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Structural changes of latex particles of ethyl acrylate–methacrylic acid copolymers during neutralization in the presence of methanol

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Abstract: Using a combination of static light scattering, potentiometry, and viscometry, structural changes of latex particles of ethyl acrylate–methacrylic acid (20–70 wt%) copolymers during neutralization in the presence of methanol were investigated. It was found that the latex particles disintegrate into small subparticles, swell, and at a high content of methacrylic acid units dissolve. Disintegration of latex particles is explained by considering the particles as agglomerates formed during polymerization by coalescence of smaller particles.

Key words: Latex dispersions – ethyl acrylate – methacrylic acid copolymers – latex particle structure – comminution effect

Introduction

During the neutralization of latex dispersions of ethyl acrylate–methacrylic acid copolymers prepared by semicontinuous emulsion polymerization, a change in the structure of the latex particles (hereinafter, particles) has been described [1]. If these copolymers contain less than 15–20 wt% of the acid the particles only swell; at a higher acid content, the particles decompose to supramolecular aggregates, and copolymers with more than about 50 wt% of the acid dissolve molecularly.

Assuming a homogeneous structure of particles, it seemed that during neutralization the particles swell as a whole, and this eventually results in their dissolution at higher contents of methacrylic acid. The particles can also swell and dissolve when an organic solvent is added to the dispersion medium. We supposed that a study of the neutralization of particles preswollen by an organic solvent could provide a more detailed elucidation of the changes in the particle structure occurring during this process.

These changes were attended by a characteristic increase in the apparent dissociation constant K_{app} with increasing degree of dissociation to the maximum extent [2, 3]. It was assumed that this increase reflects the gradual accessibility of the carboxylic groups inside the particles to the dispersion medium and, hence, its penetration into the solid structure of the particles [3]. At the K_{app} maximum the accessibility of most of the carboxylic groups is achieved which, together with the simultaneous decrease in the optical turbidity of the latices (clarification of latices), indicates complete swelling of the particles. As the addition of alkali continued, the dispersions showed a behavior typical of water-soluble polyacids, i.e., the K_{app} decreased as dissociation of further carboxylic groups became more difficult due to the increase in the electrostatic interactions. Since the changes in particle structure affected the hydrodynamic properties of the latices, potentiometry and viscometry combined with static light scattering were used in this study.

Experimental

Dispersions

Three types of ethyl acrylate–methacrylic acid latex copolymers with varying contents of methacrylic acid (hereinafter, MAA) and differing in their behavior under neutralization were used: EM 20 (21.8 wt% of MAA) – particles swelled, EM 50 (49.0 wt% of MAA) – particles partly dissolved with the formation of supramolecular aggregates and EM 70 (69.1 wt% of MAA) – copolymer dissolved molecularly. The latices were prepared by a semicontinuous emulsion polymerization with monomer emulsion feed, as described previously [1]. This procedure ensured a relatively homogeneous composition of the statistical copolymers. After polymerization, the latices contained 25 wt% of solids, and the pH was 1–2. Standard latex samples were prepared by removing low-molecular-weight ions by dialysis (Dialysierschlauch Kalle AG, Wiesbaden, FRG) first against distilled and then against twice-distilled water ($\kappa = 2 - 3\ \mu S \cdot cm^{-1}$) to constant conductivity. The content of acid groups was determined by conductometric titration with NaOH (OK 104 conductoscope, Radelkis, Hungary). The hydrodynamic diameters of the particles, determined by photon correlation spectroscopy (Nano Sizer, Coulter Electronic, Ltd., England) were 100 nm (EM 20), 137 nm (EM 50), and 285 nm (EM 70). Poly(methacrylic acid) (PMAA) used as a reference polyacid was prepared by radical polymerization [4]. Its molar mass $\bar{M}_\eta = 140\,000$ was calculated from the relationship $[\eta] = 66 \cdot 10^{-3} \cdot M^{0.5}$ from the intrinsic viscosity measured in 0.002 M HCl [5].

