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Synthesis, characterization and thermal stability of different polystyryl quaternary ammonium surfactants and their montmorillonite complexes

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ABSTRACT

Three polystyryl quaternary ammonium salts have been synthesized from the reactions of trimethylamine with chloromethyl polystyrenes which were prepared by three different methods: free-radical co-polymerization, chloromethylation of polystyrene and anionic polymerization. Then the polystyryl-modified montmorillonites have been obtained from the ion exchange of sodium ions in the montmorillonites with polystyryl quaternary ammonium salts. The polystyryl quaternary ammonium salts have been characterized using proton nuclear magnetic resonance spectrometer (^{1}H NMR), Fourier-transformed infrared spectrometer (FT-IR), and gel permeation chromatography (GPC). The thermal stability of the quaternary ammonium salts and their corresponding modified montmorillonites have been studied by thermo gravimetric analysis (TGA). TGA data have shown that the polystyryl ammonium salt and its modified montmorillonites obtained from the reactions of chloromethyl polystyrene which was prepared by anionic polymerization are the most stable ones respectively. X-ray diffraction (XRD) and transmission electronic microspectroscopy (TEM) analysis of these polystyryl-modified clays have shown that they are of intercalated structures or partial exfoliation with stacked clay layers.

1. Introduction

Polymer layered silicate nanocomposites have attracted much interest over two decades as a result of the potentially enhanced properties compared to their virgin polymers. Now, it is no doubt that a very low percentage of layered montmorillonites could lead to a significant enhancement of many properties of the polymers, such as stiffness and strength [1,2], flame retardancy [3,4], gas barrier properties [5,6], solvent resistance [7], modulus [7,8], permeability [9] and thermal stability [9,10].

Generally, the preparation of clay nanocomposites could be achieved using melt blending [11–13], solution blending [14,15], in situ polymerization [16,17] and mechano-chemical processing [18]. In most cases, the montmorillonites have to be organically modified to be compatible with polymer matrix and to be exfoliated in the processing to achieve the full enhancements [19]. Now it is well known that the exfoliation process and compatibility of the montmorillonites with virgin polymer are strongly affected by the thermal stability, polarity and reactivity of the organically modified montmorillonites. But most of the work that have been carried out to modify montmorillonites is using cationic surfactants such as alkyl ammonium [20] or alkylphosphonium [21,22], which contain at least one long alkyl chain. These modified montmorillonites have disadvantages, such as low thermal stability or incompatibility [23]. Recently a new series of oligomeric polystyryl-modified montmorillonites have gathered attention from a lot of researchers for their outstanding thermal stability especially for preparation of high melting polymers clay nanocomposites [24–28]. Wilkie et al. have also studied a series of polymerically modified clays and the affection of different ammonium groups on the stability of polystyryl surfactants and their modified clays [29]. Their study has shown that the thermal stability of the polystyryl surfactants and their modified clays are strongly dependent on the pendent groups. But there is no report of the affection on the thermal stability from the main chain of polystyryl surfactants prepared by different methods.

It is recognized that the preparation methods play a very important role in the degradation behavior of polymers. In this paper, three methods will be selected to prepare polystyryl quaternary ammonium salts (PQAS) which will be applied in the modification of montmorillonites. The thermal stability of these polystyryl surfactants and their modified clays will be evaluated.

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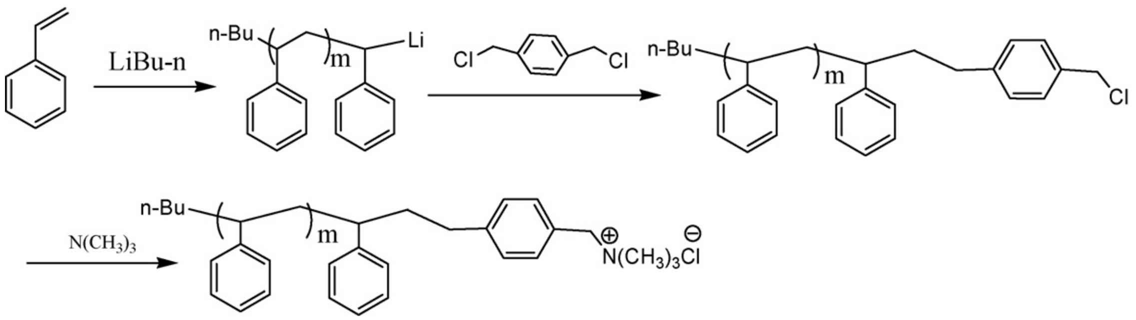

Fig. 1. Scheme for the preparation of AP-PSQAS.

