

Synthesis and Characterization of Novel Swelling Tunable Oligomeric Poly(styrene-co-acrylamide) Modified Clays

Ruyi Chen, Fubing Peng, Shengpei Su

College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Received 13 October 2007; accepted 7 December 2007

DOI 10.1002/app.27860

Published online 21 February 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The oligomeric poly(styrene-acrylamide-vinylbenzylchloride) (P(St-AM-VBC)) quaternary ammonium salts have been prepared from the reactions of trimethylamine with the corresponding P(St-AM-VBC)s, which were synthesized by free-radical polymerization of a mixture of styrene, acrylamide, and vinylbenzylchloride. Then the swelling tunable oligomeric poly(styrene-co-acrylamide) modified clays have been prepared through cation exchange of the sodium ions in the clay with the corresponding P(St-AM-VBC) quaternary ammonium salts. The P(St-AM-VBC) and its modified clays have been characterized by infrared spectra (IR), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), proton nuclear magnetic resonance (^1H NMR), X-

ray diffraction (XRD), and transmission electron microscopy (TEM). The solvent-swelling capacity of poly(styrene-co-acrylamide) modified clays have also been tested, and the experimental results have indicated that these clays are novel swelling tunable organic clays. XRD and TEM studies have shown that these novel swelling tunable clays are well-intercalated or exfoliated. Furthermore, TGA analysis shows that these polymerically modified clays have high thermal stability for nanocomposites by melt blending. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2712–2717, 2008

Key words: swelling tunable; poly(styrene-acrylamide-vinylbenzylchloride); quaternary ammonium salt; clay

INTRODUCTION

Polymerically modified clays are among the most promising organically modified clays because of their easily tuned surface properties using a variety of functional polymers. They have been widely used in many industrial fields, e.g., as catalysts,^{1,2} adsorbents,^{3–5} and fillers in preparing polymer-clay nanocomposites,^{6–11} etc. In general, polymerically modified clays could be obtained from absorption of organics, surface chemical grafting,^{12–14} or ion exchange with surfactants.^{5,15,16} The properties of these polymerically modified clays are affected by the polymers used as well as the preparation methods, and in most cases their applications are limited by their properties. For the polymerically modified clays prepared by physical absorption, their application fields are limited because of the weak force between polymer and clay surface. The method adapting the high-cost chemical grafting process to prepare the

polymerically modified clays is most often appeared in the scientific research. Ion exchange of the sodium ions in the gallery of the clays with the polymeric quaternary ammonium ions is a most favorable method used in industries because of its lower cost.^{8,17}

Polyacrylamide is a specialty polymer,^{18–22} and widely used as a matrix in gel electrophoresis,^{23,24} a flocculator in water treatment,²⁵ a soil-conditioning agent to improve soil texture,²⁶ a vesicle in drug delivery,²⁷ a phase in extraction,^{28,29} a carrier for enzyme-activity, etc.³⁰ Recently, polyacrylamide clay nanocomposites have attracted some interests from researchers to reinforce virgin polymer's mechanical properties³¹ and swelling properties.¹⁶ But most of the researches are focused on the *in situ* polymerization of acrylamide in clays.

In this study, oligomeric poly(styrene-co-acrylamide) modified clays have been prepared through cation exchange of the sodium ions in the clay with the P(styrene-co-acrylamide) quaternary ammonium salts. One of the objectives of this study, is to find the relationships between the swelling property of these modified clays and the compositions of the polymers used; the other objective is to investigate the thermal stability of these modified clays for the applications in nanocomposites by melting process.

Correspondence to: S. Su (sushengpei@gmail.com).

Contract grant sponsor: Xiaoxiang Scholar Foundation, Hunan Normal University; contract grant number: Chem 050613.