Measurement of static light scattering

The static light scattering (SLS) was measured (FICA 40000 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 $K = (2\pi/\lambda) \cdot \sin\theta/2$, where λ is the wavelength of light in solution, was determined. For colloid dispersions, $R(K)$ is given by the superposition of internal and external interference of the scattered light [6, 7]. 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 the equation [8]:

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

where D is particle diameter. In the dilute latices studied maxima on the experimental dependencies $R(K)$ vs. K at low K values were observed. This phenomenon was caused by the effect of external interference as a consequence of non-random arrangement of uniform particles in space. Thus, to estimate the particle diameter D, the $P(K)$ functions were compared with the experimental plots $R(K)$ vs. K in the range of high values of K ($\theta > 90°$).

The diameters of the particles determined by this method in water as a dispersion medium were in correspondence with those obtained by photon correlation spectroscopy.

Measurement of pH and Viscosity

Dispersions containing 0.2 wt% of the copolymer were prepared by dilution of the dialyzed latex with twice-distilled water and addition of a certain amount of high purity methanol (Lachema, Czech Republic) and NaOH solution. The pH was measured in a nitrogen atmosphere (PHM64 digital pH-meter, combined G 2321 electrode, Radiometer, Copenhagen). This electrode consists of a glass electrode and a reference silver chloride electrode. As the same results were obtained with antimony and saturated calomel electrodes (K 401, Radiometer, Copenhagen), any specific effect of methanol on the measurement of the pH with the glass electrode could be excluded. The electrodes were calibrated using standard buffers in water.

The degree of dissociation of carboxylic groups, α, was calculated using the relationship:

$$\alpha = ([Na^+] + [H^+])/c_{MAA} , \quad (2)$$

where $[Na^+]$ corresponds to the molar concentration of NaOH added, $[H^+]$ is the molar concentration of hydrogen ions calculated from the pH assuming the activity coefficient of the hydrogen ions $\gamma = 1$, and c_{MAA} is the molar concentration of MAA monomeric units. The apparent dissociation constant K_{app} was calculated from the equation:

$$pK_{app} = pH + \log[(1 - \alpha)/\alpha] . \quad (3)$$

The relative viscosity $\eta_r = \eta/\eta_0$ was calculated from the viscosities of the latices η and the viscosity of the dispersion medium η_0, measured in Ostwald-type viscometers at 25 ± 0.02 °C.

pH, viscosity, and light scattering of latex samples were always measured 24 h after their preparation. The methanol content in the dispersion medium is given in vol%.

Results

Structural changes of particles prior to neutralization

At constant polymer concentration and for large K values, the slope of the $R(K)$ function for the particles of latex EM 20 in 20, 40 and 60% of methanol obviously did not change (Fig. 1a). The $R(K)$ values decreased in this order and the effect of external interference gradually diminished, i.e., the height of the maximum found at low K values decreased or the maximum completely disappeared.

Generally, the intensity of the scattered light of dispersions containing spherical latex particles depends on their size and concentration and is much higher than that of dissolved macromolecules, see text below and Fig. 3. Hence, the change of shape (external interference maxima) and the decrease in the $R(K)$ values with increasing methanol content indicate a slight decrease in the amount of original particles. As the intensity of light scattering is controlled primarily by large particles (z-moment of the size distribution), the amount of original particles remaining in the system can be estimated by comparing the concentrations of latex in water and in a water–methanol mixture required to achieve approximately the same $R(K)$ value. Using this procedure it was found, for example, that the amount of particles with the original diameter decreased to about 30% in 60% methanol and probably to 5% in 80% methanol, where due to the swelling the particle diameter rose approximately 1.5 times (Fig. 1b).

