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ORIGINAL CONTRIBUTION

O. Quadrat
L. Mrkvičková
Z. Walterová
L. Titkova
P. Bradna
J. Šňupárek

Structure and flow behavior of crosslinked ethyl acrylate–methacrylic acid copolymer dispersion particles

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O. Quadrat (✉) · L. Mrkvičková
Z. Walterova
Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
16206 Prague 6
Czech Republic
E-mail: quadrat@imc.cas.cz

L. Titkova
Institute of Petrochemical Synthesis
Academy of Sciences of Russia
117912 Moscow B-71
Russia

P. Bradna
Spofa-Dental Co.
Černokostelecká 84
10030 Praha 10
Czech Republic

J. Šňupárek
Department of Polymer Materials
University of Pardubice
53210 Pardubice
Czech Republic

Abstract Changes in viscosity, pH and static light scattering behavior on alkali addition of model dispersions of statistical copolymers of ethyl acrylate with 15 and 50 wt% of methacrylic acid prepared by semicontinuous emuslion copolymerization and crosslinked with various amount of *N*,*N*′-methylenebisacrylamide were investigated. It was found that about 1% of crosslinking agent was sufficient to prevent unpredictable disintegration of dispersion particles and gauranteed reproducible flow behavior of alkalinized dispersions. The viscosity of alkalinized dispersions of crosslinked particles at low concentration is controlled by the effective hydrodynamic volume of swelled particles which decreases with the crosslinking degree of copolymer. On the other hand, at higher particle concentration close to critical concentration at which the space is filled up by swelled particles the influence of particle interaction prevails and due to lower deformability of crosslinked particles viscosity increases with a crosslinking degree. In comparison with similar dispersions prepared without a crosslinking agent these results indicated much uniform structure of dispersion particles and suppression of influence of random crosslinking due to chain transfer reactions. The study shows that dispersions of crosslinked copolymers of this type could be considered as thickners of latex binders with stable and reproducible thickening properties.

Key words Polymer colloids – crosslinked ethyl acrylate–methacrylic acid copolymers – structure of particles – flow properties

Introduction

At present polymer colloids rank among industrial products used for many practical purposes. Among them, dispersions of acrylate copolymers prepared by emulsion copolymerization of monomers carrying carboxylic groups are well known as effective thickening agents for setting up optimum flow properties of various latex materials [1, 2]. On alkalinization of originally acid dispersion, electrical charges of ionized carboxylic groups on polymer chains give rise to Coulombic interactions leading to an extension of the particle double layer, swelling of copolymer particles or, if the content of carboxylic groups is large, dissolution of particles to a polyeletrolyte solution. All these effects cause a dramatic change in flow properties of the system which may be used to advantage in the formulation of ecological water-based coatings. Addition of even a small amount of such dispersion to a latex binder may cause after akalinization a considerable increase in viscosity, yield stress and dynamic moduli of the system [3].

It was found [4, 5] that the thickening effect of dispersions of statistical ethyl acrylate–methacrylic acid copolymers prepared by semicontinuous emulsion polymerization with a monomer emulsion feed is determined by the structure and mutual interactions of dispersion particles after alkali addition. At first, it was supposed that the dispersion particles prepared by this procedure have a homogeneous structure and are composed predominantly of linear copolymers [6]. However, our previous experiments demonstrated that, due to crosslinking of polymer chains probably caused by chain transfer reactions and a coagulative mechanism of particle growth, the structure of such particles is more complex and depends on the polymerization route. It was found that even if the dispersions were prepared under the same conditions, their structure and flow properties after alkali addition may differ considerably.

In the case of dispersion prepared to high solids (about 25 wt%), our experiments revealed unexpected disintegration of original copolymer particles into small colloid subparticles on alkali addition followed by swelling or even dissolution [7–9]. For that reason, flow properties of the alkalinized particles and their interaction in multicomponent systems depend not only on the methacrylic acid content and on the particle size in the original acid dispersions but, in particular, on dimension and structure of fragments obtained after alkalinization [4, 8]. It is obvious that using such dispersions as thickners could hardly lead to reproducible results.