EXPERIMENTAL

Materials

Pristine sodium montmorillonite (Na-MMT) (CEC) = 90 mequiv/100 g) was kindly provided by Zhejiang Fenghong Clay Chemicals (Zhejiang, China). Acrylamide, styrene, vinylbenzylchloride, dimethylformamide (DMF), 30% trimethylamine aqueous solution, and *N, N'*-azobis (isobutyronitrile) (AIBN) were purchased from Shanghai Shanpu Chemical Reagent (Shanghai, China) and used without further purification. Tetrahydrofuran (THF) was purchased from Yueyang Chemical (Yueyang, China) and distilled before using.

Preparation of oligomeric P(St-AM-VBC) modified clay

The P(St-AM-VBC) quaternary ammonium salts were prepared from the reactions of trimethylamine with the corresponding P(St-AM-VBC)s, which were synthesized by free-radical copolymerization of styrene, acrylamide, and vinylbenzylchloride. The scheme for preparing P(St-AM-VBC) quaternary ammonium salts is shown in Figure 1.

Synthesis of P(St-AM-VBC)

A 500-mL three-neck round flask equipped with a condenser, a stirrer, and a thermometer were charged with 87.5 g (841 mmol) of styrene, 10.8 g (152 mmol) of acrylamide, 5.2 g (33 mmol) of vinylbenzylchloride, 5.2 g (31.5 mmol) of AIBN as initiator, and 100 mL of THF as solvent. The temperature was raised to 80°C and kept 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, then redissolved and reprecipitated for three times. The solvent was evaporated and 84 g of a white solid polymer was remained with a yield of 84%. ¹H NMR (CDCl₃): δ 7.4–6.3 (br, 54H), 4.5 (br, 2H), 2.3–0.8 (br, 43H).

Other P(St-AM-VBC)s with different amounts of acrylamide unit from the above polymer could be achieved by control of the mole ratio of styrene to acrylamide, whereas the total moles of these two monomers in the reaction system were kept unchanged.

Synthesis of P(St-AM-VBC) quaternary ammonium salts

A 1000-mL three-neck round flask equipped with a condenser, a stirrer, and a thermometer were charged with 80 g of P(St-AM-VBC) from the example in "Synthesis of P(St-AM-VBC)" section and 300 mL of THF as solvent. The mixture was stirred and all the components were completely dissolved at 40°C, then 10.1 g (49.5 mmol) (an excess amount) of 30% trimethylamine aqueous solution was added into the system dropwise. This reaction was kept overnight. Then the solvent was evaporated under vacuum and a pale yellow solid was remained. ¹H NMR (CDCl₃): δ 7.4–6.3 (br, 54H), 3.2 (br, 5H), 2.0–0.8 (br, 40H).

Preparation of the organically modified clays

A suspension of 36 g of pristine sodium clay in 900 mL of distilled water was stirred overnight at room temperature. Then, 1800 mL of THF was added dropwise and stirring was continued for 2 h. To this stirred clay suspension, a solution of 100 g of P(St-AM-VBC) quaternary ammonium salt obtained from the example in "Synthesis of P(St-AM-VBC) quaternary ammonium salts" section 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 for three times, then washed with 200 mL of 70/30 THF/water (v/v) twice, and washed with water again until no chloride ion could be detected by an acidic aqueous AgNO₃ solution. It was then dried under vacuum overnight at 90°C.

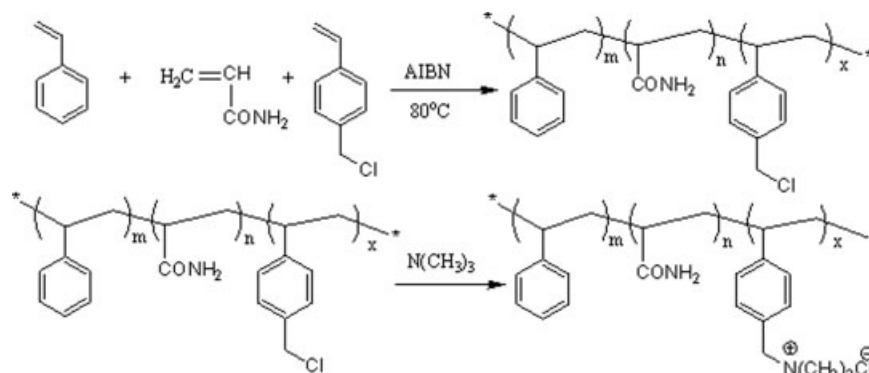


Figure 1 Scheme for the preparation of P(St-AM-VBC) quaternary ammonium salts.