2. Experiments

2.1. Materials

The majority of chemicals used in this study, including styrene, butyl lithium (*n*-BuLi), trimethyl amine, benzyl peroxide (BPO), zinc chloride, cetyltrimethylammonium bromide (CTMAB), cyclohexane and tetrahydrofuran (THF) were acquired from Baling Petrochem Co., Ltd. *p*-Dichloromethyl benzene and *p*-chloromethyl styrene were purchased from Shandong Kaima Industry and Trade Co., Ltd., while pristine sodium montmorillonite (Na-MMT) (CEC = 92 mmol/100 g) was purchased from Southern Clay Products, Inc. Monochlorodimethyl ether was prepared in this lab according to the reported method [30].

2.2. Instrumentation

The molecular weight and molecular weight distribution (MWD) of all oligomers were obtained by GPC. Analyses were performed on an Alltech Instrument (Alltech, America) using THF as the solvent eluting at a flow of 1 mL/min through a Jordi GPC 10000 A column (300 mm × 7.8 mm) equipped with an Alltech ELSD 800 detector and the 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 with 100 mg of dried KBr crystals was ground and pressed into a pellet of 13 mm in diameter. ^{1}H NMR spectra were collected using a Varian INOVA-300FT-NMR spectrometer (Varian, America) operating at 400 MHz using $CDCl_3$ as solvent. TGA was performed on a Netzsch STA409PC instrument (Netzsch, Germany) under a flowing nitrogen atmosphere from 30 to 600 °C at a scan rate of 10 °C/min. All TGA results are the average of a minimum of three determinations; temperatures are reproducible to ±3 °C, while the error bars on the nonvolatile material is ±3%. XRD was performed on a Bruker D8 instrument (Bruker, Germany); scans were taken from 2θ 1.1–10°, step size 0.1° and scan time per step of 10 s; Cu Kα X-ray radiation and a random powder mount were used. In this experiment, a razor blade was used to press the sample tight and shear the surface to obtain a good XRD. 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 diluted suspension was placed on the top of the grid, after dried in the air; the sample for TEM was obtained.

2.3. Preparation of polystyryl quaternary ammonium salts by anionic polymerization (AP-PSQAS)

Cyclohexane and THF were purified by distillation over sodium.

A four-necked flask equipped with a thermometer, a condenser and a stirrer was purged with N_2, and then cyclohexane (700 mL, 6.80 mol) and styrene (60 mL, 0.52 mol) were added under N_2 atmosphere with stirring. After cooling down to −5 °C, a little *n*-BuLi was added to remove impurities in the system, and then a stoichiometric amount of *n*-BuLi (60 mL, 0.24 mol) as initiator was added to the flask using syringe. During the course of the reaction, the color of the reaction mixture turned to red. Once the addition of *n*-BuLi was finished, the temperature of the mixture was raised to 40 °C in 30 min, and then kept at this temperature for another 1 h. After this reaction was completed, the red reaction mixture was then transferred into a solution of *p*-dichloromethyl benzene at room temperature under N_2. Once the red color in the flask with *p*-dichloromethyl benzene was disappeared, the reaction was stopped. The crude product (polystyryl benzyl chloride) was obtained by vacuum evaporation, and then the crude was dissolved in 200 mL of THF and poured into 500 mL of violently stirred methanol. The precipitation was filtered and retreated several times by using a mixture solvent (THF/methanol = 200/500 (v/v)) until no dichloromethylbenzene was detected by HPLC. This purified polystyryl benzyl chloride was dissolved in 500 mL of THF with stirring, and then introduced into an excessive trimethylamine aqueous solution, stirring for 24 h at room temperature. After the solvent was removed, the remaining solid was dried under vacuum at 70 °C, and 51 g of a pale yellow solid (polystyryl quaternary ammonium salts) was obtained (88%) (Fig. 1). ^{1}H NMR: polystyryl

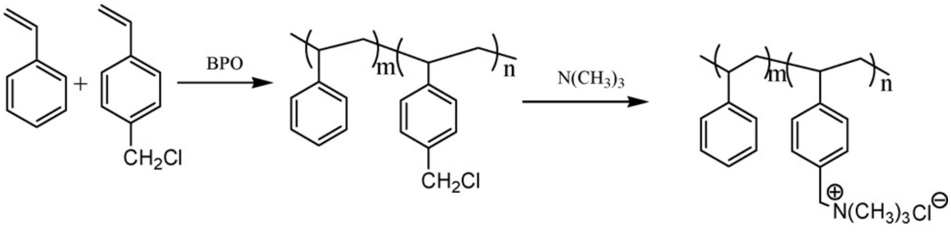

Fig. 2. Scheme for the preparation of CP-PSQAS.

