Interaction between a Tertiary Amine Methacrylate Based Polyelectrolyte and a Sodium Montmorillonite Dispersion and Its Rheological and Colloidal Properties

A. Alemdar,[1] V. Bütün[2]

[1]Faculty of Science and Letters, Istanbul Technical University, Maslak, 34469, Istanbul, Turkey
[2]Faculty of Science and Letters, Meselik Campus, Osmangazi University, 26480, Eskisehir, Turkey

ABSTRACT: The rheological and colloidal properties of sodium montmorillonite dispersions were investigated in the presence of a special type of cationic polymer [modified poly(ethylene glycol)]. 2-(Dimethylamino) ethyl methacrylate was polymerized with monomethoxy-capped oligo(ethylene glycol) via aqueous atom transfer radical polymerization. The tertiary amine residues of the resulting polymer were then quaternized with methyl iodide to obtain a cationic polyelectrolyte. The rheology and ζ-potential experiments showed that the cationic polymer adsorbed onto the sodium montmorillonite surface strongly. The rheological parameters (plastic viscosity and yield value) were obtained with a rotational low-shear rheometer. The results indicated a gradual increase in gelation with the addition of the cationic polymer, which reached a maximum at a cationic polymer concentration of 0.4–0.8 g/L. This gel-like dispersion showed pronounced thixotropy. A further increase in the polymer concentration resulted in a reduction in this gelation. The adsorption of the cationic polymer onto the clay surface reduced the ζ potential to small values, but no isoelectric point was observed. The basal-spacing measurements showed that the cationic polymer strongly adsorbed onto the sodium montmorillonite instead of entering the montmorillonite layers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 300–306, 2005

Key words: polyelectrolytes; rheology; water-soluble polymers; sodium montmorillonite; zeta potential

INTRODUCTION

Over the past few years, interest in polymers has increased considerably because of their technological applications, such as flocculating agents for the control of the stability of colloidal dispersions. Smectite group minerals have large adsorption capacities for polymer compounds and surfactants because of their unique crystal structures. Investigations of the adsorption ability of smectites for polymers (or polyelectrolytes) are multipurpose.[1–3] Montmorillonites are powerful adsorbents and are much cheaper than common adsorbents such as activated carbon. The adsorption and interaction of nonionic poly(ethylene oxide) (PEO) with clay components have been widely investigated.

Parfitt and Greenland[4,5] studied the effects of different molecular weights on the adsorption of poly(ethylene glycol) (PEG) onto clay minerals. In a previous article,[6] we reported the effects of nonionic PEG on the electrokinetic and rheological properties of clay dispersions.

The clay type, polymer concentration, and molecular weight were the parameters that modified the rheological properties of the system. We showed that nonionic PEG was added to the interlayers of the clays. The delamination of the clay layers increased with the molecular weight of PEG. A small decrease in the ζ potential as a function of the polymer concentration indicated that some of the PEG molecules attached to the clay surface. The clay dispersions (2% w/w) did not show a significant yield value in the presence of PEG. Recent studies have shown that the structure of the polymer plays an important role in the adsorption behavior of colloidal clay particles and thus affects the stability and rheological properties of the dispersion. Liang et al.[7] investigated the influence of the copolymer structure, temperature, and electrolyte concentration on the stability of titanium dioxide dispersions by means of rheological measurements and microscopy observations. They reported that the structure of the graft copolymer affected the adsorption behavior on the particles and the rheological properties of the dispersions. The copolymer, which contained more poly(methacrylic acid) groups in the backbone, stabilized the dispersion, but the dispersion weakly flocculated in the presence of other copolymers.

In this work, we extend our previous research[6] with a 2-(dimethylamino) ethyl methacrylate (DMA) based novel polyelectrolyte as the additive. We first polymerized DMA with monomethoxy-capped oligo(eth-

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TABLE I
Chemical Composition (wt %) of Sodium Montmorillonite

Sample	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	K_2O	MgO	MnO	TiO_2	P_2O_8
SNaM	62.66	19.31	6.10	2.36	0.22	0.72	2.48	0.01	0.78	0.04

ylene glycol) [OEG; mean degree of polymerization = 7–8, number-average molecular weight (M_n) = 350 g/mol] with aqueous atom transfer radical polymerization (ATRP). The tertiary amine residues of the resulting polymer were then quaternized with methyl iodide (MeI) to obtain a cationic polyelectrolyte. Second, the clay particle–particle interactions were studied, in the presence of the polymer, with rheological and electrokinetic techniques. The yield value, plastic viscosity, and ζ potential offer particularly sensitive means of detecting and evaluating the extent of stability and flocculation in colloidal systems. In addition to rheology and ζ-potential measurements, with X-ray diffraction (XRD) measurements, we could obtain information about whether the polymer adsorbed onto the clay surface or entered the clay lamellar layers.