A qualitatively similar effect was also observed for latex EM 50 (Fig. 2). However, the effect of

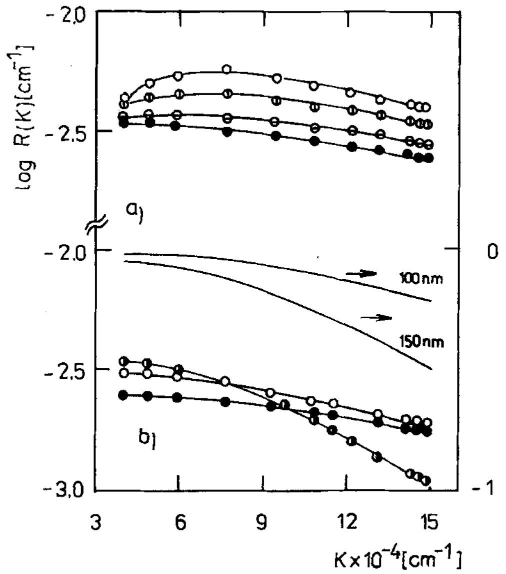

Fig. 1. Light-scattering function $R(K)$ of latex EM 20 at copolymer concentration (weight %) and methanol content (volume %), respectively: a) (○) $2 \cdot 10^{-2}$, 0; (⦶) $2 \cdot 10^{-2}$, 20; (⊖) $2 \cdot 10^{-2}$, 40; (●) $2 \cdot 10^{-2}$, 60. b) (○) $5 \cdot 10^{-3}$, 0; (●) $1.5 \cdot 10^{-2}$, 60; (◑) $1.5 \cdot 10^{-1}$, 80. The particle scattering factors $P(K)$ were calculated according to Eq. (1) and were parametrized by particle diameter D in nm

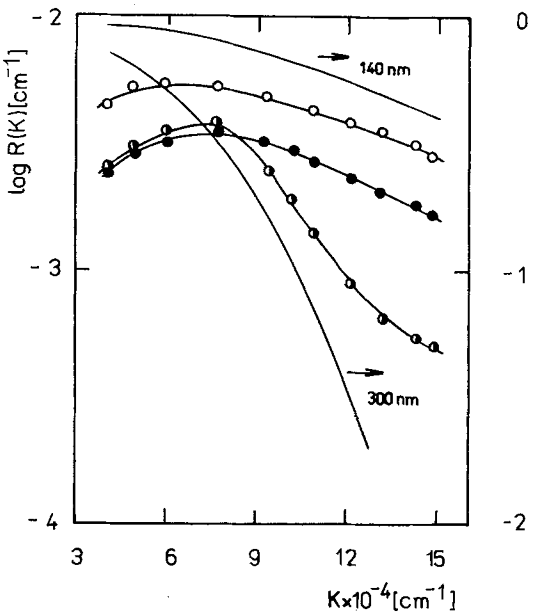

Fig. 2. Light-scattering function $R(K)$ of latex EM 50 at copolymer concentration (weight %), and at methanol content (volume %), respectively: a) (○) $5 \cdot 10^{-3}$, 0; (●) $5 \cdot 10^{-2}$ 60; (◑) $5 \cdot 10^{-1}$, 80. The particle scattering factors $P(K)$ were calculated as in Fig. 1

methanol was stronger in this case. In 60% methanol, the amount of original particles decreased to 5%, and in 80% methanol, to much less than 1% while the diameter of particles approximately doubled. At larger MAA content, with latex EM 70 in 60% methanol, complete molecular dissolution of copolymer was observed; the diameter of copolymer coils was much smaller than the dimensions of the particles in the original dispersion (Fig. 3).

Structural changes of particles during neutralization

The presence of methanol in the dispersion medium greatly affected the shape of the dependences of K_{app} and the relative viscosity on the degree of dissociation. For the EM 20 latex (Fig. 4a), the K_{app} values first decreased with increasing degree of dissociation, apparently as a consequence of an increase in the intensity of the electrostatic interactions during dissociation of the carboxylic groups on the surface of the particles. After exceeding a certain critical degree of dissociation, the K_{app} values rapidly increased to a maximum and the latex clarified. The relative viscosity reflecting the change in the hydrodynamic volume increased very slowly during neutralization and its greatest increase occurred at higher degrees of dissociation than for changes in K_{app}.