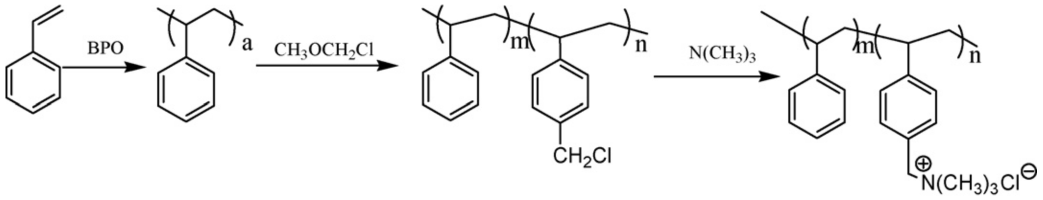

Fig. 3. Scheme for the preparation of CM-PSQAS.

benzyl chloride (PSBC): ^{1}H NMR (CDCl$_3$, δ): 7.9–6.5 (br, m, 115H), 4.6 (br, 2H), 3.0–0.8 (br, 80H). Polystyryl quaternary ammonium salts (PSQAS): ^{1}H NMR (CDCl$_3$, δ): 7.9–6.3 (br, m, 115H), 4.5 (br, 2 H), 3.5–3.1 (br, 9H), 5–1.0 (br, 80H).

2.4. Preparation of polystyryl quaternary ammonium salts by free radical co-polymerization (CP-PSQAS)

In a 500-mL three-necked flask equipped with a thermometer, a condenser and a stirrer, 50 g of styrene (0.48 mol), 7.2 g of *p*-chloromethyl styrene (0.047 mol), and 12.3 g of BPO (0.05 mol) were added and stirred. Once a transparent solution was formed, the temperature of this reaction mixture was raised to 80 °C. After the solution became viscid, the reaction was stopped and the mixture was dissolved in 200 mL of THF, and then poured into 400 mL of methanol. The precipitate was filtered and dried under vacuum at 80 °C for 24 h. 48 g of a white solid was obtained (92%). After this above solid was dissolved in 200 mL of THF, then 20 mL of 30% trimethylamine was added at room temperature, and the reaction was kept for 24 h. Then the reaction was stopped and the solvent was removed by distillation, and 47 g of the residue (CP-TMPAC) was obtained after dried under vacuum at 80 °C for 24 h (91%) (Fig. 2). Polystyryl benzyl chloride by free radical co-polymerization: ^{1}H NMR (CDCl$_3$, δ): 7.9–6.3 (br, m, 82 H), 4.5 (br, 2H), 2.5–1.0 (br, 55H). Polystyryl quaternary ammonium salts: ^{1}H NMR (CDCl$_3$, δ): 7.9–6.3 (br, m, 82H), 4.5 (br, 2H), 3.5–3.1 (br, 9H), 2.5–1.0 (br, 55H).

2.5. Preparation of polystyryl quaternary ammonium salts by chloromethylation (CM-PSQAS)

In a 250-mL round-bottom flask equipped with a mechanical stirrer and a cold water condenser, were placed 80 g of styrene (0.77 mol), 100 mL of THF, and 4 g of BPO (0.017 mol). This mixture was stirred until a transparent, homogeneous solution formed at room temperature, and then the flask was immersed in a water bath at 80 °C. After the reaction was maintained at 80 °C for another 2 h, this mixture was then cooled and poured into 500 mL of violently stirred methanol. The precipitate was filtered and dried in a vacuum oven. 75 g of polystyrene was obtained (Fig. 3). ^{1}H NMR (CDCl$_3$, δ): 7.5–6.3 (br, m, 394H), 4.5 (br, 18H), 2.5–1.0 (br, 260H).

In a 250-mL round-bottom flask equipped with a mechanical stirrer and a cold water condenser, were placed 50 g of PS made above and 50 mL of THF. After the PS was completely dissolved and a transparent solution was formed, 25 mL of monochlorodimethyl ether and 5 g of zinc chloride (0.036 mol) were added. Then the temperature was raised to 38 °C and maintained for another 0.5 h. This mixture was then poured into 250 mL of stirred water. The precipitate was filtered and washed by methanol-water (50/50, v/v) solution for three times, then dried and transferred into a round-bottom flask with 100 mL of THF. A slight excess of trimethylamine was added and this mixture was stirred over night. After most of the solvent was removed by rotary evaporation, the residue was washed three times with water and dried. 41 g of polystyryl quaternary ammonium salts by chloromethylation (82%) was obtained. ^{1}H NMR (CDCl$_3$, δ): 7.6–6.3 (br, m, 394H), 4.5 (br, 18H), 3.5–3.1 (br, 81H), 2.5–1.0 (br, 260H).