TABLE I
GPC Analysis Data of P(St-AM-VBC) with Different Acrylamide Contents

No.	St (g)	VBC (g)	AM (g)	The contents of AM (%)	AIBN (g)	Yield (%)	M_w	M_n	MWD
1 ^a	88.06	5.18	5.18	5	5.18	85	8,400	5,559	1.51
2 ^a	82.88	5.18	10.36	10	5.18	88	9,181	5,692	1.61
3 ^a	72.52	5.18	20.72	20	5.18	84	10,618	6,913	1.54
4 ^b	51.80	5.18	41.44	40	5.18	84	10,938	6,752	1.62
5 ^b	31.08	5.18	62.16	60	5.18	83	9,785	5,939	1.64
6 ^b	0	5.18	93.24	100	5.18	75	7,236	3,808	1.90

^a Using THF as eluting solvent.

^b Using DMF as eluting solvent.

Instrumentation

The molecular weight and molecular weight distribution (MWD) of all oligomers were obtained using GPC. Analyses were performed on an Alltech instrument (Alltech) using THF as the solvent eluting at a flow of 1 mL/min through a Jordi GPC 10,000 A column (300 mm × 7.8 mm) equipped with an Alltech ELSD 800 detector. This system was calibrated with standard polystyrenes. IR studies were carried out on a WQF-200 instrument (Rayleigh, China) using conventional KBr pellets. A mixture of 1 mg of sample powder with 100 mg of dried KBr crystals was pressed into a pellet of 13-mm diameter. ¹H NMR spectra were collected using a Varian INOVA-300FT-NMR spectrometer (Varian) operating at 400 MHz using CDCl₃ as solvent. TGA scans were made from 30 to 600°C using a Netzsch STA409PC instrument (Netzsch, Germany) under a flowing nitrogen atmosphere at a scan rate of 10°C/min. All TGA results are the average of a minimum of three determinations; temperature is reproducible to ±3°C, while the error bars on the nonvolatile material is ±3%. XRD patterns were collected from 1.1° to 10° and a scan time

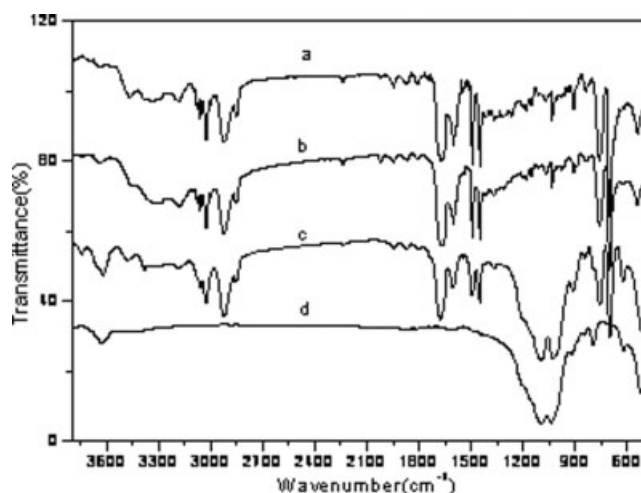


Figure 2 IR spectra obtained from (a) P(St-AM-VBC), (b) P(St-AM-VBC) quaternary ammonium salt, (c) P(St-AM-VBC) quaternary ammonium salt modified clay, and (d) pure clay.