The behavior of latex EM 20 in 20% methanol was similar to that of the dispersion in water. However, at a methanol content of 40 and 60%, the K_{app} values increased rapidly from the very beginning of the neutralization, although the relative viscosity did not show any significant change (Figs. 4b, c). At the same time, maximum K_{app} and the points of clarification occurred at lower degrees of dissociation. A different shape of the K_{app} vs. degree of dissociation dependence was found in 80% methanol: the K_{app} maximum disappeared and the K_{app} values decreased monotonously only (Fig. 4d). The dispersion clarified at $\alpha = 0$ and the

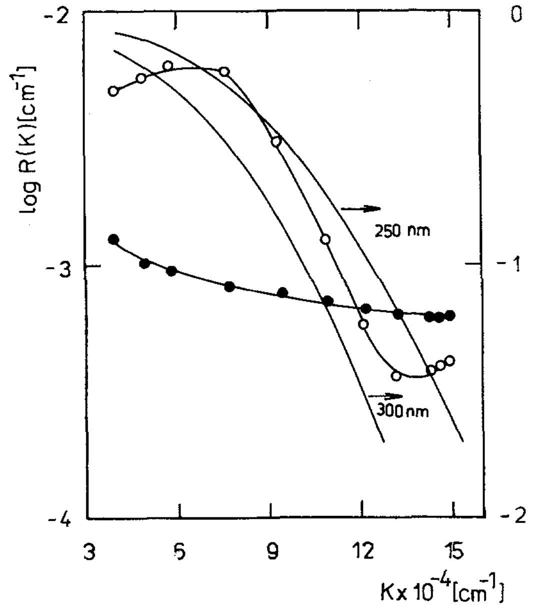

Fig. 3. Light-scattering function $R(K)$ of latex EM 70 at copolymer concentration (weight %) and methanol content (volume %), respectively: (○) $5 \cdot 10^{-3}$, 0; (●) 1.0, 60. The particle scattering factors $P(K)$ were calculated as in Fig. 1

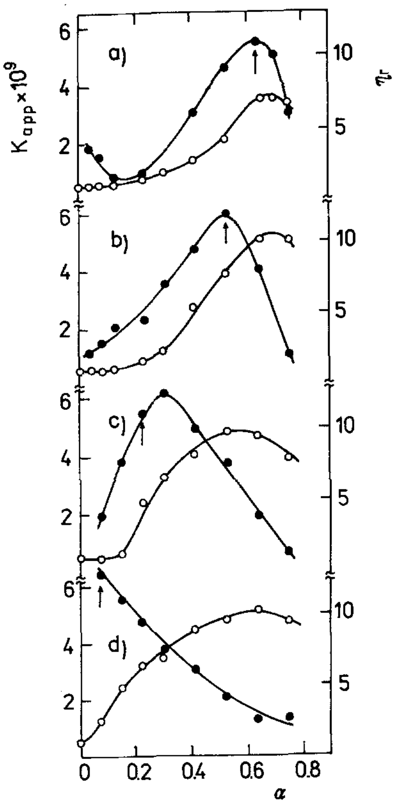

Fig. 4. K_{app} (●) and relative viscosity η_r (○) of latex EM 20 as a function of the degree of dissociation, α, at methanol content (volume %): a) 0%, b) 40%, c) 60% d) 80%. Vertical arrows indicate the points of clarification of dispersions

relative viscosity rapidly increased from the very beginning of the neutralization.

These results indicate that with increasing methanol content structural changes and complete swelling of the EM 20 latex particles occurred at lower degrees of dissociation and, at the highest methanol content (80%), the particles swelled even prior to neutralization.