2.6. Preparation of PSQAS and alkyl surfactant-modified MMTs

5 g of AP-PSQAS quaternary ammonium salt was dissolved in 30 mL of THF while 2 g of sodium montmorillonite was dispersed in 100 mL of distilled water over 24 h. Then 200 mL of THF was added to the montmorillonite suspension and this mixture was violently stirred for 2 h. To this montmorillonite suspension the solution of AP-PSQAS quaternary ammonium salt mentioned above was added dropwise. A voluminous white precipitate was observed and this ion exchange process was maintained overnight. Finally, the slurry was filtered and washed repeatedly with THF solution (water/THF = 100/200 (v/v)) three times until no chlorine ion could be detected by an acidic aqueous AgNO$_3$ solution. Then the resulting modified MMT was dried in a vacuum oven at 70 °C for 12 h. The AP-PSQAS-modified montmorillonite was obtained.

The CM-PSQAS, CP-PSQAS and CTMAB-modified montmorillonites were prepared by a procedure similar to the above one. The composition of ion exchange system is shown in Table 1. The mass ratio of quaternary ammonium salt to montmorillonite was calculated based on the amount of quaternary ammonium functional groups in the polymer which is determined by ^{1}H NMR and the CEC of the pristine sodium montmorillonite. In general, 20% of excess polystyryl quaternary ammonium salts was used to make sure that all the sodium ions in the montmorillonites could be exchanged. All polymerically modified clays were washed to make sure that there were no non-ionically bonded polystyryl quaternary ammonium salts, and the affect from the undesired degradation of ammonium salts was avoided [31].

Table 1
The composition of ion exchange system for the preparation of polystyryl-modified montmorillonites

	QAS (g)	Na-MMT (g)	THF (mL)	Water (mL)
AP-PSQAS	11.5	5	700	300
CP-PSQAS	8	5	500	400
CM-PSQAS	5	5	600	400
CMTAB	2.5	5	100	600

Note: QAS is quaternary ammonium salt.

Table 2
Molecular weight and molecular weight distribution of polystyryl quaternary ammonium salts

Material	M_n	M_w	M_w/M_n	Mass/charge	Polymerization method
AP-PSQAS	2500	2975	1.19	2500	Anionic polymerization
CP-PSQAS	1869	3027	1.62	1800	Free-radical polymerization
CM-PSQAS	9800	17150	1.75	1200	Free-radical polymerization

Note: Molecular weight and molecular weight distribution were obtained by GPC.