We suppose that, to prevent the unexpected behavior, particles of ethyl acrylate–methacrylic acid copolymers intentionally crosslinked with a small amount of a crosslinking agent could be used. This paper reports the results of investigation of such model material with the aim to obtain dispersions with better controlled properties suitable in paint industry as well defined thickners of acrylic latices.

Experimental

Dispersions

Two series of model dispersions of the ethyl acrylate copolymer, with a low content (15 wt%-L dispersions) and with a high content (50 wt%-H dispersions) of methacrylic acid, each with 0, 0.25, 1.25, 2.5 and 5 wt% *N*,*N*′-methylenebisacrylamide (MBA) as a crosslinking agent, were prepared by a semicontinuous emulsion polymerization with a monomer emulsion feed (Table 1). Polymerization initiated with 1 wt% ammonium peroxodisulfate (relative to the monomers) was carried out in a stainless-steel reactor under nitrogen atmosphere at 80 °C. Disponil AES 60 (sodium alkylaryl ether polyglycol sulfate, Henkel), in an amount of 3.25 wt% of active component (relative to the monomers) was used as an emulsifier. Such process guarantees statistical composition of the copolymer of dispersion particles [10–12].

Emulsions of technical grade ethyl acrylate (Chemical Works, Sokolov, Czech Republic) with methacrylic acid (Roehm, Darmstadt, Germany) and MBA (American Cyanamide) were fed into the reactor at a constant rate for 20 min followed by heating at 80 °C for 90 min. After polymerization, the polymer solids made about 7 wt%; pH was 2–3. We suppose that the low solids content reduces crosslinking of dispersion particles by chain transfer.

Table 1 Polymerization recipes

Reactor charge (in grams)					
	Water			400	
	Disponil AES 60			1.3	
	Ammonium peroxodisulfate			0.4	
Monomer emulsion feed (in grams)					
	L/0	L/0.25	L/1.25	L/2.5	L/5
Water	80	80	80	80	80
Disponil AES 60	1.3	1.3	1.3	1.3	1.3
Ethyl acrylate	34.0	33.9	33.5	33.0	32.0
Methacrylic acid	6	6	6	6	6
Methylenebisacrylamide	0	0.1	0.5	1.0	2.0
	H/0	H/0.25	H/1.25	H/2.5	H/5
Water	80	80	80	80	80
Disponil AES 60	1.3	1.3	1.3	1.3	1.3
Ethyl acrylate	20	19.9	19.5	19.0	18.0
Methacrylic acid	20	20	20	20	20
Methylenebisacrylamide	0	0.1	0.5	1.0	2.0

Conductometric titration

The content of acid groups in the copolymers was determined by conductometric titration with NaOH (OK-104 conductoscope, Radelkis, Hungary).

Sample preparation

Samples for pH, viscosity and light scattering measurements were prepared by adding NH_4OH solution to the originally acid materials to reach a required pH value. Samples for light scattering measurements were also prepared in the recovered acid form – an acetic acid solution was added to fully alkalinized dispersion (pH ~ 9) to reach again the original pH ≈ 3.

The degree of alkalinization was calculated as $\alpha = [NH_4^+]/c_{MAA}$, where $[NH_4^+]$ is the molar concentration of NH_4OH added and c_{MAA} is the molar concentration of methacrylic acid monomeric units. All measurements were carried out at 25 °C, with samples stabilized for 1 day after alkalinization or acid recovery.

pH and viscosity mesurement

pH changes accompanying the addition of ammonium hydroxide to the dispersions at 0.4 wt% of solids were followed by means of a digital pH meter 64 (Radiometer Copenhagen) with a combined electrode GK 2321 C.

Viscosity of dispersions in the course of alkalinization was measured with a glass capillary viscometer of the Ostwald type at a shear stress about 0.6 Pa. The same viscometer was used for the measurement of the viscosity–particle concentration dependence of moderately concentrated dispersions alkalinized to pH 9.2.