The effect of methanol on the dissociation and hydrodynamic behavior of latices with higher MAA content (EM 50 and EM 70) was more pronounced than for latex EM 20, (Fig. 5). At a given methanol content, a rapid increase in K_{app} and the relative viscosity, similar to the maximum of K_{app} and point of latex clarification were observed at lower degrees of dissociation. With latex EM 50 in 60% methanol and EM 70 in 40% methanol a monotonous decrease in the K_{app} values with degrees of dissociation was found almost from the beginning of the neutralization, indicating practically complete swelling of the particles in these media prior to neutralization. Thus, in these latices, methanol has a far greater effect on the particle structure than with latex EM 20.

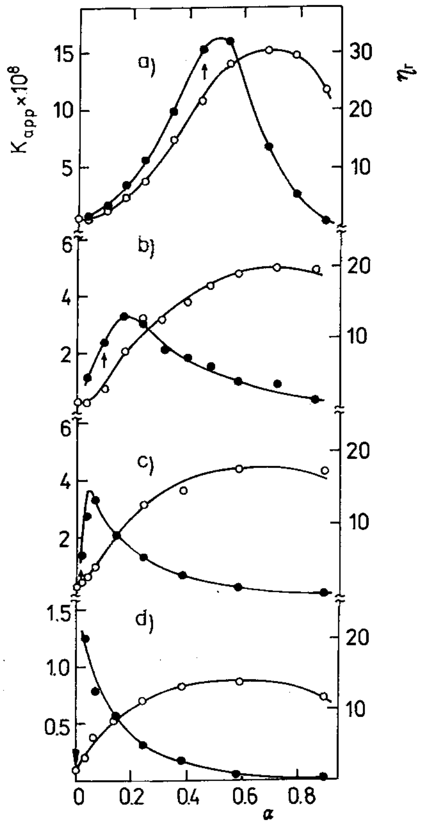

Fig. 5. K_{app} (●) and relative viscosity η_r (○) of latex EM 50 as a function of the degree of dissociation, α, at methanol content (volume %): a) 0%, b) 40%, c) 60% d) 80%. Vertical arrows indicate the points of clarification of dispersions

Discussion

In general, methanol can affect both the dissociation constant of carboxylic groups and also solvent power of the dispersion medium. To determine the effect of these factors during the neutralization of the latices, the influence of methanol on the dissociation and hydrodynamic behavior of PMAA was studied. As indicated by the shape of the dependencies of K_{app} vs. degree of dissociation (Fig. 6), methanol greatly suppresses the dissociation of carboxylic groups of PMAA. As a similar decrease in K_{app} was also observed during the neutralization of low-molecular-weight acetic acid, then this behavior can be explained in terms of a decrease in the dielectric constant of the dispersion medium with increasing methanol content.

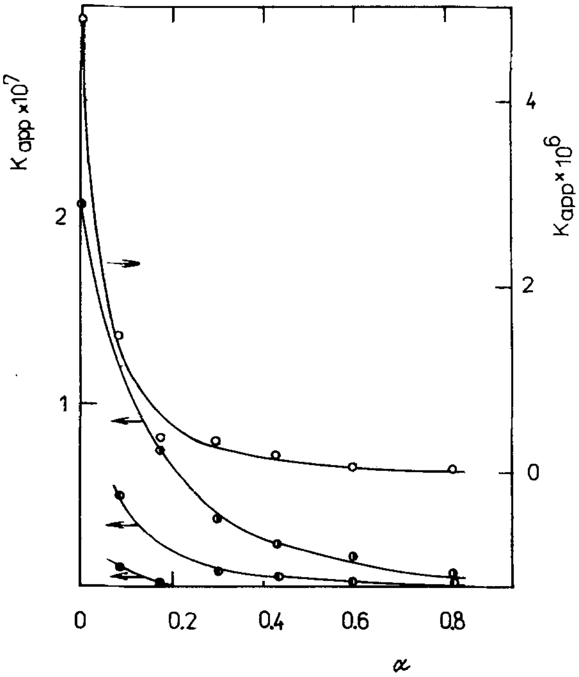

Fig. 6. Changes in K_{app} of poly(methacrylic acid) with the degree of dissociation, α, at methanol content (volume %): (○) 0%, (◑) 40%, (◐) 60%, (●) 80%