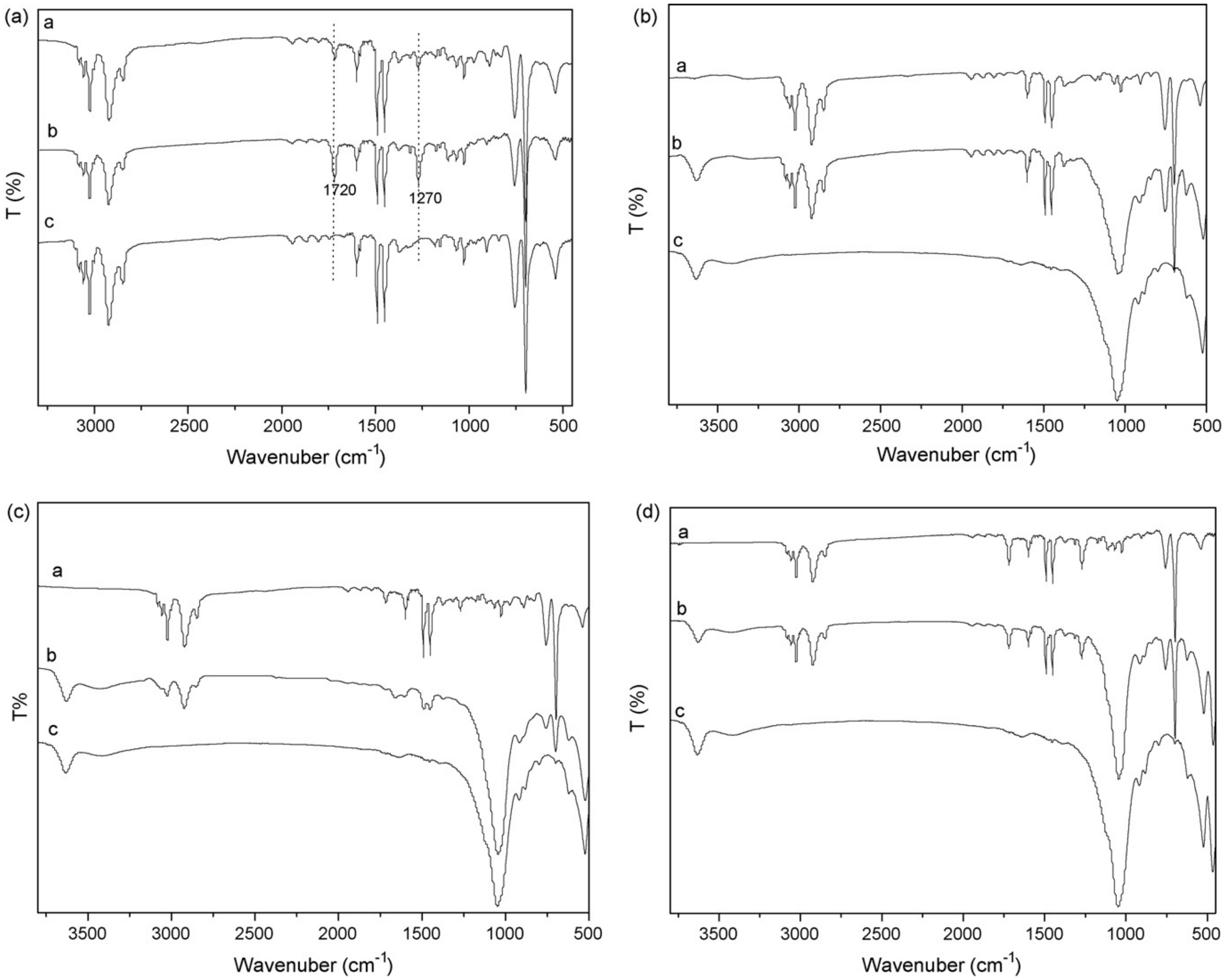

Fig. 4. (A) FT-IR spectra obtained from polystyryl quaternary ammonium salts: (a) CM-PSQAS; (b) CP-PSQAS; (c) AP-PSQAS. (B) FT-IR spectra obtained from AP-PSQAS and AP-PSQAS-modified MMT: (a) AP-PSQAS; (b) AP-PSQAS-modified MMT; (c) Na-MMT. (C) FT-IR spectra obtained from CM-PSQAS and CM-PSQAS-modified MMT: (a) CM-PSQAS; (b) CM-PSQAS-modified MMT; (c) Na-MMT. (D) FT-IR spectra obtained from CP-PSQAS and CP-PSQAS-modified MMT: (a) CP-PSQAS; (b) CP -PSQAS-modified MMT; (c) Na-MMT.

3. Results and discussion

3.1. Molecular weight and molecular weight distribution of quaternary ammonium salts

The size of polystyryl chain and the number of quaternary ammonium groups on it are two important factors to be considered in the preparation of polystyryl cationic surfactant-modified montmorillonites. In some extreme cases, such as a long chain with many cations, we may observe the blocking of the layers due to the ion exchange happened in different galleries [32]. To avoid the situation of a severe blocking, in this experiment, three polystyryl quaternary ammonium salts (AP-PSQAS, CP-PSQAS and CM-PSQAS) with short chain or few cations on per chain are prepared by different methods, and their sizes are tuned by the mole ratio of initiator to monomer in the preparation of the polystyrenes which are the main chains of polystyryl quaternary ammonium salts. The number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and polydispersity index (M_w/M_n) were measured using GPC and results are summarized in Table 2. It is obvious that AP-PSQAS has a relative small value of polydispersity index which indicates a narrow molecular weight distribution. Compared to AP-PSQAS CP-PSQAS and CM-PSQAS have a relative large value of polydispersity index due to the polystyryl main chains that were prepared by free-radical polymerization. Because an excess of dichloromethylbenzene is used to terminate the chain reaction in the anionic polymerization step, and an excess of trimethylamine is used in the following ammonium reaction, so there is only one quaternary ammonium group on each polystyryl chain for the AP-PSQAS. But the situation for both CP-PSQAS and CM-PSQAS is different, the ammonium groups on each chain of these two polystyryl ammonium salts have to be measured from ^{1}H NMR experiments. The calculated result for mass/charge (the mass per ammonium group) ratios of polystyryl ammonium salts are also summarized in Table 2. Once we know the above information and CEC of the montmorillonite, we can easily calculate the mass ratio of polystyryl ammonium salt to MMT to make sure the sodium ions in MMT will be completely ion exchanged.

3.2. FT-IR spectrum

To obtain a short polystyryl chain, a high ratio of BPO to styrene was used in the preparation of CP-PSQAS and CM-PSQAS by free radical polymerization, and a relative high ratio of butyl lithium to