of 10 s/step using a Bruker D8 instrument (Bruker, Germany) with a step size of 0.1°. Cu K α X-ray radiation and a random powder mount were used. TEM images were obtained from a JEOL-1230 instrument (Jeol, Japan) under an accelerating voltage of 100 kV. To coat the clays on Cu-grids, a suspension of the organically modified montmorillonite sample in chloroform was mixed with a formvar/chloroform solution. A drop of this above mixture was placed on the top of the grid, and after dried in the air, the sample for TEM was obtained. The solvent-swelling properties of the modified clays were characterized using the method described in literature.³²

RESULTS AND DISCUSSION

The molecular weight and molecular weight distribution

The molecular weight and molecular weight distribution have been measured by GPC. The GPC analysis data are shown in Table I. The results have indicated

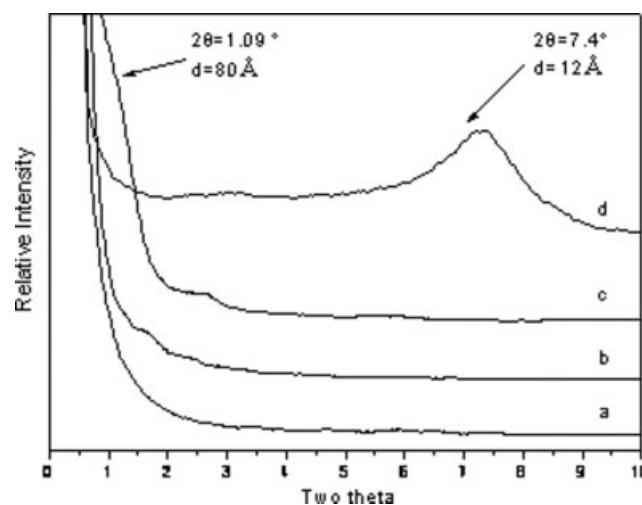


Figure 3 X-ray diffraction traces in reflection mode obtained from clays modified with P(St-AM-VBC) quaternary ammonium salt with different acrylamide contents: (a) P(St-AM5-VBC), (b) P(St-AM10-VBC), (c) P(St-AM20-VBC), and (d) pure clay.

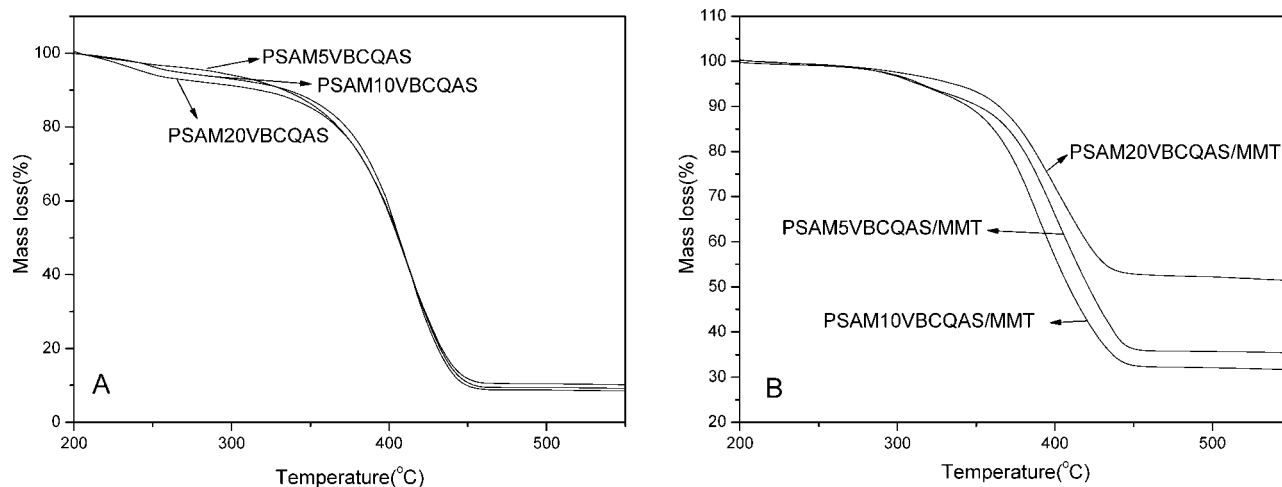


Figure 4 TGA traces obtained from (A) P(St-AM-VBC) quaternary ammonium salts and (B) P(St-AM-VBC) modified clay. Note: The numbers in the sample names are the percent contents of acrylamide units in the polymers.