The hydrodynamic volume of the alkalinized dispersion particles at infinite dilution (intrinsic viscosity) was measured in a capillary dilution viscometer of an Ubbelohde type.

Static light scattering

The static light scattering (SLS) was measured (FICA 40 000 photogoniodiffusometer) in the range of scattering angles $\theta = 30–150°$ with vertically polarized light of the wavelength $\lambda_0 = 546$ nm. The samples were filtered (Jena Glass F4 filter) and measured at 25 °C. The dependence of the excess Rayleigh ratio $R(K)$ (reduced intensity of scattered light) on the scattering vector $K = (2\pi/\lambda)\sin\theta/2$, where λ is the wavelength of light in solution, was determined. For colloidal dispersions, $R(K)$ is given by superposition of internal and external interference of the scattered light [13, 14]. When the dimensions of scattering particles are larger than $\lambda/20$, the internal interference is given, in principle, by a single scattering factor $P(K)$. For monodisperse spherical particles at infinite dilution, $P(K)$ is defined by equation [15]:

$$P(K) = [(3/K^3D^3)(\sin KD - KD\cos KD)]^2\ , \qquad (1)$$

where D is particle diameter. In the dilute dispersions studied, maxima on the experimental dependences $R(K)$ vs. K were observed at low K values. This phenomenon was caused by the effect of external interference as a consequence of nonrandom arrangement of uniform particles in space and it can be expressed by $S(K)$ function. Thus, to estimate the particle diameter D (z-moment of the size distribution) regarding proportionality $R(K) \approx P(K)\,S(K)$, the calculated $P(K)$ functions were compared with the experimental plots $R(K)$ vs. K in the range of high values of K ($\theta > 90°$) (cf. Fig. 1).

Results and discussion

Behavior of dispersions in the course of alkalinization

Changes in particle structure

To obtain direct information about changes in the particle size due to alkalinization, the multiangle static light scattering as the best method for the purpose was used. Original aqueous dispersions (pH ≈ 3) showed characteristic experimental dependences of the reduced intensity of scattered light $R(K)$ (Rayleigh ratio) vs. K with external interference maxima at small K-values. After alkalinization, an increase in the slope of the $R(K)$ function in the range of higher K values (increase in internal interference) indicates an increase in the original particle diameter.

Depending on the content of both carboxylic groups and crosslinking agent, the alkalinization produced particles ranging from the molecular to colloidal size. In addition to particle swelling, disintegration or even dissolution of original dispersion particles took place. Thus, an increase in particle diameter is controlled primarily by some surviving originally swelled particles and is associated with a considerable decrease in $R(K)$ values and diminishing of the external interference effect (maximum $R(K)$ function gradually disappeared) [16]. This behavior was just observed for the dispersion with no or a small content of crosslinking agent. In that case, the intensity of the scattered light in samples L-0 and H-0 decreased during alkalinization twice and four times, respectively, and the values of the slope of $R(K)$ function were unreliable. Consequently, the recovery process (alkali treatment to pH ≈9 followed by acidification to pH ≈3) [8] showed unreproducible results. A slight disintegration of original particles is also assumed in alkalinized samples L-0.25 and H-0.25, as follows from a low decrease in the particle size after recovery (Table 2).

Starting from medium contents of MBA, the recovery confirmed a greater stability of dispersion particles. It can be assued that these alkalinized systems consisted predominantly of swelled original particles. Particles of L-dispersions swelled less than those of H-dispersions and swelling was gradually suppressed by the increasing content of MBA. Table 2 shows that if the MBA content is large, the swelling is no more controlled by the content of ionized carboxylic groups in the copolymer. For that reason, the difference in swelling between samples L-5 with 15 wt% of methacrylic acid and H-5 with 50 wt% of methacrylic acid was lower.