EXPERIMENTAL

Sodium montmorillonite

The material used here was an aqueous suspension of montmorillonite consisting of platelike particles. The natural bentonite sample was obtained from the bentonite deposits in Enez, Turkey (Bensan Co.). A Philips PW 1040 model X-ray diffractometer instrument (Eindhoven, Netherlands) was used to determine the types of clay minerals. The dominant clay mineral was found to be dioctahedral montmorillonite; there were minor amounts of illite and kaolinite. Quartz was always present in the clay fraction. There was no other clay or nonclay mineral in the sample. Purified sodium montmorillonite (SNaM) was prepared from the corresponding bentonites with various treatments: First, iron oxides were removed with a sodium citrate and sodium dithionate buffering technique. For the removal of the carbonate, the bentonite dispersion was mixed with an NaCl/HCl solution and centrifuged several times and was then washed by water. The organic material was oxidized with a hydrogen peroxide solution at 80°C. The less-than-2-μm fraction was separated by sedimentation with Stoke's law. The dispersion was then sodium-saturated, dialyzed, and freeze-dried.[6,8,9] The layer charge, determined by the alkyl ammonium method, was 0.283 (equiv/mol). The cation-exchange capacity of montmorillonite was 0.7 mequiv/g.[10]

The major elements of the sample were determined with a Rigaku model 3070 X-ray fluorescence instrument (Tokyo, Japan) and with the rock standards of the Geological Survey of Japan. The results of the chemical analyses of the sample are given in Table I. The particle size distributions (PSDs) of the sodium montmorillonite were determined by the sedimentation technique method. A SA-CP4L photocentrifugal particle size analyzer (Shimadzu Corp., Kyoto, Japan) was used for particle size measurements. The sample was put into distilled water and dispersed ultrasonically for 10 min under 50 W of power. No dispersing reagents were used. The PSD measurements revealed that the size of 90% of the particles was less than 0.5 μm.

Polyelectrolytes

Since it was first developed independently by Matyjaszewski's group[11] and Sawamoto and Kamigaaito,[12] ATRP has been extensively studied. This new living polymerization chemistry is applicable to a wide range of monomers, including styrenics,[11,13,14] (meth)acrylates,[15] and acrylonitrile.[16] ATRP has provided a new and efficient way of conducting controlled radical polymerization. The ATRP of methacrylates with various alkyl halides as initiators and with a catalyst consisting of a transition metal complexed by a bidentate nitrogen-based ligand [e.g., Cu(I)X/2,2'-bipyridine (bipy)] proceeds in a controlled, living fashion.[17,18] The resulting polymers can have remarkably narrow polydispersities [the weight-average molecular weight/number-average molecular weight ratio (M_w/M_n) can be as low as 1.06]. The rate of polymerization depends on the initiator structure activity, catalyst activity, solvent polarity, monomer type, and temperature.[19] ATRP is usually performed either in bulk or in nonaqueous media and is remarkably tolerant of functional groups. Recently, ATRP has been extended to the polymerization of neutral and anionic water-soluble monomers in aqueous media. For example, Armes and coworkers reported the polymerization of sodium methacrylate,[20] sodium 4-vinylbenzoate,[21] and monomethoxy-capped OEG methacrylate[22] in aqueous media, with high yields in short reaction times at 20°C for the last two monomers.

The polymerization of DMA by ATRP was first investigated in nonaqueous media by Matyjaszewski et al.[15,23] They studied important parameters of the DMA homopolymer synthesis, including the reaction temperature, the initiator type, the use of various ligands, and the choice of solvent.