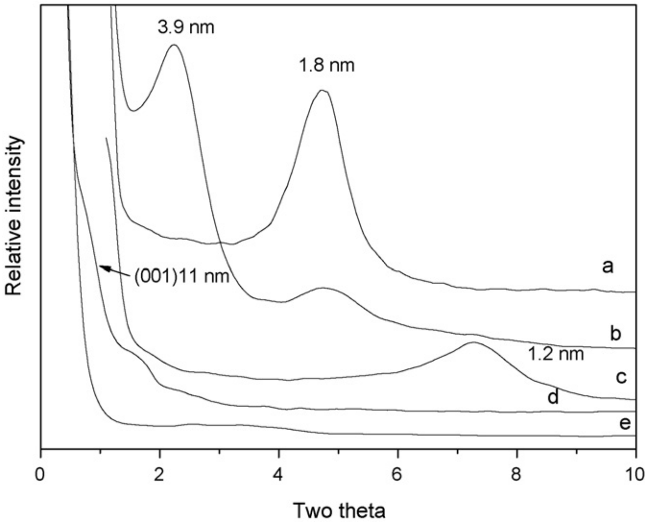

Fig. 5. XRD traces obtained from pristine sodium MMT and surfactants modified MMT: (a) CTMAB-modified MMT; (b) CM-PSQAS-modified MMT; (c) Na-MMT; (d) AP-PSQAS-modified MMT; (e) CP-PSQAS-modified MMT.

styrene was used in the preparation of AP-PSQAS. It is well known that the amount of initiator used in the chain reaction will affect the structure and properties of the polymer such as terminal groups and thermal stability. IR analysis of these three polystyryl quaternary ammonium salts has been performed to obtain the chemical structural information, and their IR spectra have been presented in Fig. 4A. It is obvious that there are two bands at 1720 and 1270 cm^{-1} that could be attributed to the ester group in the IR spectra of CP-PSQAS and CM-PSQAS while these two bands were not present in the IR spectra obtained from AP-PSQAS. These ester groups on the styryl chain are due to the free radical formed from the BPO or chain transfer to BPO in the preparation of short chain polystyrene by free-radical polymerization.

The comparison of the IR spectra of Na-MMT, polystyryl quaternary ammonium salt, and polystyryl-modified MMT was performed and the results are shown in Fig. 4B–D. In Fig. 4B, spectrum (a) is a typical IR spectrum obtained from AP-PSQAS, and bands at 3022, 2940, 1600, 1487, and 695 cm^{-1} are attributed to the vibrations of polystyrene; spectrum (c) is a typical IR spectrum obtained from Na-MMT, the absorption band near 3635 cm^{-1} is attributed to O–H stretching and the band at 1046 cm^{-1} is attributed to Si–O stretching; In spectrum (b), all the typical absorption bands for AP-PSQAS and Na-MMT could be observed, indicating that AP-PSQAS-modified MMT has been achieved. The IR analysis has also been performed on other polystyryl-modified MMTs