Table 2 Diameters of origial, D_o and recovered, D_r, dispersions measured by static light scattering

	L/0	L/0.25	L/1.25	L/2.5	L/5
D_o[nm]	100	100	90	115	140
D_r [nm]	—	80	90	115	140
	H/0	H/0.25	H/1.25	H/2.5	H/5
D_o[nm]	80	110	150	170	150
D_r [nm]	—	80	140	200	150

Changes in pH

In our previous papers, it was reported [17] that changes in particle structure of ethyl acrylate–methacrylic acid copolymers during the alkali treatment are sensitively reflected in the change in pH of the dispersion. Also in the case of crosslinked particles, the method showed characteristic results. Titration curves obtained during alkalinization of dispersions with particle concentration $c_p = 4 \times 10^{-3}$ g ml^{-1} are presented in Figs. 1 and 2. The curves can be divided into several characteristic parts, each of

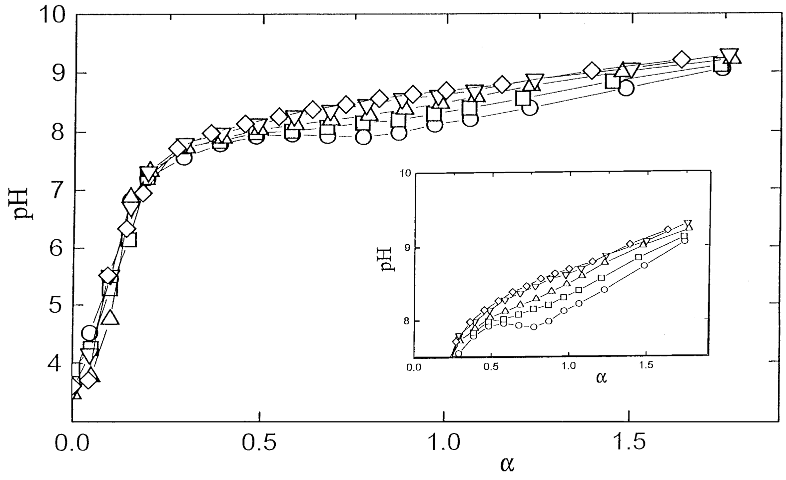

Fig. 1 Dependence of pH on the degree of alkalinization α; Particle concentration 0.4 wt%. Dispersions: (○) L/0, (□) L/0.25, (△) L/1.25, (▽) L/2.5, (◇) L/5

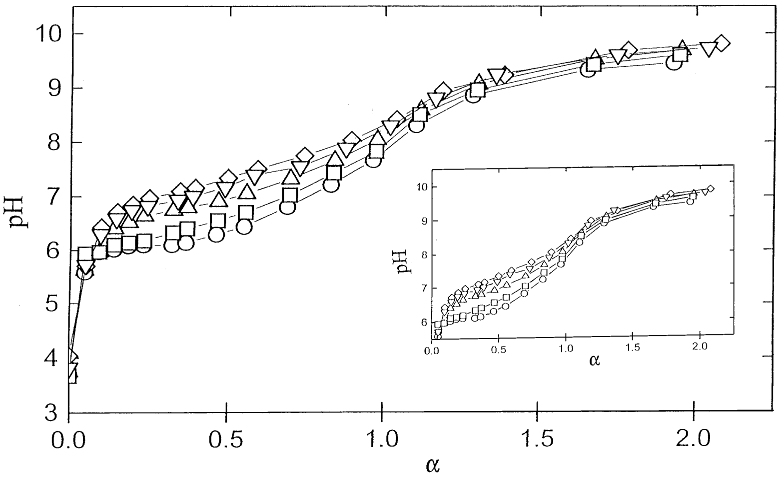

Fig. 2 Dependence of pH on the degree of alkalinization α; Particle concentration 0.4 wt%. Dispersions: (○) H/0, (□) H/0.25, (△) H/1.25, (▽) H/2.5, (◇) H/5

them corresponding to a different change in particle structure.