Bütün and coworkers[24–27] homopolymerized and block-copolymerized DMA with three other tertiary amine methacrylates with group transfer polymeriza-
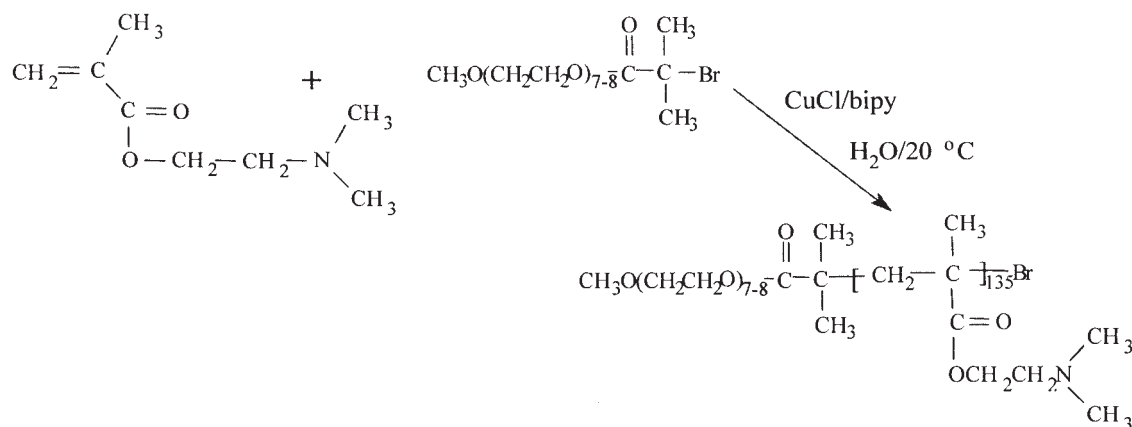
Figure 1 General reaction scheme for the polymerization of the DMA monomer via ATRP at 20°C.

tion and investigated their aqueous solution properties. They reported that the DMA homopolymer was water-soluble in both acidic and neutral media at room temperature. However, it could be precipitated from neutral or basic aqueous solutions at 32–46°C, given the appropriate molecular weight.[24] Both the selective quaternization of these new diblocks and the synthesis of shell crosslinked micelles (nanospheres) from their micelles have been also studied in detail.[25,26] In a recent article,[27] they also reported adsorption studies of a novel series of nearly monodisperse tertiary amine methacrylate based water-soluble diblock copolymers containing a quaternized DMA sequence as the first block onto a planar silica surface. These cationic diblock copolymers exhibited interesting pH-regulated adsorption at the silica–water interface.

Homopolymerization of DMA via ATRP

DMA (Aldrich) was passed through a basic alumina column to remove the hydroquinone inhibitor before use. Monomethoxy-capped OEG was kindly donated by Laporte (Hythe, UK) and was used as received. 2-Bromoisobutryl bromide, triethyl amine, copper(I) chloride (CuCl), and bipy were all purchased from Aldrich (Gillinhham-Dorset, UK) and used as received. The synthesis of a bromo-capped, oligo (ethyleneglycol)-based initiator (OEGBr), through the reaction of monomethoxy-capped oxyethylene glycol with 2-bromoisobutyryl bromide in toluene, was carried out with procedures reported elsewhere.[21,22]

Figure 1 describes the general procedure for the synthesis of the DMA homopolymer by ATRP in an aqueous solution at room temperature with copper(I) chloride as the catalyst, bipy as the ligand, and OEGBr as the ATRP initiator. Typically, the OEGBr initiator (0.5 g, 1 mmol, 1 equiv) was dissolved in doubly distilled water (20.0 mL) and purged with nitrogen for 30 min. The CuCl catalyst (0.1 g, 1 mmol, 1 equiv) and bipy ligand (0.4 g, 2.6 mmol, 2.6 equiv) were added to

another two-necked, round-bottom flask and purged with nitrogen for 30 min. The initiator solution was transferred to the flask containing the CuCl–bipy catalyst via a cannula under nitrogen and was stirred for 30 s; this was followed by the addition of the DMA monomer (19.4 mL, 115 mmol, 115 equiv) under nitrogen. The reaction mixture became dark-brown and more viscous within 5–10 min. Termination occurred rapidly upon exposure to air, as indicated by the color change from brown to blue [oxidation of Cu(I) into Cu(II)].

