Characteristic changes of pH during the alkalization of latex dispersions of the ethyl acrylate – methacrylic acid copolymers

O. Quadrat, L. Mrkvičková, E. Jasná and J. Šňupárek, Jr.¹

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia
1) Research Institut for Synthetic Resins and Lacquers Pardubice, Czechoslovakia

Abstract: The titration curves of latex dispersions of ethyl acrylate - methacrylic acid copolymers have a rather complex shape which indicates a strong dependence of the apparent dissociation constant of carboxylic groups on the degree of neutralization and copolymer composition. These dependences seem to be related to changes in the macroscopic structure (swelling and disintegration) of dispersion particles during alkalization.

Key words: Latex dispersions, copolymers of ethyl acrylate with methacrylic acid, titration curves

Introduction

It has been reported [1, 2] that during the alkalization of latex dispersions of the copolymer of ethyl acrylate with 33 or 20 wt. % of methacrylic acid, the pH values steeply rise at the beginning, go through a broad plateau and rise again to the equivalence point. Systematic experiments over a broader range of copolymer composition carried out in this laboratory have shown, however, that the shape of the titration curves of those materials is more complex and depends on the copolymer composition. The results are presented and discussed below.

Experimental

Latex dispersions of the statistical copolymers of ethyl acrylate with 10–55 wt. % of methacrylic acid (weight fraction w2=0.1-0.55), denoted EM-10-EM-55, were prepared by a semi continuous emulsion polymerization with a monomer emulsion feed. Such a procedure of preparation ensured a homogeneous composition of the copolymer of latex particles [3-5]. The amount of dissolved polymer in serum obtained by centrifugation (Ultra centrifuge Beckman L8-55, 15 000 rpm, 2h) was only several tenths of a per cent and its influence on the titration curves was negligible. The diameter of dispersion particles in acid dispersions, measured by the autocorrelation spectroscopy of scattered laser light using a Coulter Nano Sizer (Coulter Electronics Ltd., England), lay in the range 90–118 nm.

The pH of the dispersions was monitored during the alkalization with ammonium hydroxide at a concentration 0.2 wt. % of polymer solids by means of a digital pH Meter 64 (Radiometer Copenhagen) with a combined electrode GK 2321 C. The content of polymer solids in the original dispersions was 25 wt. %. After partial dilution and addition of the corresponding quantity of ammonium hydroxide, the volume of the samples was adjusted by water to the required concentration. All pH measurement took place at 25 °C after oneday of stabilization of the samples following the alkalization.

Results and discussion

Titration curves are presented in Fig. 1. The initial part is very steep and similar for all copolymers, but the subsequent part becomes more complex the larger the weight fraction, w2, of methacrylic acid in the copolymer. While the curves for copolymers comprising 10 wt. % MA (w2=0.1) are monotonous, those for copolymers with w2=0.15 display a broad plateau and those for w2 ≥ 0.20 have a low maximum and a shallow minimum which are the more displaced to low pH values the higher the acid content. At w2 ≥ 0.40 the curves seem to display another plateau (in addition to the maximum and minimum) in the region preceding the equivalence point. On the other hand, the titration curve of poly-methacrylic acid, w2=1, is monotonous.
It is to be emphasized that the shape virtually does not change even after the samples, alkalized to the respective pH, have been left standing for several months. This fact rules out the possibility that the unusual shape of the titration curves, especially the minimum, is an artifact caused by the nonequilibrium of the dispersion particles.

A quantity which facilitates the interpretation of the titration curves of polyelectrolytes is the apparent dissociation constant, $K_{app}$, of the carboxylic groups [6]. It reflects the average electrostatic interaction of dissociated groups on the polymer chain and of low-molecular-weight ions in the dispersion medium. It is calculated by

$$pK_{app} = pH + \log \left( \frac{1 - \alpha}{\alpha} \right).$$

The degree of dissociation $\alpha$ was calculated using $\alpha = ([NH_4^+] + [H^+])/c_{MA}$, where $[NH_4^+]$ is the consumption of NH$_4$OH, $[H^+]$ is the concentration of H$^+$ ions calculated from the measured pH (the activity coefficient of H$^+$ ions being neglected), and $c_{MA}$ is the molar concentration of methacrylic acid units.

In Fig. 2 the values of $K_{app}$ are plotted against $\alpha$. The shape of curves depends on the copolymer composition, and seems to be related to changes in the macroscopic structure of the dispersion particles during alkalization. In a previous work [7] we have shown, with the same dispersion samples, that the macroscopic appearance and structure of particles typically change during alkalization. (a) At $w_2 \leq 0.20$, the particles only swell. Since their refractive index differs considerably from that of the dispersion medium, the dispersion remains opalescent throughout the whole titration. (b) At $w_2 \leq 0.20$, the dispersion clarifies on alkalization. It is remarkable that the clarification sets on around the minimum of the titration curves. This seemingly indicates dissolution of the latex particles. In fact, however, the swollen particles do not dissolve completely, but only partly disintegrate into swollen units formed by aggregates of macromolecules. (c) At $w_2 \leq 0.40$, the copolymer begins to dissolve; the fraction of aggregates decreases with an increase in $w_2$. At $w_2 = 0.55$, the copolymer is virtually completely dissolved.

Figure 2 shows that the dependences of $K_{app}$ vs $\alpha$ increase monotonously if $w_2 \leq 0.35$. With the dispersions, which only swell (EM-10 and EM-15), the increase is moderate, whereas with those which disintegrate into supermolecular aggregates or macromolecules, it is steep. It is steeper as the structure of the dispersion particles during alkalization becomes looser.

This fact leads us to propose the following interpretation. It is similar to that used in a study of copolymers of methacrylic acid and 2-hydroxyethyl methacrylate [8]. Swelling and disintegration of latex particles raise their degree of hydration and, con-