The initial part of the curves due to neutralization of carboxylic groups on the particle surface is very steep and similar for all samples. In the case of L-dispersions (Fig. 1) without crosslinking agent, an inrease in pH diminishes at $\alpha \approx 0.2$ and pH ≈ 7 and reaches a flat maximum at $\alpha \approx 0.5$ pH. It was assumed [17] that at that time alkali begins to penetrate the swelling particles, which start to disintegrate into smaller subparticles. The alkali required for neutralization of newly uncovered carboxylic groups is greater than the alkali addition and pH decreases to a shallow minimum. When disintegration of particles ceased and the remaining carboxylic groups are gradually neutralized, pH slowly increases.

If MBA in the copolymer is present, disintegrations of particles is suppressed. Then, after neutralization of the surface carboxylic groups, the minimum disappears and only a pH increase indicates a gradual neutralization of carboxylic groups inside the swelled particles. The higher content of MBA, the smaller particles swelling can be assumed and, also, at the same α a higher pH value of the dispersion appears.

Due to higher contents of carboxylic groups in the copolymers of H-dispersion the swelling of particles at the same degree of alkalinization is greater than in the previous case. For the sample without MBA, after an initial steep pH rise, only a plateau (much lower than in the L-dispersions) and a continuous slight increase follow (Fig. 2). This suggests that disintegration of particles is more pronounced and leads to the dissolution of the copolymer. On the other hand, in the presence of MBA, neutralization of carboxylic groups of the swelled particles is similar to the L-dispersions, however, it occurs at lower pH values.

Changes in viscosity

Swelling and disintegration of particles during alkalinization caused characteristic changes in viscosity of dispersions (Fig. 3). During a steep pH increase in the initial part of the titration curves, viscosity remained practically constant, which indicated that the particle size and shape remained unchanged. An increase in viscosity when a particle swelling began. Here the steepness of the rise to the maximum viscosity reflects the superposition of swelling and disintegration of particles.

The comparison of the $\eta - \alpha$ plots for samples with low and high contents of methacrylic acid shows both common and different features. In both cases, the maximum increase in viscosity sets in for dispersions with a 0.25 wt% content of MBA, while in the case of dispersions without MBA, the increase was smaller. For other samples, maximum viscosities of the alkalinized dispersions were much lower and decreased with the MBA content in the copolymer. In the case of uncrosslinked sample H-0 the maximum was very flat due to a considerable particle disintegration starting at much lower α-values [16]. Maximum viscosity for sample H-0.25 was several times higher than that for the sample L-0.25 and was shifted to lower α values. It was followed by a pronounced viscosity decrease. We suppose that it is a consequence of a gradual disintegration or even dissolution of weakly crosslinked structure of particles.

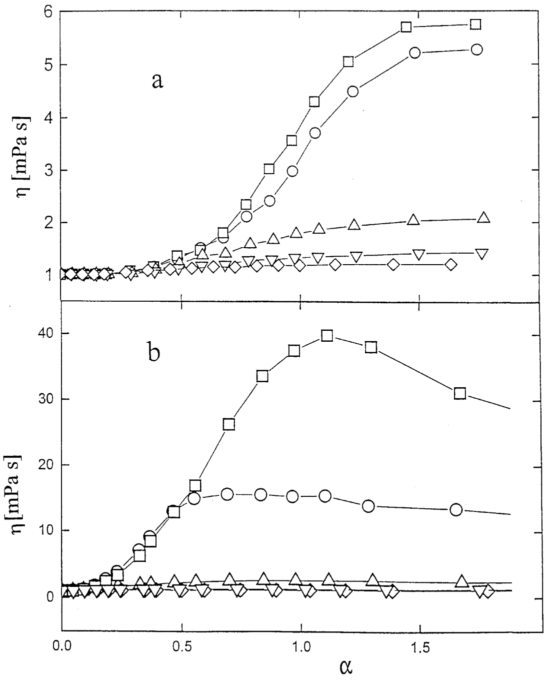

Fig. 3 Dependence of viscosity η on the degree of alkalinization α; (a): L-dispersions, (b): H-dispersions. (For the point denotation, see Figs. 1 and 2.)