In the purification of the OEG–DMA homopolymer, a different method from the literature[16–18] was used to remove the copper catalyst. After polymerization, a 50% aqueous polymer solution was diluted 10-fold with water and heated above the cloud point of the DMA block (50°C). The copolymer was precipitated from this hot aqueous solution by the addition of a small amount of the KOH solution (2.0M). The white precipitate was quickly washed with hot water for the removal of excess KOH and was dried *in vacuo*. The white color indicated that the level of the copper catalyst contamination was very low.

Aqueous gel permeation chromatography (GPC) studies (with PEO standards) indicated that the original OEG block had a low polydispersity ($M_w/M_n < 1.10$) and an M_n value of approximately 350, which corresponded to a degree of polymerization of 7–8 for ethylene oxide residues. With this ethylene oxide block treated as an end group, an inspection of the ^{1}H-NMR (D$_2$O) spectrum of the precursor OEG–DMA homopolymer indicated an average degree of polymerization for the DMA block of 135. Thus, the overall M_n value of the OEG–DMA homopolymer was calculated to be 21,700. GPC studies [with tetrahydrofuran (THF) as an eluent] of the homopolymer indicated a polydispersity (M_w/M_n) of 1.15.
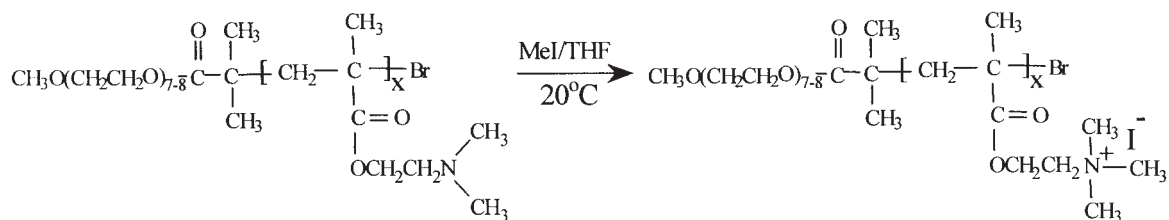
Figure 2 Reaction scheme for the quaternization of the DMA homopolymer with MeI in THF at 20°C.

Quaternization of the tertiary amine methacrylate homopolymers

The quaternization of the OEG–DMA homopolymer was carried out with MeI at 20°C (see Fig. 2). The DMA homopolymer (15.0 g) was dissolved in THF (250.0 mL), and then MeI (25.0 mL) was added. The methylation of the DMA homopolymer was very fast and was completed within 20 min at 20°C in THF. Because the resulting quaternized homopolymer was insoluble in THF, the excess quaternizing agent was readily removed by Soxhlet extraction.

The extent of quaternization was assessed with ^{1}H-NMR spectroscopy. In the ^{1}H-NMR spectrum of the DMA homopolymer in D_2O (not shown), the six dimethylamino protons appeared at $\delta = 2.3$–2.4. After quaternization, nine quaternary ammonium protons ap-

peared at $\delta = 3.3$. A comparison of the peak integral of this signal with that of the oxymethylene proton signal at $\delta = 4.1$ and the absence of any unquaternized dimethylamino protons at $\delta = 2.3$–2.4 indicated 100% quaternization (see Fig. 3). The molecular weight of the quaternized OEG–DMA homopolymer (OEG–QDMA) was then calculated from ^{1}H-NMR analyses of the quaternized homopolymer, through a comparison of the integral of peak A with the integral of peak B (see Fig. 3), with 100% quaternization assumed, to be 40,900.