that the molecular weight and molecular weight distribution could be tuned by adjusting the molar ratio of initiator to monomers. Typical M_w is about 9000, and MWD is about 1.5.

FTIR spectrum

FTIR spectra of P(St-AM-VBC), P(St-AM-VBC) quaternary ammonium salt, P(St-AM-VBC) modified clay, and pure clay are shown in Figure 2. The changes in the structure of the organoclay will be observed through changes in the infrared spectra. Figure 2 (curve a) describes the aromatic C—H stretching region ($3103\text{--}3000\text{ cm}^{-1}$), aliphatic C—H stretching region ($2993\text{--}2800\text{ cm}^{-1}$), NH_2 stretching region ($3467, 3300, \text{ and } 3175\text{ cm}^{-1}$), C=O stretching

(1668 cm^{-1}), NH_2 bending (1620 cm^{-1}), and $\text{CH}_2\text{—Cl}$ wagging band (1264 cm^{-1}) in the FTIR spectra of P(St-AM-VBC) copolymer. The disappearance of band at 1264 cm^{-1} in Figure 2 (curve b) indicates the rupture of $\text{CH}_2\text{—Cl}$ bond, and it is confirmed that P(St-AM-VBC) quaternary ammonium salt has been obtained. The position of the band, related to the $\nu(\text{OH})$ stretching vibration (3627 cm^{-1}), $\nu(\text{Si—O})$ stretching vibration (1043 cm^{-1}), and $\nu_s(\text{Si—O—Si})$ bending vibration ($620\text{--}513\text{ cm}^{-1}$) of pristine MMT is shown in Figure 2 (curve d). As shown in Figure 2 (curve c), the FTIR spectrum displays the characteristic absorbance bands of P(St-AM-VBC) quaternary ammonium and pure MMT. This indicated a novel P(St-AM-VBC) quaternary ammonium-modified MMT was obtained.

