Polym. Bull. (2010) 64:677–690
DOI 10.1007/s00289-009-0210-4

ORIGINAL PAPER

Preparation and rheological properties of SEM-25 containing associative thickener latexes and their mechanisms of thickening

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Received: 16 March 2009 / Revised: 11 November 2009 / Accepted: 18 November 2009 /

Abstract Hydrophobically modified alkali-soluble acrylic latexes were prepared using varying level of SEM-25, triphenylethyl phenoxy polyoxyethylene ether methacrylate, a functional monomer bearing a long segment of ethylene oxide and a hydrophobic tetraphenyl group. Sharp increases in viscosity and light transmittance of the diluted associative thickener latexes were observed with ascendant pH starting from 7. And with further increase in the pH, viscosity of the thickener latexes rapidly fell down, while the light transmittance was kept relatively constant. It was revealed that a critical content of SEM-25 in the thickener copolymer, 5% in the present case, was required in order for the associative thickener to outperform the SEM-25 free counterpart. When used in thickening a latex of P(St–BA) (Poly(styrene–Butyl acrylate)) copolymer using a thickener copolymer with 12 wt% of SEM-25, addition of 0.34 wt% of the thickener polymer relative to P(St–BA) was necessary to have a higher viscosity than the same latex thickened using the thickener free of SEM-25. It seemed that incorporation of 0.275 mol% of SEM-25 was indispensable for the associative thickener to exceed the performance of conventional thickener.

Keywords SEM-25 functional monomer · Hydrophobic group · Associative thickener · Light transmittance · Rheological property

Introduction

Polymeric thickeners are employed by latex paint formulator to provide the appropriate viscosity profile across the entire shear range encountered in paint applications [1, 2]. Thickeners traditionally used are water-soluble polymers, for

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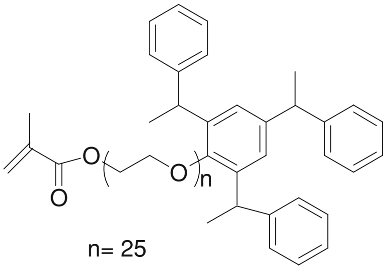
example, derivatives of cellulose. These derivatives thicken the medium because of chain entanglements between the long polymer molecules, which are solvated and extended in aqueous media [3, 4]. Water-soluble associative polymers are currently gaining importance as thickeners, or viscosity modifiers, in a number of waterborne applications. Associative thickeners are water-soluble polymers containing hydrophobic moieties [5, 6], such as hydrophobically modified alkali-soluble emulsion (HASE), hydrophobically modified ethylene oxide urethane block copolymer (HEUR) and hydrophobically modified hydroxy ethylcellulose (HMHEC) [7]. A mechanism of associative thickening is put forth, in which hydrophobic segments are attached by adsorption to latex and pigment particles. Thus, the particles bridged by thickener macromolecules form a physical network structure, which can be gradually destroyed in the shear field, thus controlling the flow properties of the system [8]. Besides, hydrodynamic interaction between the latex particles and macromolecules of the thickener or their aggregates (clusters, micelles) may be highly important in the thickening process. The mechanism of flow of latex coatings thickened with associative compounds is not yet fully understood. It may be assumed that in application, the shearing destroys associative bonds and the network from thickener macromolecules and latex particles disintegrates into smaller isolated aggregates which can freely rotate in the flow field. These reduce the coating viscosity. As the associative bonds are fairly resistant to higher shear forces, the shear thinning is much lower than that observed with classical alkali-swellable thickener [9].

HASE polymers are increasingly being used to replace the long-chain cellulosic polymers due to their enhanced performance and economic advantages [10]. HASE polymers generally offer excellent viscosity building, wide formulation latitude, excellent biostability, ease of dosing and are supplied as high solids latex, free of organic cosolvents. They are usually obtained by emulsion polymerization [11–14], inverse emulsion polymerization [15–20], or precipitation polymerization [21]. Polyacrylic acid or polyacrylamide modified with hydrophobic comonomers with long alkyl groups are usually studied using inverse emulsion polymerization. Typically, HASE polymers are synthesized using conventional semi-continuous emulsion polymerization. Ji et al. [11], Feng et al. [12], and Jassal et al. [14] discussed the polymerization of methacrylic acid (MAA)-ethyl acrylate (EA)-diallyl phthalate (DAP) copolymer using semi-continuous emulsion polymerization. The effect of reaction condition on viscosity was studied at pH 8. Tam and Jenkins et al. [13, 22–29] reported a series of studies on HASE of Union Carbide Corporation based on MAA, EA, and a functional macromonomer capped with a hydrophobic group.