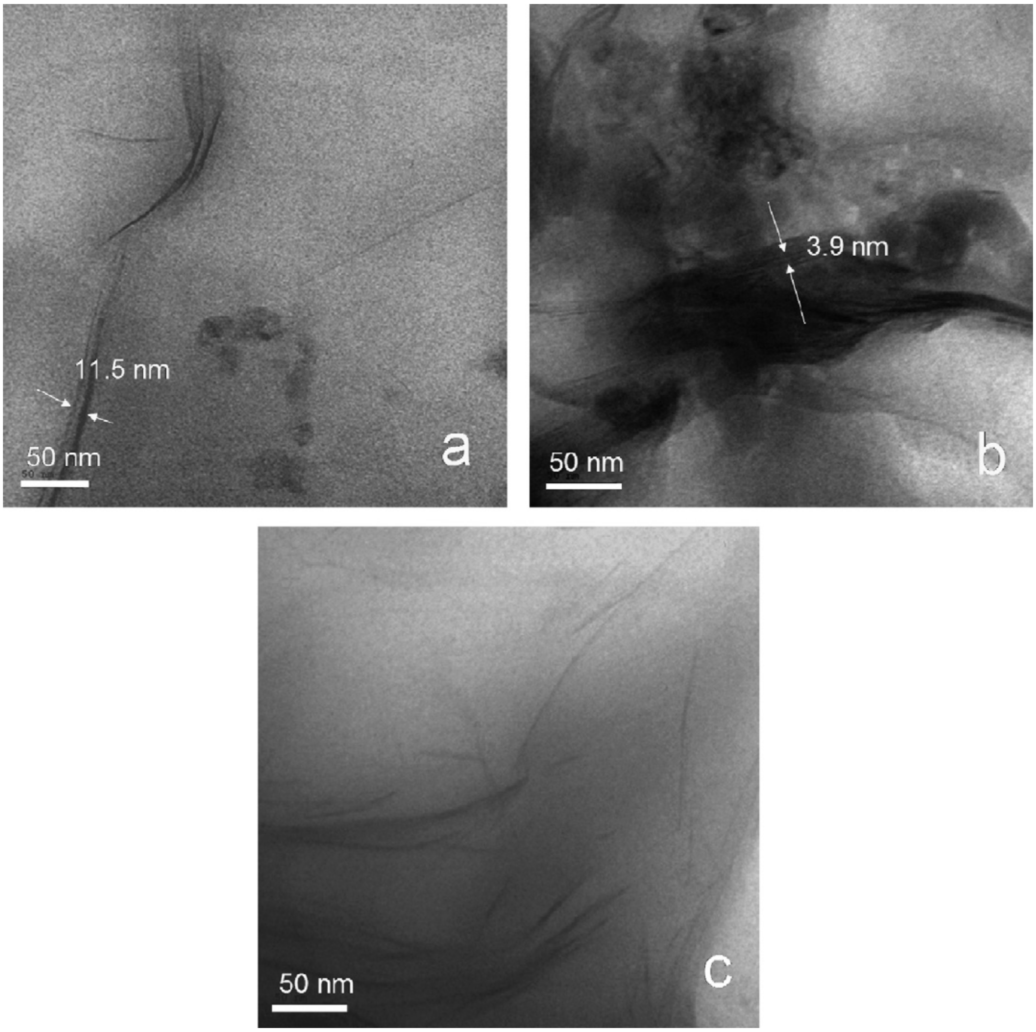

Fig. 6. TEM images of modified MMTs: (a) AP-PSQAS-modified MMT; (b) CM-PSQAS-modified MMT; (c) CP-PSQAS-modified MMT.

samples, and the results have indicated that CM-PSQAS- and CP-PSQAS-modified MMT have also been achieved (see Fig. 4C and D).

3.3. XRD measurement

Generally, the *d*-spacing of pristine sodium montmorillonite is about 1.2 nm, when organic ammonium salts are intercalated into the galleries of MMT, the *d*-spacing will be increased. Fig. 5 shows the XRD patterns of four different organically modified montmorillonites. The CTMAB-modified MMT exhibits a basal reflection peak (0 0 1) at $2\theta = 4.75^\circ$ corresponding to a gallery gap of 1.8 nm. As for CM-PSQAS-modified MMT, the incorporation of polystyryl ammonium salt has expanded the *d*-spacing of the MMT to a value of 3.9 nm. The AP-PSQAS-modified MMT reveals a peak (0 0 1) at about $2\theta = 0.8^\circ$ corresponding to a gallery gap of 11 nm. There are no significant peaks that could be observed from the XRD trace of CP-PSQAS-modified MMT, and indicates this modified clay are of an exfoliated or completely disordered structure. These differences of *d*-spacing among the different organically modified montmorillonites are related to the ratio of mass to charge of the surfactants (Table 2). The mass/charge of CTAB is 283, and it has an intercalated structure with a *d*-spacing of 1.8 nm; CM-PSQAS has a mass/charge of 1200, and the *d*-spacing of its modified MMT is 3.9 nm; When the mass/charge values for the polystyryl-modified MMTs are bigger than 1800, there are no significant peaks in XRD traces could be observed, and indicates a structure with exfoliation or disordering.

To confirm these conclusions from XRD analysis, TEM was performed and the experimental result is discussed in the following section.

3.4. TEM results

The TEM images have been taken to confirm the structures of polystyryl-modified montmorillonites evaluated from XRD analysis. Fig. 6(a) is a typical TEM image for AP-PSQAS-modified MMT. It shows an intercalated structure with a *d*-spacing of 11.6 nm and partial exfoliation with stacked clay layers. This *d*-spacing is consistent with the result from XRD analysis. CM-PSQAS-modified MMT shows a well-intercalated structure with a *d*-spacing of 3.9 and CP-PSQAS-modified MMT are completely exfoliated.

3.5. TGA characterization

The thermal stability of different polystyryl quaternary ammonium surfactants and their modified montmorillonites were evaluated by TGA. The results are presented graphically in Figs. 7 and 8. Generally, information obtained from TGA analysis includes: the 10% weight loss temperature (T_{10}), a measure of the onset degradation; the 50% weight loss temperature (T_{50}), the midpoint of the degradation process; and the fraction of material which remained at 600 °C, denoted as char.

The CTAB is a long alkyl chain ammonium and has a low onset degradation temperature due to the Hoffmann β-elimination reaction [33]. The CP-PSQAS and AP-PSQAS are of much higher onset temperatures compared to that of CTAB because of no-presence of β-hydrogen. It is obvious that, although CM-PSQAS is also a styryl ammonium salt, but it has a lowest onset degradation temperature compared to that of CP-PSQAS and AP-PSQAS. This comes from the different polymerization methods used in the preparation of polystyrenes. The polystyrene for CM-PSQAS is prepared by free radical polymerization at 80 °C; the reaction undergoes termination by a combination of coupling and disproportionation, and it has terminal vinyl groups on the chain [34]. In the following chloromethylation reaction, the electrophilic addition of hydrochloride existing in monochlorodimethyl ether to these terminal vinyl groups will give chloromethyl groups [35]. So there are two types of chloromethyl groups: one is on the end of main styrene chain; the other is on the benzyl ring. When these two types of chloromethyl groups are transferred to ammonium groups with excess trimethylamine in this research, then two different kinds of ammonium groups are obtained, and the degradation mechanisms of these two types of quaternary ammoniums are different. This difference leads to an even lower onset degradation temperature for CM-PSQAS compared to that of CTAB.