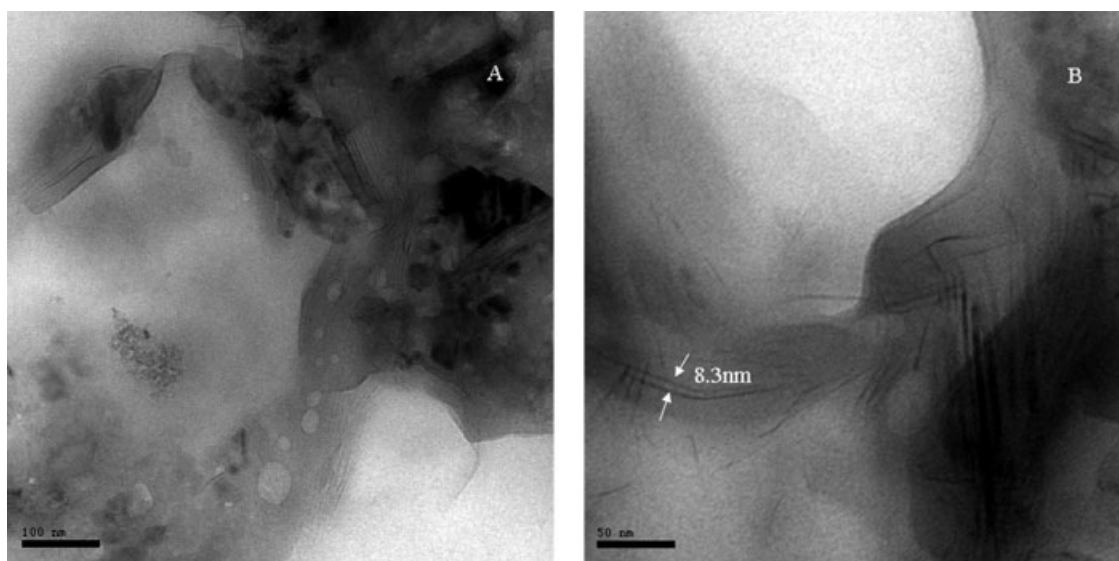


Figure 5 TEM images of the typical P(St-AM-VBC) modified clay.

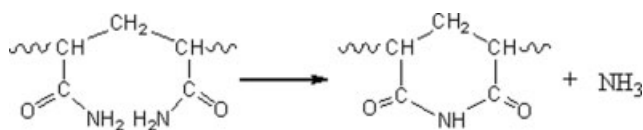


Figure 6 The equation of amine group cyclization.

XRD and TEM results

XRD traces of the polymerically modified clays are shown in Figure 3. The pure clay shows an apparent peak at $2\theta = 7.4^\circ$, which is corresponding to a basal spacing of 1.2 nm, while the P(St-AM10-VBC/MMT) [Fig. 3 (curve b)] and P(St-AM20-VBC/MMT) [Fig. 3 (curve c)] show a weak broad peak at $2\theta = 1.09^\circ$, corresponding to a basal spacing of 8.0 nm. The XRD trace obtained from P(St-AM5-VBC/MMT) [Fig. 3 (curve a)] does not show a characteristic basal structure, and indicates that the silicate layers of clay in P(St-AM5-VBC) are disordered or exfoliated. To confirm these deduced structures from XRD results, TEM has been performed on the clay samples. Figure 5 shows the TEM images of typically modified clay. The images of the sample show a well-intercalated structure for the modified clay. And the d -spacing is around 8.3 nm. This result is consistent with that obtained from XRD analysis. It is well-known that this great enlargement of d -spacing between the clay layers makes these novel clays possible for the preparation of exfoliated nanocomposites.

TGA characterization

TGA traces obtained from P(St-AM-VBC) quaternary ammonium salts and their modified clays are shown in Figure 4. It is obvious that there are two steps in the thermal degradation of these quaternary ammoniums [Fig. 4(A)]. The initial degradation temperature of the first step is above 205°C , and it is related to the content of acrylamide unit in the copolymers. The more the content of acrylamide unit in the copolymer is, the lower is the initial degradation temperature. As reported, this initial degradation is

TABLE II
Characteristic Temperature Obtained by the TG Analysis for the P(St-AM-VBC) QAS and P(St-AM-VBC) QAS/MMT Degradation

Mass loss	P(St-AM-VBC) QAS with different contents of AM (%)			P(St-AM-VBC) QAS/MMT with different contents of AM (%)		
	5	10	20	5	10	20
5%	231	247	230	258	276	310
10%	312	319	288	319	330	353
50%	403	404	404	390	394	387

caused by a side-group cyclization reaction.³³ A scheme for this side-group cyclization reaction is proposed in Figure 6.

The TGA data for both P(St-AM-VBC) quaternary ammonium salts and their corresponding modified clays are shown in Table II. It has shown that the ammonium salt has a better thermal stability when the acrylamide content is 10% in the polymer, and the modified clay has highest thermal stability when there was 20% of the acrylamide unit in the polymer. The typical 10% weight loss degradation temperature of these novel polymer quaternary ammonium salts is 50°C higher when compared with the long-chain alkyl group quaternary salts as reported.^{34,35} This advantage offers these polymer-modified clays possibility for the application in preparation of nanocomposites where high-melting blend temperature is required.