They studied the rheological properties of HASE in ionic or non-ionic surfactant solutions, salt or salt/SDS solutions, and observed aggregation behavior of MAA/EA copolymer in dilute solutions using static light scattering and dynamic light scattering. In this study, a new hydrophobic comonomer, triphenylethyl phenoxy polyoxyethylene ether methacrylate, abbreviated as SEM-25, was used to prepare hydrophobically modified polyacrylic acid emulsion. The structure of this comonomer is shown in Scheme 1. The effects of SEM-25 content and latex solids on the viscosity and light transmittance of the latexes at different pH were studied.



Scheme 1 Chemical structure of SEM-25

Experimental

Materials

Ethyl acrylate (EA) and methacrylic acid (MAA), both chemical pure, were purchased from Guoyao Chemicals Ltd.; diallyl phthatale (DAP) was from Shanghai Chemical Reagent Ltd.; Surfactant OP-21 and OP-9, both industrial grade, were from Tianjin Hongmei Chemical Ltd. Sodium dodecyl benzene sulfonate (SDBS), chemical pure, was from Shanghai Chemical Reagent Supply Association. Except EA and MAA which were distilled under reduced pressure before use, all chemicals were used as received. SEM-25 is a functional monomer from Rhodia, USA. Poly(styrene-co-butyl acrylate) (P(St–BA)) latex was prepared in our laboratory.

Preparations of thickeners and styrene (St)–butyl acrylate (BA) copolymer latex

Emulsion polymerization was used to prepare the thickener latex. The formula for the latex was comprised of 100 g of water, 40 g of monomers including EA, MAA, 0.10 wt% of cross-linker DAP based on all monomers and SEM-25 at varying levels. SDBS, OP-21, and OP-9 of 1.0, 0.5, and 0.5 wt%, respectively, based on total mass of the monomers, were used as surfactants. Ammonium persulfate (APS) was used as initiator. Semi-batch process was employed for the polymerization, in which 1/2 of the water was initially charged into the reactor, and the rest of the water was used to prepare a pre-emulsion. This pre-emulsion was fed into the reactor at a constant rate during 3 h. The polymerization temperature was fixed at 85 °C, kept for 1 h after the completion of the pre-emulsion addition.

P(St–BA) latex was prepared by semi-batch emulsion polymerization at 80 °C using sodium dodecyl sulfate, OP-9 and OP-40 as surfactants, APS as initiator. The theoretical solids of the latex was designed to be 50 wt%, in which the monomer composition was of 45% of BA, 53% of St, and 2% of MAA, all expressed by weight. Particle size of the latex was of 168 nm determined by light scattering, and the size distribution was monomodal.

Characterization of thickener latexes

The solids of the latexes and monomer conversions were determined by gravimetry. Particle size and its distribution was detected using Nano-ZS dynamic light scattering particle sizer (Malvern, UK). The particle morphology of latexes was investigated by JEM-100CX transmission electron microscope (TEM, Jeol, Japan) with phosphotungstic acid as staining agent. The viscosity of the original and diluted thickener latexes and P(St–BA) latexes containing thickener were determined using Ubbelodhe viscometer (diameter 1.0–1.1 mm) in a thermostat at 25 °C or DV-II+ Pro. viscometer (Brookfield, USA) at ambient temperature. The light transmittance at different pH was followed by 662 photometer and 808 Titrando (Metrohm, Switzerland).

Results and discussion

Basic properties of thickener latexes

In Table 1 are given the basic properties of thickener latexes. It can be seen that viscosity of thickener latexes increased with the addition of SEM-25. This increase may be attributed to the presence of hydrophilic polyethylene oxide segments in SEM-25. Owing to their hydrophilicity, these segments were not expected to be adsorbed tightly on the particle surface, but extended, at least part of them, into the surrounding water phase. When their number is large, an entanglement could occur between these segments due to their terminal hydrophilic multiphenyl groups. This entanglement would surely contribute to the increase in apparent latex viscosity, and this increase would be further enhanced with increase of SEM-25. In the present latexes, this entanglement seemed not to be occurring because the viscosity augmentation was not significant. Table 1 shows also that particle size of these latexes increased at first, followed by a decrease when content of SEM-25 reached 5%. It is to note that particle size of the thickeners with SEM-25 was all superior to the sample T00, the one without SEM-25. Particle size distribution of all thickeners with SEM-25 was obviously narrower than that free of SEM-25, but without any regularity with SEM-25 content. Due to the presence of MAA, pH in all these thickeners was around 3.0. Histograms of the particle size distribution in the latexes are also displayed in Fig. 1, which showed a reasonable narrow particle size