The results mentioned above were characteristic of $c_p = 4 \times 10^{-3}\,\mathrm{g\,ml^{-1}}$. It will be shown in the next part that the dependences of the maximum viscosity of dispersions reached in the course of alkalinization on the content of MBA in the copolymer at other particle concentrations considerably differ.

Viscosity of alkalinized dispersions

The hydrodynamic volume of alkalinized dispersion particles at infinite dilution (intrinsic viscosity) $[\eta]$ obtained after extrapolation of the reduced specific viscosity to the zero particle concentration for samples both with low and

Table 3 Intrinsic viscosity $[\eta]$, volume swelling raio ϕ_s/ϕ_o and critical concentration c_{cr} of particles in fully occupied space of dispersion

	L/0	L/0.25	L/1.25	L/2.5	L/5
$[\eta]$ [ml g^{-1}]	795	725	249	110	31
$\phi_s \times 10^2$ [g mol^{-1}]	365	333	114	50	14
$c_{cr} \times 10^2$ [g ml^{-1}]	0.31	0.34	1.0	2.3	8.0
	H/0	H/0.25	H/1.25	H/2.5	H/5
$[\eta]$ [ml g^{-1}]	2950	1650	290	92	54
$\phi_s \times 10^2$ [g mol^{-1}]	1350	990	133	42	25
$c_{cr} \times 10^2$ [g ml^{-1}]	0.08	0.15	0.86	2.7	4.6

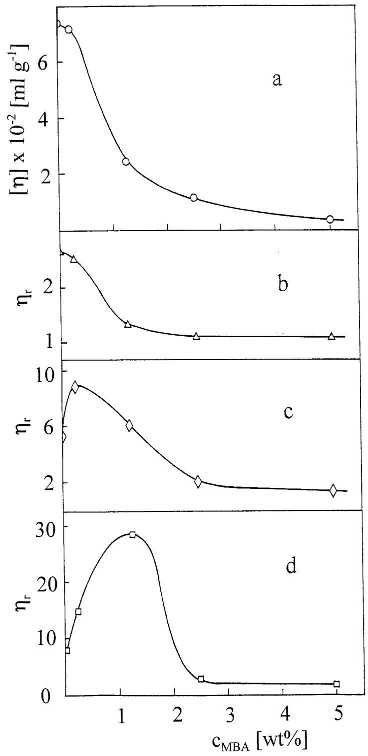

Fig. 4 Dependence of the particle hydrodynamic volume (intrinsic viscosity) $[\eta]$ and relative viscosity η_r of L-dispersions on the concentration of MBA in the copolymer c_{MBA}; concentration of dispersion particles (g cm^{-3}): (a) 0, (b) 1×10^{-3}, (c) 5×10^{-3}, (d) 1×10^{-2}

high contents of methacrylic acid only decreases with the increase in c_{MBA} (Table 3), i.e. the highest value corresponds to the non-crosslinked copolymer (Figs. 4a and 5a). Similar dependences were found for relative viscosity at a low (1×10^{-3} g ml^{-1}) concentration of dispersion particles (Fig. 4b). On the other hand, when the particle concentration increased to 5×10^{-3} g ml^{-1} (and also to 4×10^{-3} g ml^{-1}, Fig. 3), maxima on the plots appeared at 0.25 wt% of MBA (Figs. 4c and 5b).

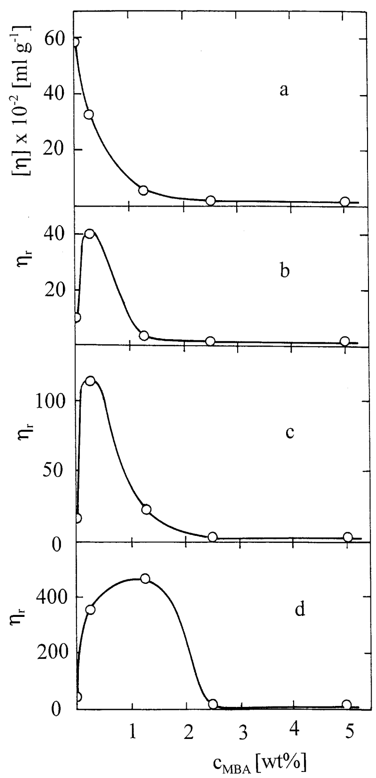

Fig. 5 Dependence of the particle hydrodynamic volume (intrinsic viscosity) $[\eta]$ and relative viscosity η_r of H-dispersions on the concentration of MBA in the copolymer c_{MBA}; concentration of dispersion particles (g cm^{-3}): (a) 0, (b) 5×10^{-3}, (c) 1×10^{-2}, (d) 2×10^{-2}