The swelling ability of different solvents on the polymer-modified clays

Solvent-swelling ability of clays modified by P(St-AM-VBC) quaternary ammonium salts containing different amount of acrylamide unit was tested in solvent such as water, methanol, THF, and chloroform. The experimental data in Figure 7 indicate that the swelling ability of these novel polymer modified clays is related to the polarity of the solvent and the composition of the polymers used. Water has the lowest swelling ability when the content of acrylamide units is less, while this is sharply improved as the content of acrylamide unit increased because of the hydrogen bonding between water and amide group. The swelling behavior of chloroform is greatly different from that of water; it has shown a

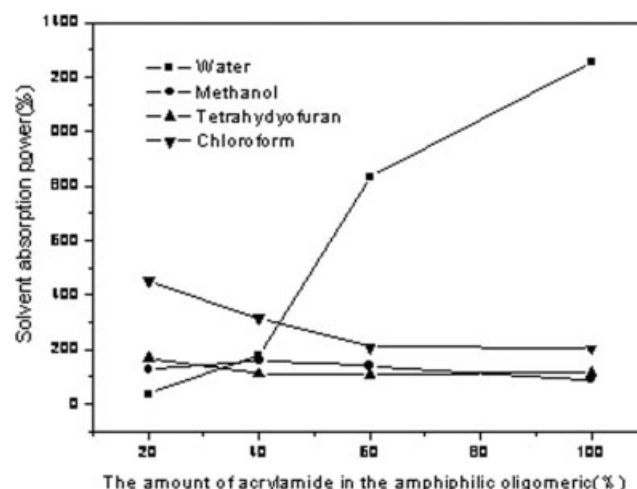


Figure 7 The relationships between the solvent-swelling ability and the amount of acrylamide units in P(St-AM-VBC) quaternary ammonium salts in the clay.

higher swelling ability when there are more styrene units and a lower swelling ability for more acrylamide units in the polymeric quaternary ammonium. The swelling ability of methanol and THF is not so sensitive to the content change of styrene and acrylamide units in the polymer modified clays. So, till now, a conclusion could be made that the solvent-swelling behavior of this series of poly(styrene-*co*-acrylamide) modified clays could be tuned through adjusting styrene or acrylamide unit in poly(styrene-*co*-acrylamide) for water and chloroform.

CONCLUSIONS

These novel polymer-modified clays could offer an advantage in thermal stability when compared with conventional long-chain alkyl ammonium salt modified clays. The remarkably improved thermal stability is confirmed by TGA. The solvent-swelling ability of these novel polymer-modified clays could be tuned through adjusting the ratio of styrene to acrylamide unit in the polymer. The aforementioned high thermal stability and adjustable swelling ability have offered this novel series of polymer-modified clays as promising nanofillers in the preparation of polymer nanocomposites, especially where the high-melt blending temperature and compatibility are required.

The authors appreciate Zhejiang Fenghong Clay Chemicals Co. Ltd. for clay products, adjunct professor Chen, College of Life Sciences, Hunan Normal University, for obtaining the TEM images, and Dr. Cao, College of Chemistry and Chemical Engineering, Hunan University, for obtaining the digital X-ray diffraction patterns.