Table 1 Basic properties of thickener latexes

Sample	SEM-25[a] (%)	Solids (%)	Monomer conversion (%)	Dp (nm)	PDI	pH	Viscosity[b] (mPa s)
T00	0.00	27.40	97.11	86.7	0.095	2.74	11.0
T05	0.52	28.32	99.90	144.0	0.059	3.10	17.0
T11	1.10	28.30	99.61	161.0	0.072	2.53	16.0
T16	1.60	27.63	97.02	162.6	0.050	2.59	15.0
T50	5.00	29.36	99.00	118.0	0.079	3.09	21.7
T120	12.00	30.91	99.80	120.0	0.070	3.58	21.8

[a] SEM-25 content by weight based on all monomers

[b] Brookfield viscosity using 3# spindle at 60 r/min

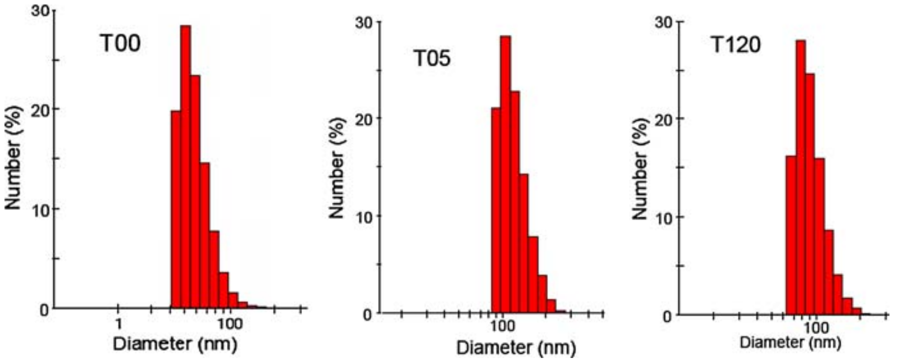
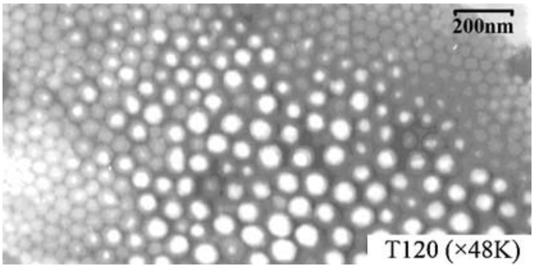


Fig. 1 Particle distribution histograms of the thickener latexes (T00, SEM-25 free; T05, 0.5% of SEM-25; T120, 12% of SEM-25)

Fig. 2 TEM pictures of thickener latexes T120 with 12% of SEM-25



distribution, in agreement with the results in Table 1. As supplementary information, TEM photographs of the particles in the thickener latex with 12 wt% of SEM-25 are also given in Fig. 2.

Effect of solids on thickeners properties

In a first set of tests, thickener latexes of different SEM-25 content were diluted to different solids, i.e. 0.1, 0.25, 0.50, and 0.65%, all expressed by weight, and their pH gradually varied from 6 to 12. The viscosity of the diluted latex thickeners and light transmittance were determined, and the results are shown in Figs. 3 and 4. It is seen that viscosity of the latex thickeners sharply increased to a maximum from pH 6 to 8, then followed by a decrease with further pH increase. It is believed [14] that the maxima corresponds to the maximal dissolution of thickener polymer, or disintegration of latex particles due to disassociation of carboxylic acid in polymer chains upon alkali addition, which leads to ionization of polymer chains and therefore entraining polymer dissolution into aqueous phase because of the static repulsion of negatively charged carboxylate groups. Particle size evolution in these latexes were also followed by light scattering, which showed that the particle size rapidly increased at the same pH, concomitantly with the viscosity increase starting at around pH 6, followed by a slight decrease from pH 8 to 10, and then abruptly became not detectable once pH past 12. Since light scattering detected were