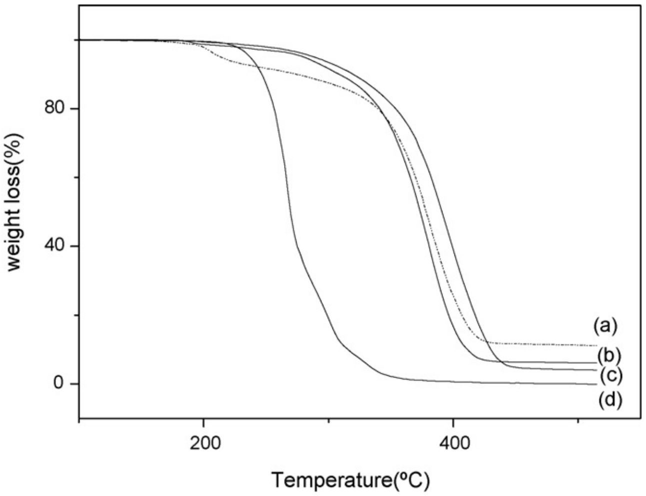

Fig. 7. TGA traces obtained from quaternary ammoniums: (a) CM-PSQAS; (b) CP-PSQAS; (c) AP-PSQAS; (d) CTMAB.

The TGA traces obtained from quaternary ammonium salts and their modified montmorillonites are shown in Fig. 8. The TGA results have shown that onset degradation temperatures of CM-PSQAS, CP-PSQAS, and AP-PSQAS-modified montmorillonite are 46%, 52%, and 56%, higher respectively compared to that of CTMAB-modified montmorillonite. This is not a surprise, since the C—C bonds in aromatics are much stronger than that in aliphatic compounds. The π bond between the aromatic rings and the 2p orbitals of the oxygen atoms in the silicate layer have further stabilized the polymers intercalated in the silicate layers [36]. In addition, the polymers were confined in the interlayer and could not move freely,

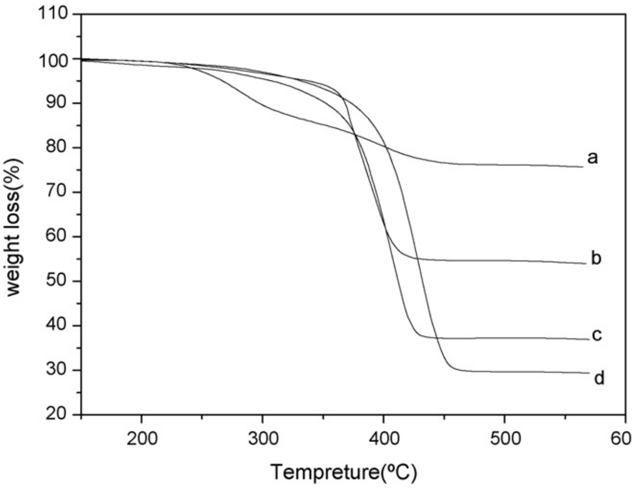

Fig. 8. TGA trace obtained from quaternary ammonium-modified montmorillonites: (a) CTMAB-modified MMT; (b) CM-PSQAS-modified MMT; (c) CP-PSQAS-modified MMT; (d) AP-PSQAS-modified MMT.

so the degradation process was also changed [37]. Hence, the degradation temperature of this polymerically modified montmorillonite series was higher.

4. Conclusions

Three series of different molecular weight polystyryl quaternary ammonium salts (PSQAS) and their MMT complexes have been successfully obtained from the chloromethyl polystyrenes which are prepared by three different methods: free-radical copolymerization, chloromethylation of polystyrene and anionic polymerization. The TEM and XRD results have indicated that the polystyryl-modified montmorillonites are of partial exfoliation with stacked clay layers or intercalated structures, and the structures are affected by the mass/charge ratios. TGA analysis indicates that all of the polymerically modified montmorillonites have an advantage of greater thermal stability than conventional long-chain alkylammonium-modified montmorillonites. The thermal degradation of polystyryl ammonium salts and their modified montmorillonites do affected by the preparation methods for the main styryl chain, and both of the polystyryl ammonium salt and its modified clay obtained from the chloromethyl polystyrene prepared by anionic polymerization are the most stable ones, respectively.

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