References

1. Pinnvaia, J. J. *Science* 1983, 220, 365.
2. Noyan, H.; Onal, M.; Sarikaya, Y. *Clays Clay Miner* 2006, 54, 375.
3. Maes, N.; Heylen, I.; Cool, P.; De Bock, M.; Vanhoof, C.; Vansant, E. F. *J Porous Mater* 2005, 3, 47.
4. Mortland, M. M.; Sun, S. B.; Boyd, S. A. *Clays Clay Miner* 1986, 34, 581.
5. Erim, F. B.; Alemdar, I.; Fresenius, J. *Anal Chem* 1998, 361, 455.
6. Ahmadi, S. J.; Huang, Y. D.; Li, W. *J Mater Sci* 2004, 39, 1919.
7. Xie, W.; Hwu, J. M.; George, J. J.; Buthelezi, T. M.; Pan, W. P. *Polym Eng Sci* 2004, 43, 214.
8. Su, S. P.; Jiang, D. D.; Wilkie, C. A. *Polym Adv Technol* 2004, 15, 225.
9. Su, S. P.; Jiang, D. D.; Wilkie, C. A. *Polym Degrad Stab* 2004, 83, 321.
10. Su, S. P.; Jiang, D. D.; Wilkie, C. A. *Polym Degrad Stab* 2004, 83, 333.
11. Su, S. P.; Jiang, D. D.; Wilkie, C. A. *J Vinyl Addit Technol* 2004, 10, 44.
12. Piletsky, S. A.; Piletska, E. V.; Chen, B. N.; Karim, K.; Weston, D.; Barrett, G.; Lowe, P.; Turner, A. P. *F. Anal Chem* 2000, 72, 4381.
13. Anbarasan, R.; Vasudevan, T.; Gopalan, A. *Eur Polym J* 2000, 36, 1725.
14. Tsubokawa, N. *Prog Polym Sci (UK)* 1992, 17, 417.
15. Rheinlander, T.; Klumpp, E.; Schwuger, M. J. *J Dispersion Sci Technol* 1998, 19, 379.
16. Xu, S. H.; Boyd, S. A. *Langmuir* 1995, 11, 2508.
17. Su, S. P.; Wilkie, C. A. *Polym Degrad Stab* 2004, 83, 347.
18. Chu, Y. H.; Chen, J. K.; Whitesides, G. M. *Anal Chem* 1993, 65, 1314.
19. Jackson, P. *Biochem J* 1990, 270, 705.
20. Okuzawa, K.; Franzén, D. B.; Lindholm, J.; Linder, S.; Hirano, T.; Bergman, T.; Ebihara, Y.; Kato, H.; Auer, G. *Electrophoresis* 1993, 15, 382.
21. Ghannam, M. T. *J Chem Eng Data* 2002, 47, 274.
22. Xia Y. Q.; Guo T. Y.; Song, M. D.; Zhang, B. H.; Zhang, B. L. *Biomacromolecules* 2005, 6, 2601.
23. Huang, G.; Zhang, Y.; Yang, J.; Baeyens, R. G. *Anal Chim Acta* 2006, 577, 137.
24. Nováková, Z.; Man, P.; Novák, P.; Hozák, P.; Hodný, Z. *Electrophoresis* 2006, 27, 1277.
25. Bhasakar, S. G.; Ako, J. E. *Eur Food Res Technol* 2005, 221, 746.
26. Youssef, N. N. U.S. Pat. 4,762,545 (1988).
27. Ranquin, A.; Versees, W.; Meier, W.; Steyaert, J.; Van Gelder, P. *Nano Lett* 2005, 5, 2220.
28. Li, K. M.; Rivory, L. P.; Clarke, S. J. *Curr Pharm Anal* 2006, 2, 95.
29. Chen, W. Z.; Shen, J.; Yin, X. F.; Yu, Y. N. *Mass Spectrom* 2007, 21, 35.
30. Bajpai, A. K.; Bhanu, S. *Colloid Polym Sci* 2004, 282, 76.
31. Somasundaran, P.; Chakraborty, S.; Qiang, Q.; Deo, P.; Wang, J.; Zhang, R. *Int J Cosmet Sci* 2004, 27, 135.
32. Zhang, J. P.; Liu, R. F.; Li, A.; Wang, A. Q. *Polym Mater Sci Eng* 2005, 21, 169.
33. Maria Elisa, S. R. E. S.; Eider, R. D.; Valdir, M.; Machado, J. C. *Polym Degrad Stab* 2000, 67, 491.
34. Xie, W.; Gao, Z. M.; Liu, K. L.; Pan, W. P.; Vaia, R.; Hunter, D. *Thermochim Acta* 2001, 367, 339.
35. Xie, W.; Gao, Z. M.; Pan, W. P.; Hunter, D. *Chem Mater* 2001, 13, 2979.