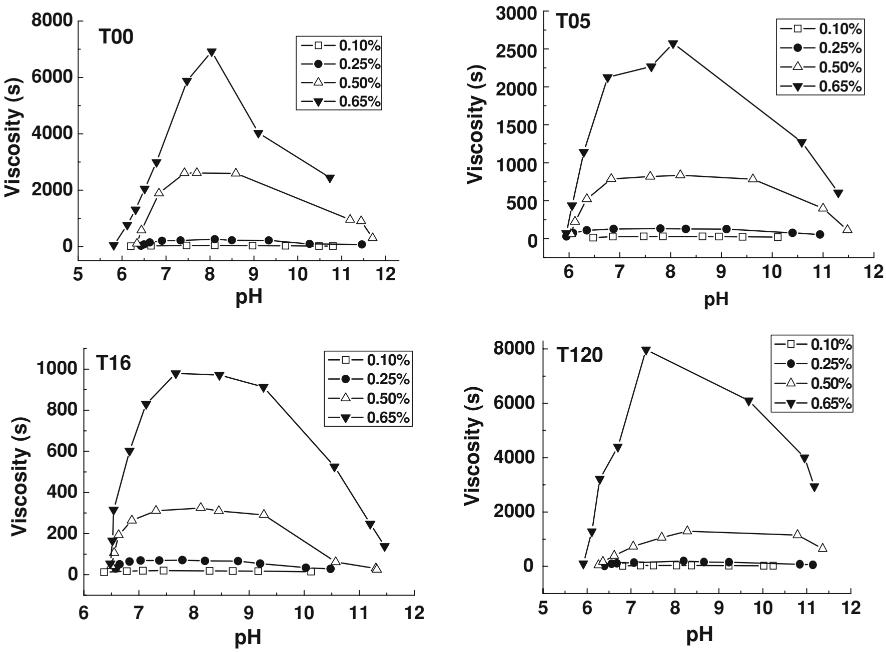


Fig. 3 Viscosity variation of latex thickener with different SEM-25 content diluted to different solids (T00, 0%; T05, 0.5%; T16, 1.6%; T120, 12% of SEM-25)

hydrated particles, particle size increase indicated alkali swelling, and the subsequent disappearance should be taken as an indication of particle disintegration.

The subsequent viscosity decrease was caused by addition of sodium hydroxide solution, which made the polymer solution further diluted. It is to point out that Fig. 3 also revealed that the viscosity increase was significant only for the samples with solids higher than 0.5%, below which only a slight viscosity increase was observed around pH 8. Careful comparison between the viscosity curves of the thickener latexes revealed that only sample T120 at 0.65% solids displayed a higher viscosity than T00, the SEM-25 free sample. All other thickeners showed lower viscosity than sample T00 at equal solids. This indicated that a critical polymer concentration and a critical SEM-25 level in the thickener polymer were both needed in order for the latex thickener to have a good performance. This observation was in good agreement with previously reported results, which stated that the performance of associative thickeners was concentration related [30].

As to the light transmittance of the diluted latex thickeners, a sharp increase was also observed with ascendant pH in all thickener latexes of different solids, followed by a plateau with continuous increase in pH as shown in Fig. 4. The maxima of light transmittance in T00 at all solids were highest among all the samples tested, indicating a high degree of latex particle dissolution. It is also seen that the maxima of light transmittance for samples rich of SEM-25, T120 and T50 (T50 similar to T120, not shown in Fig. 4) for instance, were all very high regardless of their solids, indicating a similar extent of latex particle disintegration to T00. However, for those

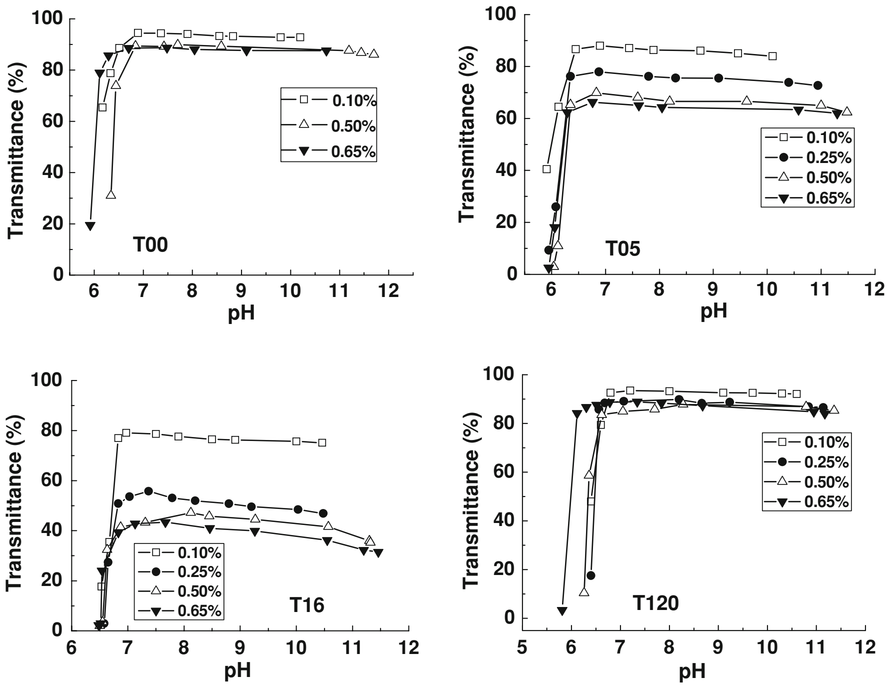


Fig. 4 Transmittance variation of latex thickener with different SEM-25 content diluted to different solids (T00, 0%; T05, 0.5%; T16, 1.6%; T120, 12% of SEM-25)