At higher particle concentrations, the shape of the η_r–c_{MBA} dependences for L and H dispersions differed. While for $c_p = 1 \times 10^{-2}$ g ml^{-1} of L–dispersions, the maximum viscosity was shifted to 1.25 wt% of MBA (Fig.4d), for H–dispersions its position at 0.25 wt% remained unchanged (Fig. 5c); to shift it to the higher c_{MBA} value, a higher particle concentration (about 2×10^{-2} g ml^{-1}) was needed (Fig. 5d).

To explain this viscosity behavior, three main factors – hydrodynamic volume, concentration of dispersion particles and their interaction must be considered. Our previous experiments revealed [18] that the hydrodynamic volume of particles (intrinsic viscosity) in acid dispersions of acrylate copolymers containing carboxylic groups is very close to Einstein's theoretical value [19] of 2.5 for rigid undeformable spheres. Thus, considering the experimental values of intrinsic viscosity of swollen alkalinized particles $[\eta]$, an increase in the particle hydrodynamic volume during alkalinization can be expressed as the effective particle volume swelling ratio

$$\phi_s/\phi_o = \rho[\eta]/2.5 \; . \qquad (2)$$

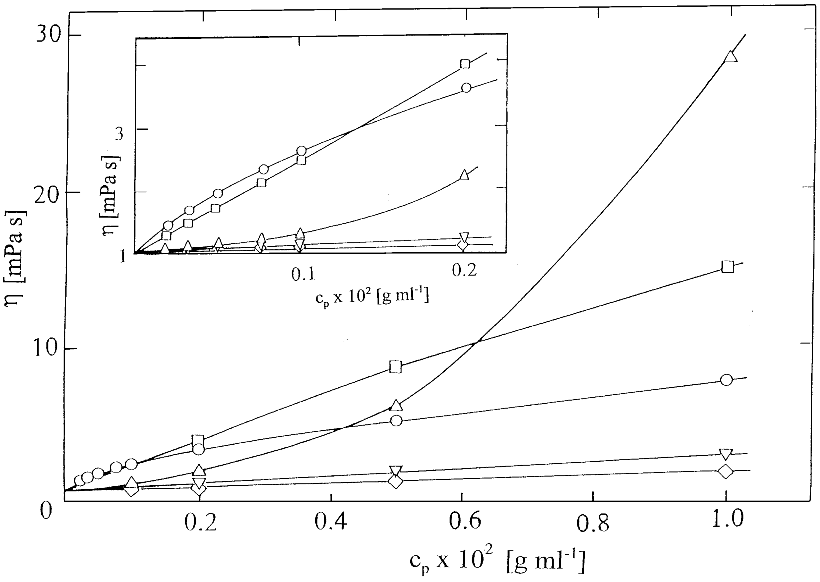

Fig. 6 Dependence of the viscosity η of L-dispersions on the particle concentration c (For the point denotation, see Fig. 1)

Here ϕ_s is the volume fraction of the alkalinized (swollen) particles and ϕ_o is the volume fraction of original particles of density ρ (1.15 $\mathrm{g\,cm^{-3}}$). Accordingly, the critical concentration (in $\mathrm{g\,ml^{-1}}$)

$$c_{cr} = 2.5/[\eta] \, , \tag{3}$$

at which the space occupied by the alkalinized dispersion is completely filled by swollen (or disintegrated) particles ($\phi_c = 1$) can be estimated (Table 3).