Methods

The flow behavior of the dispersions was measured with a Brookfield DVIII+ low-shear rheometer at 24 ± 1°C. The maximal shear rate was $\gamma = 328$ s^{-1}. The
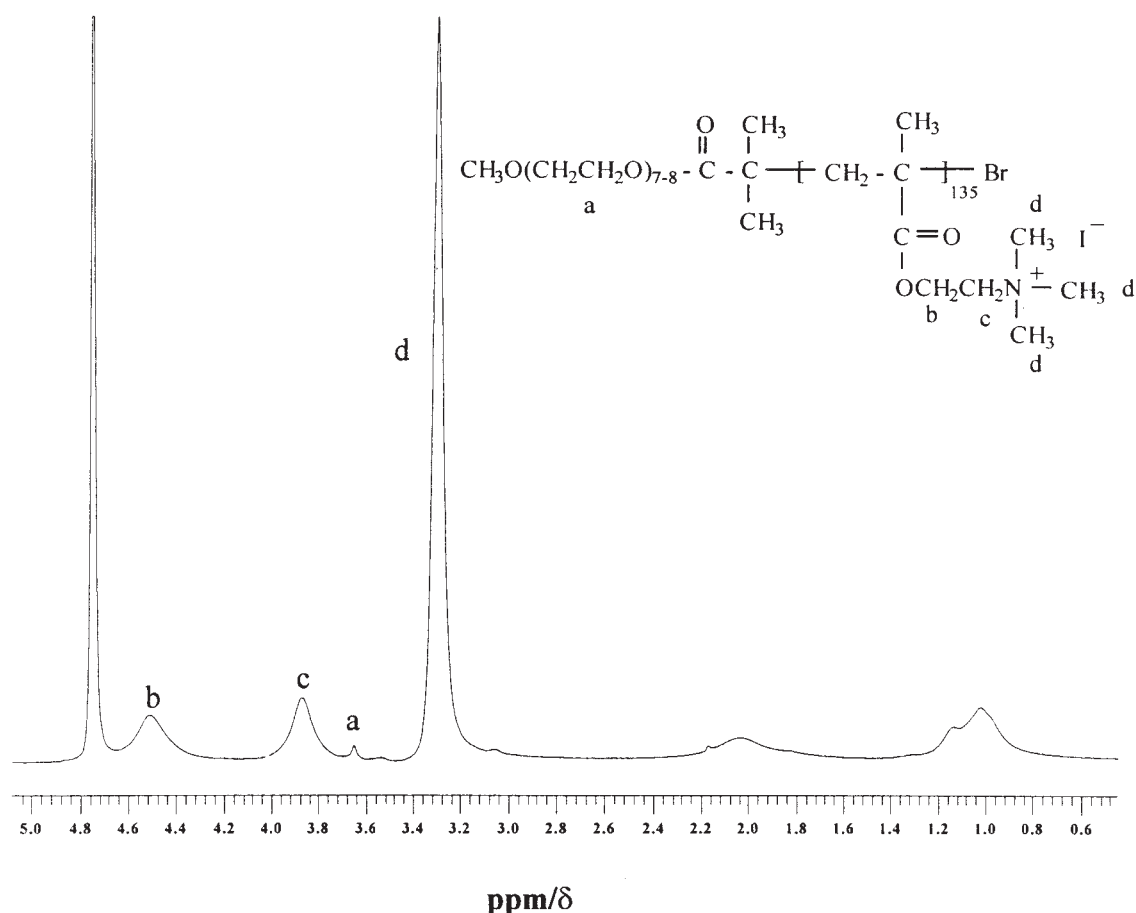

ppm/δ

Figure 3 ^{1}H-NMR spectrum of the OEG–QDMA homopolymer in D_2O at 20°C ($M_n = 40,900$, polydispersity = 1.15)

sample was dispersed in water (2% w/w) and was shaken intensively for 24 h. The polymer solution was then added to the clay dispersion in a concentration range of 0.005–10 g/L. An adsorption time of 24 h was adopted for the OEG–QDMA homopolymer. Once the curve of the shear stress versus the shear rate was obtained for sodium montmorillonite under the given experimental conditions, the value of the extrapolated shear stress was determined from the intersection of the extrapolated linear portion of the curve with the axis. The method of least squares was used to determine the values of this intersection. The plastic viscosity was derived from the slope of this linear section. All the suspensions exhibited Bingham plastic behavior. The degree of thixotropic and antithixotropic behavior was measured from the area of the hysteresis loop.[28]

The electrophoresis measurements were then carried out, with a small portion of the sample injected into the cell of a Zetamaster 2000 instrument (Worcestershire, UK) at room temperature. The pH of all the samples was approximately 5–6. Multiple measurements of the electrophoretic mobility of the particles were made, and the electrophoretic mobility was then converted into the ζ potential with established theories.

The XRD data were taken with a Philips PW 3020 goniometer. The X-ray source was Cu Kα (40 kV, 40 mA). A uniform mixture from the sodium montmorillonite dispersion and polymer was prepared through simple mixing and was left for 24 h in the shaker. The samples were then spread on glass tiles gently and dried at room temperature.