with low SEM-25 content (T05, T16), these maxima were largely scattered. The higher were the solids; the lower was the maximum of their light transmittance at high pH, indicating a gradually reduced solubility of the polymer molecules with increase in SEM-25 when its content was at low level. This trend was kept on till SEM-25 reached 1.6%, and after this point, the light transmittance in high pH area started to increase with ascending SEM-25 in the copolymer. This observation will be further discussed in next section. Also observed in samples with low SEM-25 content was that the light transmittance manifested a slight decrease with pH increase (T05, T16) once the maxima was achieved, which might be attributable to the fact that the presence of more negatively charged hydroxyl ions might reduce the degree of ionization of carboxylate groups, and therefore to impede their extension into aqueous phase, although the addition of sodium hydroxide would lead to the opposite direction.

Effect of SEM-25 content on thickeners properties

To investigate the influence of SEM-25 content, tests were also done on samples of different SEM-25 content, and adjusted to a same solid. Figure 5 presents the comparative curves of the light transmittance. It was clearly seen from Fig. 5 that the variation of light transmittance versus pH in all samples at different solids followed a similar pattern, namely, the transmittance increased rapidly starting from

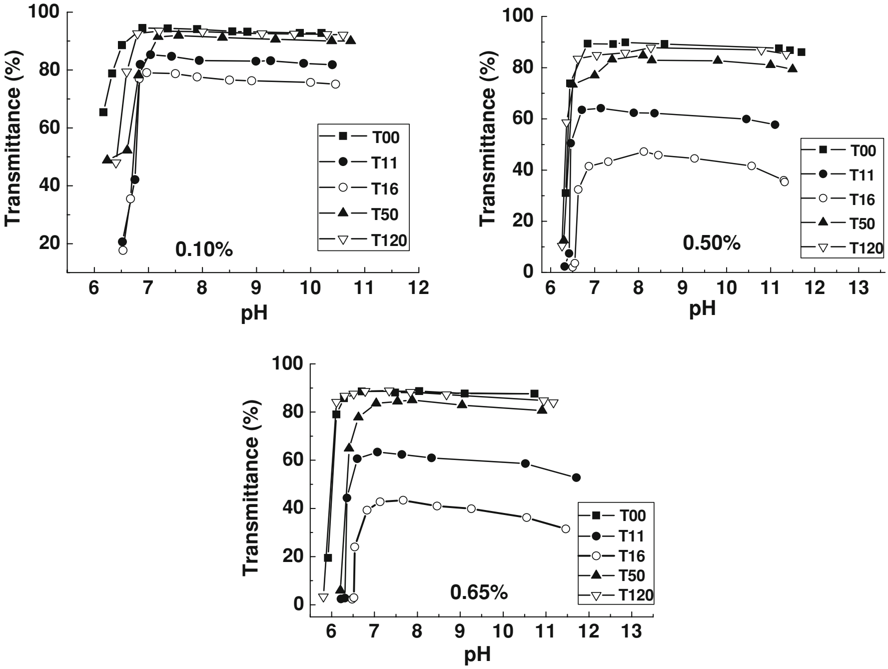


Fig. 5 Transmittance dependence on SEM-25 content in latex thickener diluted to a same solid level (T00, 0%; T11, 1.1%; T16, 1.6%; T50, 5.0%; and T120, 12% of SEM-25)

pH between 6 and 7. This increase was followed by a plateau, where the transmittance remained relatively constant with continuous pH ascending for most of the samples. The maxima of light transmittance observed in the plateau region for samples either with higher SEM-25 (T50, T120) or without SEM-25 (T00) were at 90% or higher, which was an indication of the disintegration of the latex particles, expected due to entrained disassociation of carboxylic acid in polymer chains upon alkali addition. However, more close examination revealed that the light transmittance was also dependant on SEM-25 content in the latex polymer. It is seen that, comparatively to the SEM-25 free sample, the maxima of light transmittance of the latex thickener displayed a gradual decrease when SEM-25 content was inferior to 5.0% (samples T11, T16) regardless of the polymer concentration as evidenced by Fig. 5; and thus the light transmittance of T11 (1.1% SEM-25) in high pH area was lower that T00, the SEM-25 free sample; and a lowest maximum of light transmittance was observed in sample T16 (1.6% SEM-25), which was likely the turning-point for SEM-25 content. Afterward, the maxima of the light transmittance were again increased in samples with T50 and T120, containing 5 and 12% of SEM-25, respectively.

