blending temperature is required.

IR spectra of the thermally treated poly(styrene-*co*-acrylonitrile)-clay complexes

It is well known that polyacrylonitrile and its styrene copolymer will form polyimine/enamine

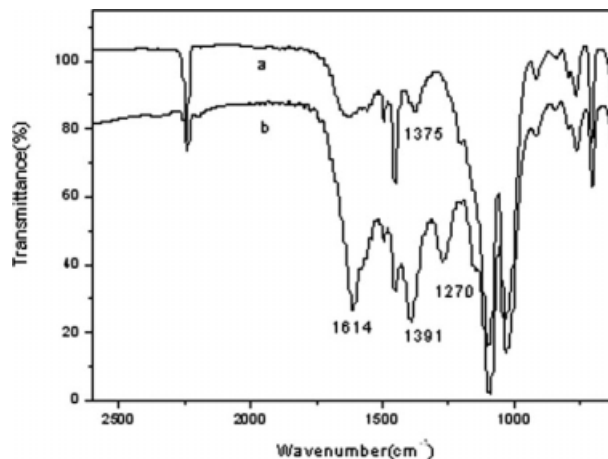


Figure 7 IR spectra obtained from poly(styrene-*co*-acrylonitrile)-clay complexes (a) before and (b) after the thermal treatment at 250°C under N₂ for 3 h.

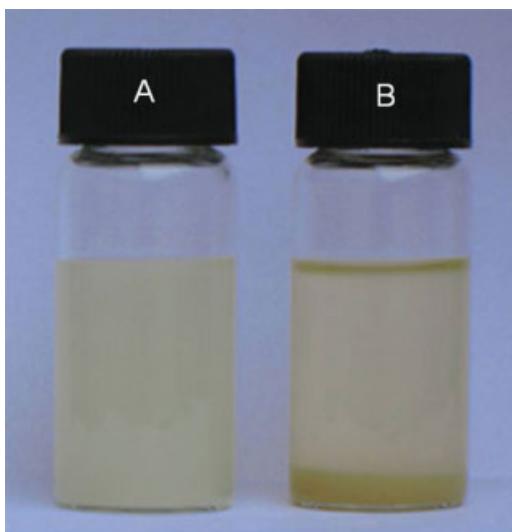


Figure 8 Photographs recorded from poly(styrene-*co*-acrylonitrile)-clay complexes (A) before and (B) after the thermal treatment at 250°C under N₂ for 3 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

structures because of the cyclization process of repetitive acrylonitrile units promoted by the thermolysis process.^{38,39} A scheme for this side-group cyclization reaction is proposed in Figure 6. Recently, this polyimine/enamine has attracted much interest as a novel vesicle for applications in NO release.²⁵ The difference between poly(styrene-*co*-acrylonitrile) and its clay complexes is that, for poly(styrene-*co*-acrylonitrile)-clay complexes, the polymers are intercalated in the silicate layers. To know whether the polyimine/enamine could also be formed after the thermal treatment of the poly(styrene-*co*-acrylonitrile)-clay complex, IR spectra were obtained from the samples before and after they were heated at 250°C under nitrogen for 3 h.

The IR spectra of Figure 7 show a significant reduction of the CN band at 2240 cm⁻¹, whereas the band at 1614 cm⁻¹ has increased, and two new bands at 1391 and 1270 cm⁻¹ are present. These observations are typical for the formation of a polyimine/enamine structure in the thermal treatment process, as previously reported.³⁸ Therefore, a novel polyimine/enamine clay complex has been obtained.

Dispersion testing of the thermally treated poly(styrene-*co*-acrylonitrile)-clay complexes

There is a great difference in the solubility in DMF between poly(styrene-*co*-acrylonitrile) and its corresponding polyimine/enamine, as previously reported.³⁹ Therefore, we performed dispersion testing in DMF for the poly(styrene-*co*-acrylonitrile)-clay complexes before and after the thermal treatment. The observations were recorded with photographs

and are shown in Figure 8. It is obvious that the thermally treated sample (B) precipitated, whereas the poly(styrene-*co*-acrylonitrile)-clay complex (A) dispersed well in DMF as expected. This also supports the conclusion of the previous section.

CONCLUSIONS

These novel poly(styrene-*co*-acrylonitrile)-clay complexes could offer an advantage in thermal stability in comparison with conventional long-chain alkyl ammonium modified clays. XRD and TEM studies have shown a great enlargement of the *d*-spacing of the clay layers due to the insertion of polymers. The aforementioned high thermal stability and large *d*-spacing demonstrate the promise of this novel series of polymer-modified clays as nanofillers in the preparation of polymer nanocomposites, especially when a high melt-blending temperature and compatibility are required. Furthermore, IR and dispersion tests in DMF have indicated that novel polyimine/enamine clay complexes can be obtained through the thermal treatment of poly(styrene-*co*-acrylonitrile)-clay complexes, and these could be promising NO release vesicles, although an application study needs to be done.

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