RESULTS AND DISCUSSIONS

Cationic polyelectrolytes are effective flocculants for many colloidal solid dispersions such as montmoril-
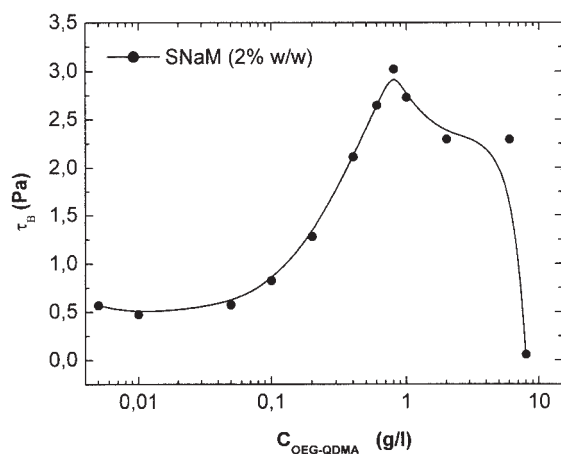

Figure 4 Influence of the OEG–QDMA homopolymer on the Bingham yield value (τ_B) of 2% (w/w) sodium montmorillonite dispersions.
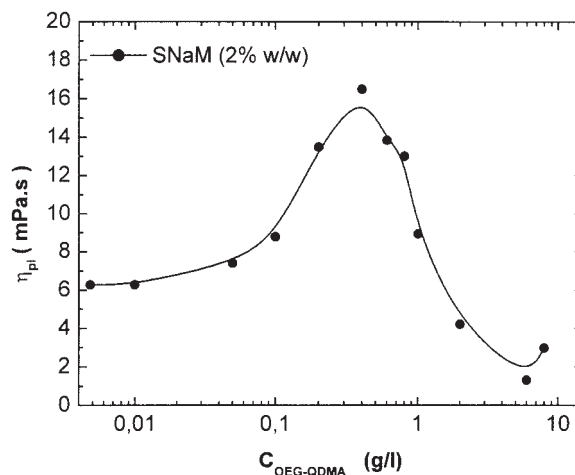

Figure 5 Influence of the OEG–QDMA homopolymer on the plastic viscosity (η_{pl}) of 2% (w/w) sodium montmorillonite dispersions.

lonites. Generally, flocculation occurs by the adsorption of polymers onto solid particles and the bridging of polymer chains between them. In the use of cationic polymers, adsorption onto negatively charged montmorillonites and consequent flocculation occur by electrostatic attraction. At higher polymer concentrations, the electrical double layers of clay particles are compressed by adsorbed polymer layers. Through the adsorption of a polymer layer onto the particle surface, a steric barrier is obtained between the particles. The magnitude of the attractive forces is reduced by the fact that the smallest possible distance between the particles is increased by the polymer chain. When a cationic polymer is used in the stabilization of the dispersion, the adsorbed polymer layer sterically stabilizes the dispersions because of the repulsive force between the cationic polymer layers.

The rheological results indicated that the addition of the OEG–QDMA homopolymer to a 2% (w/w) sodium montmorillonite dispersion led to a gradual buildup of pseudoplastic behavior until a maximum was reached around 0.8 g/L OEG–QDMA. In comparison with the effect of nonionic PEG in our previous work, the addition of cationic OEG–QDMA to a sodium montmorillonite dispersion had a yield value, which we did not observe with nonionic PEG. The results given in Figure 4 show a gradual increase in the gelation upon the addition of the OEG–QDMA homopolymer, which reached a maximum of 3.2 Pa at 0.8 g/L OEG–QDMA; a further increase in the polymer concentration resulted in a reduction in this gelation.