In Fig. 6 are presented the same curves but for the viscosity variation with pH. For all the samples tested at different solids, the viscosity rapidly increased at pH starting 6 to 7, reached a maximum at pH around 8 and then commenced to decrease afterward. This decrease in viscosity after their peak value was due to the simple

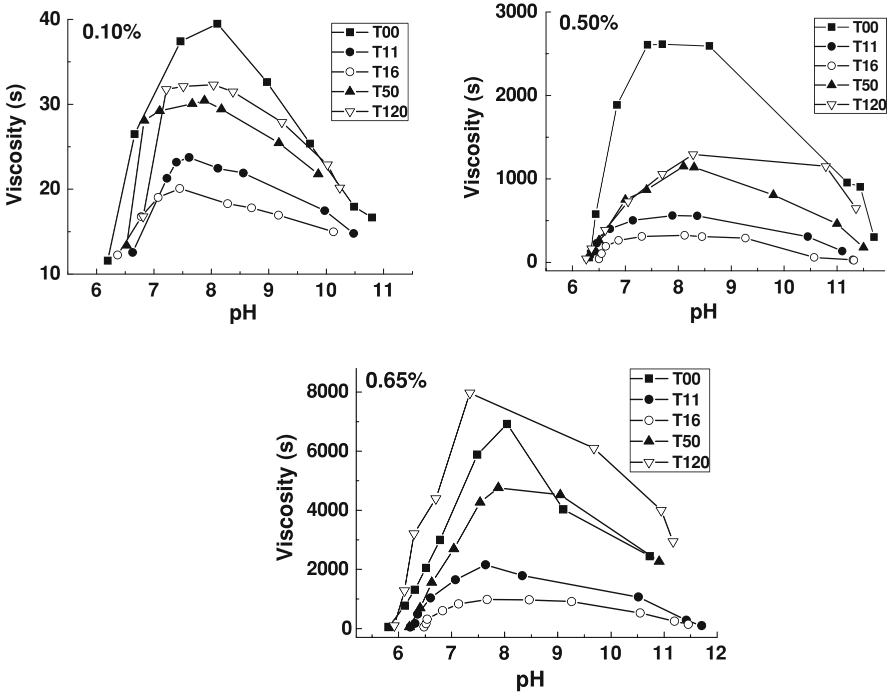


Fig. 6 Viscosity variation of latex thickener with different SEM-25 content diluted to same solids (T00, 0%; T11, 1.1%; T16, 1.6%; T50, 5.0%; and T120, 12% of SEM-25)

dilution of the polymer solution as afore-mentioned. Also, when comparing the viscosity variation of the samples at a same solid but different SEM-25 content, it was revealed that the viscosity was first largely lowered with the presence of SEM-25 in the copolymer, this way the viscosity of T11 was lower than T00, the SEM-25 free sample, and that of T16 also lower than T11. Exactly as what observed in the light transmittance test, here again T16 was the turning point, with higher SEM-25 content (T50, T120), and higher viscosity than T16 was detected.

This close dependence of light transmittance and viscosity in thickener latex on SEM-25 content was depicted clearly in Fig. 7 for samples with polymer concentration of 0.10 and 0.65% as examples. It was evidenced that incorporation of low level SEM-25 (<1.6%, for instance) did not contribute to better performance of the thickener but led to adverse effect, a positive contribution was only obtained when a critical SEM-25 content was achieved. In this case, this critical amount for SEM-25 was 5.0%. To illustrate the function of SEM-25 in the thickening, a schematic presentation was given in Fig. 8. It is commonly agreed that the hydrophobic groups, i.e. the tetraphenyl groups in SEM-25 in the present case, in the associative thickener molecules can form a micelle-like or rosette-shape aggregates due to their hydrophobic affinity by entanglement once their concentration is high enough (Fig. 8C), and different hydrophobic groups on one single thickener molecule are assumed to be able to participate in different aggregate

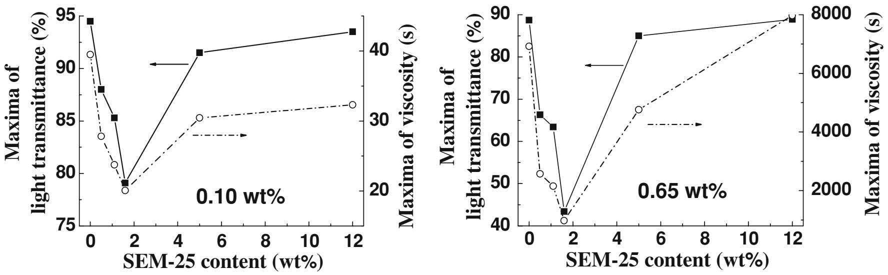


Fig. 7 Maxima of light transmittance and of viscosity at high pH for thickener latexes of different SEM-25 level at 0.10 and 0.65 wt% solids