At particle concentrations lower than the critical one ($c_p < c_{cr}$), interactions of particles are weak and the effect of hydrodynamic volume prevails. That is why the shapes of the plots $\eta_r = c_{MBA}$ for $c_p = 1 \times 10^{-3}\,\mathrm{g\,ml^{-1}}$ and $[\eta] - c_{MBA}$ are alike. On the other hand, at a higher particle concentration ($5 \times 10^{-3}\,\mathrm{g\,ml^{-1}}$) for samples L/0, L/0.25, H/0 and H/0.25 the space available is completely filled up with swollen soft particles (or subparticles) and strong particle interactions leading to high η are operative. In spite of the highest intrinsic viscosity of non-crosslinked samples a maximum viscosity occurs at c_{MBA} 0.25 wt% due to a greater stiffness of crosslinked particles.

However, when particle concentration rises to $1 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$, the space is filled up also for sample L/1.25. Disintegration of this copolymer is very low and thus, with regard to the compact crosslinked structure of particles, their interaction is extremely strong so that the system reaches a much higher (maximum) viscosity than the other samples. On the other hand, swelling of particles with higher MBA contents is only slight and their interaction in non-filled space is limited.

No doubt, at the particle concentration of $1 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$ in H/1.25 dispersion, the space is filled up by swollen particles similar to in L/1.25, but due to stronger interactions of tightly arranged particles of H/0.25, its maximum viscosity does not change.

The same specific influence of hydrodynamic volume and particle interaction on the viscosity of dispersions is reflected by similar dependences of viscosity on particle concentration at low and high contents of methacrylic acid in the copolymer (Figs. 6 and 7). In both cases, the steepest initial increase in viscosity sets in for the non-crosslinked copolymers, where the intensity of interactions is controlled by a relatively large size of swollen particles and the particle interaction is negligibly small. In this range of particle concentrations, the viscosity increase in dispersions of more compact crosslinked particles is lower. At higher particle concentrations, however, an increase in viscosity of non-crosslinked sample diminishes because interaction of more compact crosslinked particles, especially in the vicinity of critical concentration, becomes the main factor influencing the energy dissipation during flow.

Conclusion

Semicontinuous emulsion copolymerization of ethyl acrylate with methacrylic acid and a small amount of *N*,*N*′-methylenebisacrylamide provided dispersions of particles with a compact and homogeneous structure, which after

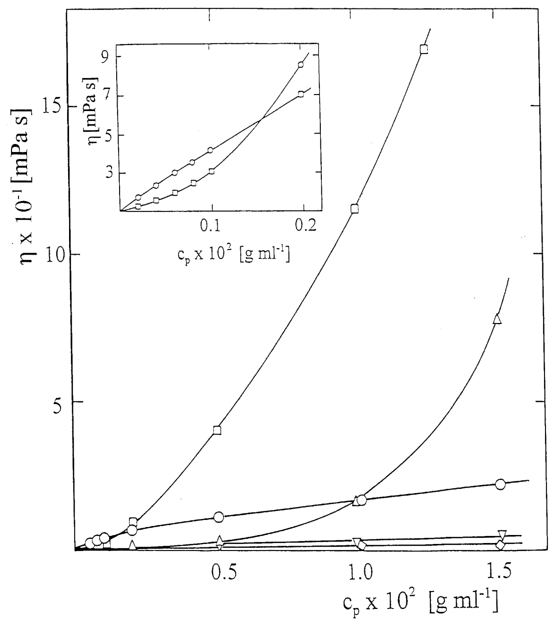

Fig. 7 Dependence of the viscosity η of L-dispersions on the particle concentration c (For the point denotation, see Fig. 2)

alkalinization do not unpredictibly disintegrate as described for dispersions without a crosslinking agent studied in the past. Only about 1% of MBA proved to be sufficient to prevent disintegration of particles and to obtain material with reproducible structure and flow properties. We believe that these results could be a good base for a detailed elucidation of the mechanism of the thickening effect of these materials, whose study is in progress in our laboratory.

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