Both the measured plastic viscosity and the yield values showed the same trend with the OEG–QDMA concentration. The plastic viscosity of the sodium montmorillonite dispersion increased to a sharp maximum of 16.5 mPa s at a polymer concentration of approximately 0.4 g/L (see Fig. 5).
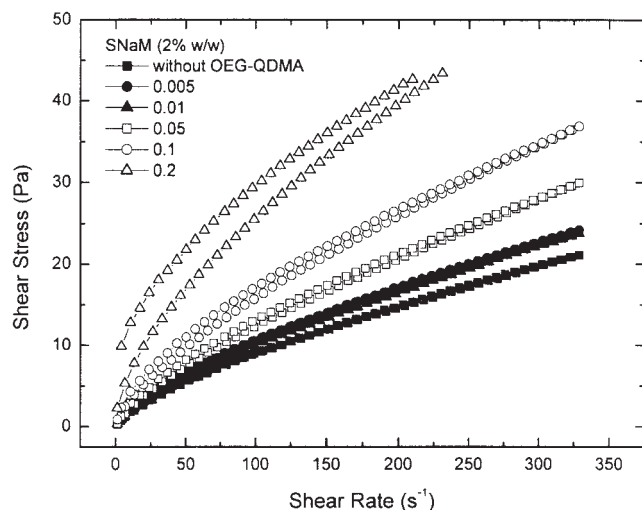
Figure 6 Shear stress as a function of the shear rate for sodium montmorillonite dispersions in the presence of the OEG–QDMA homopolymer.

Both the high plastic viscosity and the yield value indicated a strong interaction between the clay particles and cationic OEG–QDMA homopolymer, as we expected. Being a cationic polyelectrolyte, the OEG–QDMA homopolymer could presumably interact with the negatively charged sodium montmorillonite through cation exchange. This interaction could occur in two ways. First, the OEG–QDMA homopolymer, having a positively charged quaternary amine group on each DMA residue (see Fig. 2), adsorbs onto the negatively charged sodium montmorillonite through the resulting complexation between the polymer and clay particle, and stabilization takes place. Second, the cationic OEG–QDMA homopolymer may also interact with different clay particles at the same time and form bridges between particles so that a voluminous network occurs.

The flocculation of the dispersions was greatly increased by a small addition of the OEG–QDMA homopolymer, and a maximum was reached at a OEG–QDMA homopolymer concentration of 0.8 g/L. A further increase in the OEG–QDMA concentration led to a reduction in the flocculation of the dispersions. The OEG–QDMA concentrations at which the maximum yield value is obtained should correspond to the optimum polymer dosage for particle bridging. Flocculation may be attributed to the bridging of micelles between the particles, which promotes the formation of a strong gel-like network.

The plastic viscosity and yield value increased with an increase in the polymer concentration. The shear stress was quite low in the absence of the cationic OEG–QDMA homopolymer. Increasing the polymer concentration caused an increase in the shear stress. The shear-stress/shear-rate measurements (flow curve) revealed that both the shear stress and yield
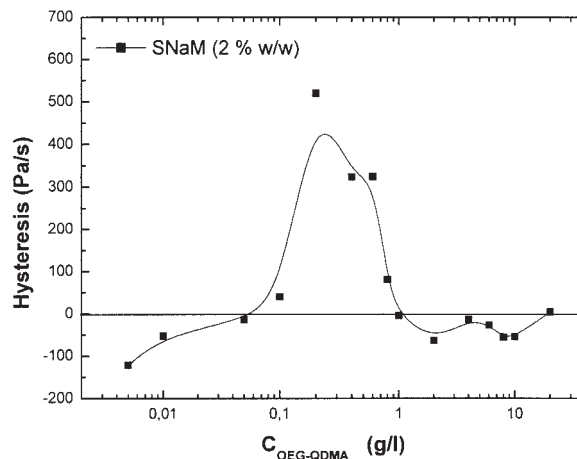
value increased with the OEG–QDMA concentration (see Figs. 4 and 6). Figure 6 shows the effect of varying the OEG–QDMA concentration on the flow behavior of sodium montmorillonite (2% w/w). The flow curve of sodium montmorillonite shows a small hysteresis loop that increases with the polymer concentration.

A hysteresis effect was observed for sodium montmorillonite dispersions. Weak antithixotropic behavior was observed for sodium montmorillonite in the absence of the polymer because shearing induced delamination. The flow behavior of the OEG–QDMA/sodium montmorillonite dispersion changed from antithixotropic to thixotropic at a polymer concentration of 0.1 g/L. An increase in the OEG–QDMA concentration, which induced bridging flocculation, also promoted the formation of a network (gel-like) in the system. For the same reason, a maximal thixotropy of 520 Pa/s was observed at 0.2 g/L OEG–QDMA (Fig. 7). The further addition of the OEG–QDMA ho-
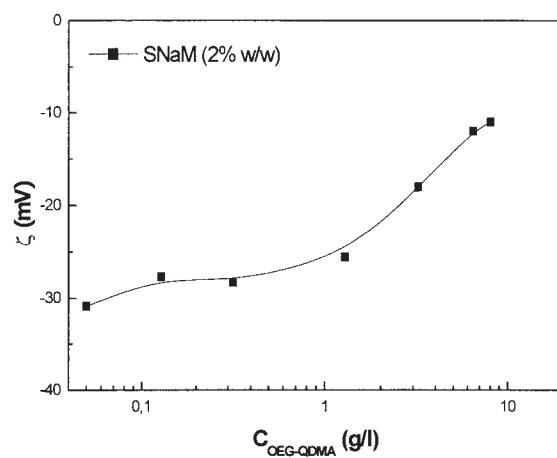