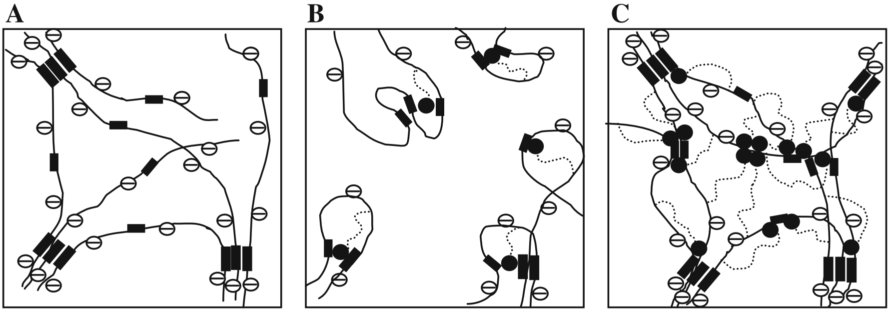
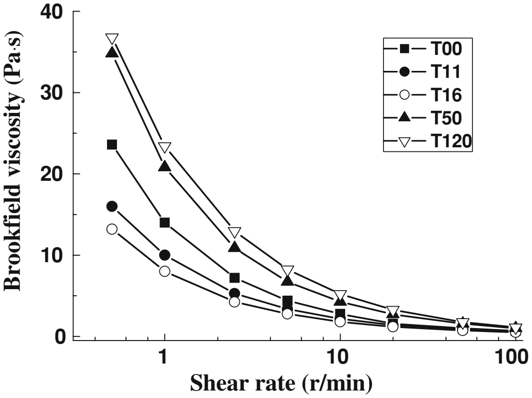


Fig. 8 Illustration of function of SEM-25 in latex thickening: **A** no SEM-25; **B** very low SEM-25; **C** high SEM-25 content to form aggregates between the hydrophobic groups. (●, hydrophobic group; ▬, soft acrylic segments; ⊖, carboxylic group)

formation, therefore building up linking or bridge between these aggregates, which are believed to be relatively stable and therefore to increase shearing resistance. A prerequisite for this aggregation to occur is that there must be enough hydrophobic groups available in the media. It is to note that the presence of very low amount of the hydrophobic groups (1.1 and 1.6%, for instance), below the critical concentration required to form the aggregates, not only did not increase the viscosity of the thickener but also entrain adverse effects, namely, reducing the viscosity and the light transmittance of the thickener polymer solution as seen in Figs. 5, 6, and 7 and illustrated in Fig. 8B. It is therefore reasonable to assume that the thickener polymer solubility was whittled when SEM-25 content was too low for their hydrophobic group to form a rosette aggregation (Fig. 8B). This could be easily understood knowing that these multiphenyl groups are hydrophobic in nature, and there was no intermolecular bridging to keep the polymer chains extended in water phase before the formation of hydrophobic aggregation. In Figs. 5 and 6, the critical SEM-25 content in copolymer, at which the minima were observed in light transmittance and viscosity in the copolymer solution, was 1.60%. Knowing the molecular mass of SEM-25 being 1,525, it is readily estimated that SEM-25 was 0.088 mol% in the copolymer, or 1 SEM-25 unit in every 1,136 monomer units on average. The same way, the point of 5.0% in T50 sample, where both light transmittance and viscosity

Fig. 9 Effect of SEM-25 content on dynamic viscosity of the latex thickeners (T00, 0%; T11, 1.1%; T16, 1.6%; T50, 5.0%; and T120, 12% of SEM-25)



started to increase after the minima observed in T16, was equaled to 0.278 mol% of SEM-25. However, in order to have a higher performance for the associative thickener than the sample with no SEM-25 (T00), 0.667 mol% (12% in T120) of SEM-25 was indispensable as shown in Figs. 5, 6 and 7.

Dynamic viscosity of the latex thickeners

Rheological behaviors of the thickeners at 1.0% solids were also tested by changing shearing rate using Brookfield viscometer. The results are shown in Fig. 9. Similar observations to those previously described were revealed, i.e., at lower SEM-25 content, for instance T11 and T16, thickener latexes showed a lower viscosity than T00 in all tested shearing range. T16 with 1.6% of SEM-25 displayed the lowest viscosity among all tested samples. With further increase in SEM-25, viscosity started to increase. Different from the static viscosity dependence on SEM-25, where the sample T50 (5.0% SEM-25) displayed a viscosity lower than T00, the dynamic viscosity in both T50 and T120 were higher than that in T00.