The slight increase in the relative viscosity of PMAA solutions with increasing methanol content at $\alpha > 0.2$, Fig. 7, may be a consequence of an improvement in solvent power of the dispersion medium with methanol content. On the other hand, at higher degrees of dissociation, the relative viscosity of PMAA solutions decreased with increasing methanol content and, in 60% methanol for $\alpha \approx 1.0$, and in 80% methanol for $\alpha \approx 0.1$ critical solubility conditions, i.e., precipitation of the polymer was achieved. This behavior suggests a deterioration in solvent power of the dispersion medium with increasing methanol content at higher degrees of dissociation of PMMA.

It is seen (Figs. 4 and 5) that the K_{app} values for dispersions neutralized to approximately $\alpha < 0.2$ (EM 20) and $\alpha < 0.1$ (EM 50) with methanol content mostly increased. As methanol reduces the dissociation of the carboxylic groups, the observed increase in K_{app} is obviously a consequence of compensation of this effect by the accessibility of a larger number of carboxylic groups inside the particle to the dispersion medium at the beginning of the neutralization. Taking into account the shift of K_{app} maximum to lower degrees of dissociation (Figs. 4 and 5), it can be concluded that the presence of a relatively small amount of methanol led to marked changes in the solid structure of the particles prior to and also during the neutralization. This finding is in good agreement with the results obtained in the study of the effect of methanol by SLS.

It can be assumed that the changes in the structure of the particles by their swelling and dissolution should lead to a marked increase in their hydrodynamic volume. From the slow initial increase in relative viscosity with degree of dissociation in media with a lower content of methanol (Figs. 4a–c, 5a, b) it is clear that the hydrodynamic volume of the particles did not change considerably. Thus, no great swelling or dissolution of the particles occurred at the beginning of the neutralization. The results seem to indicate that the original dispersed character of the systems was retained under these conditions. Consequently, the decrease in the amount of original particles after the addition of methanol observed by SLS could reflect their disintegration to subparticles, described in literature as micronization, i.e., the "comminution effect" [9]. We assume that this effect occurs simultaneously with the swelling of particles and their dissolution, effects which predominate with increased contents of MAA in the copolymer, methanol content in the dispersion medium and degrees of dissociation.

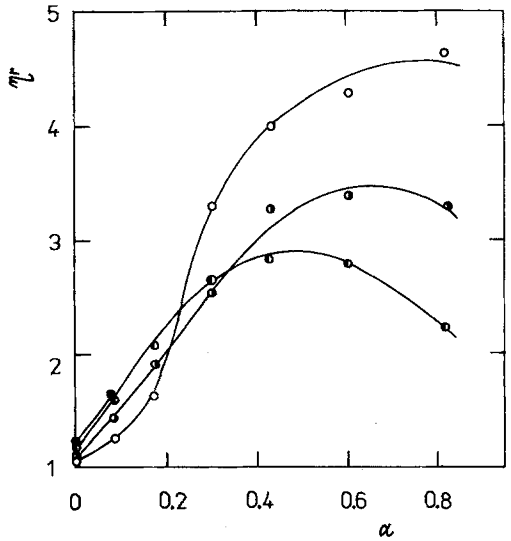

Fig. 7. Changes in relative viscosity η_r of poly(methacrylic acid) with the degree of dissociation, α. Methanol contents (volume %) denoted as in Fig. 6

Conclusion

In contrast to the, so far, assumed homogeneous structure of the latex particles of ethyl acrylate–methacrylic acid copolymers, our results indicate their heterogeneity. This could reflect the internal structure of the particles, e.g., agglomerates formed during the emulsion polymerization through coagulative mechanism of particle growth [10–13]. We suppose that these results could contribute to further elucidation of the growth mechanism of latex particles during the polymerization and the thickening effect of neutralized latices of these copolymers, utilized in practice.

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