Figure 7 Hysteresis of sodium montmorillonite dispersions in the presence of the OEG–QDMA homopolymer.

Figure 8 Influence of the OEG–QDMA homopolymer on the ζ potential of 2% (w/w) sodium montmorillonite dispersions.
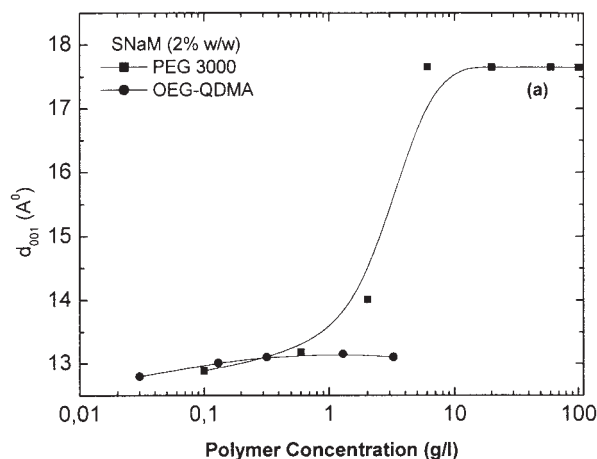
Figure 9 Basal spacing (d_{001}) for sodium montmorillonite dispersions as a function of the OEG–QDMA homopolymer concentration [(a) ref. 6].

mopolymer reduced thixotropy again (Fig. 7). These results were in good agreement with the behavior of the yield value and the plastic viscosity of the sodium montmorillonite dispersions.

The ζ potential decreased with an increasing concentration of OEG–QDMA. The initial suspension had a ζ potential of -44 mV in the natural system, but the same dispersion became more flocculated after the addition of OEG–QDMA and began to aggregate by the adsorption of cationic OEG–QDMA on the negatively charged sodium montmorillonite surface through the resulting complexation between the polymer and clay particle. The results presented in Figure 8 indicate that the potential at the plane of shear within the double layer of the sodium montmorillonite became less negative as more cations (OEG–QDMA) were forced toward the sodium montmorillonite surface by the compression of the double layer at higher OEG–QDMA concentrations.

The XRD measurements carried out to investigate the change in the basal spacing (d_{001}) with increasing polymer concentration agreed with the rheological results. As the polymer concentration increased, the basal spacing of sodium montmorillonite did not change (Fig. 9). Other concentrations (<3.2 g/L) of the OEG–QDMA polymer in sodium montmorillonite could not studied by XRD because of the interference of polymer and sodium montmorillonite diffraction peaks. The X-ray results indicated that the interlamellar adsorption of the OEG–QDMA homopolymer did not take place on sodium montmorillonite. The cationic OEG–QDMA homopolymer was adsorbed, but interlamellar adsorption did not occur. By comparing this behavior with that of the nonionic PEG 3000 that we used in our pervious study, we found that this novel form of PEG (OEG) adsorbed onto sodium montmorillonite, whereas nonionic PEG molecules were added to the interlayer structures and revealed the expansion of d_{001} spacings up to 17.6 Å (Fig. 9).

From these investigations, we have concluded that this novel cationic polymer enhances the adsorption ability of PEG. The interactions between the cationic polymer and sodium montmorillonite particles are mainly electrostatic and induce the bridging flocculation to the polymer–clay system. The adsorbed polymer greatly changes the rheological and colloidal properties of sodium montmorillonite dispersions. With increasing polymer concentration, sodium montmorillonite dispersions show high yield values and thixotropic loops; this indicates gel-like structures in the systems.

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