Thickening of P(St–BA) latex

The criteria to judge a thickener remains in its capacity in latex thickening. The above associative thickeners of different SEM-25 content were therefore added at different levels to a P(St–BA) latex prepared as described in "Experimental" section, the solids content of the P(St–BA) latex was adjusted to 30 wt% prior to test. Results are listed in Table 2.

The thickening of P(St–BA) latex was obvious at even low level of thickeners rich of SEM-25, T50 and T120 for instance. And with the thickener of 5.0% of SEM-25 or higher, thickening was always more pronounced than sample T00, free of SEM-25. Nevertheless, the thickening was also more effective than T00 when low SEM-25 samples were added at a high level. For T05 and T11, for instance, the thickening over past T00 sample when added at 1.88%; And for T16, a higher thickening was only observed when 2.24% was used. This was in accordance with the results previously discussed and could be explained based on the same consideration.

Table 2 Brookfield viscosity of P(St–BA) latex thickened with associative thickeners of different SEM-25 content at varied thickener levels

Thickener level[a] (%)	Brookfield viscosity[b] (mPa s)					
	T00	T05	T11	T16	T50	T120
0.34	20	10	10	10	30	50
0.76	210	50	40	10	400	4000
1.12	790	320	400	120	3100	>10000
1.48	1740	1350	1220	570	9290	–
1.88	3150	3270	3170	1880	>10000	–
2.24	5470	6220	7880	6170	–	–
2.44	6270	9670	>10000	9220	–	–

[a] Thickener level expressed as pure polymer versus the copolymer in P(St–BA) latex

[b] Brookfield viscosity done using spindle #4 at 20 r/min

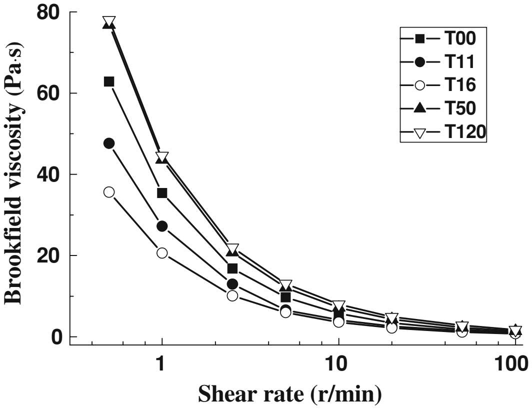


Fig. 10 Rheological properties of 30% P(St-BA) latex thickened with associative thickeners (T00, 0%; T11, 1.1%; T16, 1.6%; T50, 5.0%; and T120, 12% of SEM-25)

Finally, another set of tests was also carried out using the same P(St–BA) latex and thickeners with thickener amount fixed this time at 0.34%. The rheological behavior at different shearing was tested. Results are given in Fig. 10. By comparison to SEM-25 free sample T00, it was reconfirmed that T50 and T120 were more effective in all tested shearing range, and T16 thickener yielded the lowest performance. This enabled us to conclude that SEM-25 is an effective functional monomer for associative thickener providing that its content is above 5.0% in the thickener latex polymer when the associative thickener copolymer is added at level of 0.34% relative to the copolymer of the latex to be thickened.

Conclusions

Hydrophobically modified alkali-soluble emulsions were prepared by semi-batch emulsion polymerization using MAA, EA, and SEM-25, a functional monomer bearing a long segment of ethylene oxide terminated with a hydrophobic tetraphenyl group. Viscosity and light transmittance of the associative thickener latexes were followed. It was seen from the experiment results that sharp increases both in viscosity and light transmittance were observed with ascendant pH starting from 7. And with further pH increase, viscosity of the thickener latexes rapidly fell down, while the light transmittance was kept relatively constant. It was revealed that a critical content of SEM-25 in the thickener copolymer, 5.0% in the present case, was required in order for the associative thickener to outperform the SEM-25-free counterpart. Thickening of P(St–BA) copolymers latex using these associative thickeners was studied. It was observed that addition of 0.34% of thickener polymer of 12 wt% (0.67 mol%) of SEM-25 based on P(St–BA) copolymer was necessary for the thickened latex to have a higher viscosity than that free of SEM-25. To reach a same thickening result, more thickener was needed if its SEM-25 content was lowered. It was concluded that incorporation of 0.275 mol% of SEM-25 was indispensable for the associative thickener to exceed the performance of conventional thickener.

Acknowledgements This research is financial supported by Natural Science Foundation of China (NSFC, Grant No. 20874040) and by Doctoral Research Funds of Shandong Province, China (2006BS04032).

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