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SHORT COMMUNICATION

AGGREGATION OF THE INTERPOLYMER COMPLEX OF POLY(METHACRYLIC ACID) AND POLY(VINYL PYRROLIDONE) IN AQUEOUS SOLUTIONS

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Abstract—The aggregation of the interpolymer complexes between poly(methacrylic acid) (PMAA) and poly(vinyl pyrrolidone) (PVP) was investigated using the light scattering technique. The fast complexation of the polymers in aqueous solution is followed by aggregation which is very sensitive to pH. The aggregation behaviour was found to change noticeably when the pH increases from 3.2 to 3.9. The time dependence of the particle size as well as the size distribution at different pH was analysed. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The complex formation of PMAA is an important field of study, and it may be utilised in various fields of polymer research and technology [1–3]. Some recent examples are the studies on the template polymerisation of *N*-vinyl imidazole along with PMAA in water [4], and the investigation of the complexation of poly(ether-ester)s with PMAA [5]. In the latter, polymers containing biologically active residues were prepared. Philippova *et al.* have studied the conformational transitions of PMAA hydrogels, induced by the complexation with linear poly(ethylene oxide), PEO [6]. The complexes of the PMAA network with PEO have been suggested to be used as carriers of enzymes or drugs for their controlled release.

The most studied interpolymer complexes of PMAA are those formed either with PEO or with poly(vinyl pyrrolidone), PVP. Recently, properties of solid complexes of PMAA with PEO and PVP, respectively, have been studied by one of the present authors [7]. The precipitation of the complexes was observed to be dependent on the concentration and pH of the solutions.

Ohno *et al.* [8] have studied the solvent effect on the complex formation of PMAA and PVP. Rough values for molar masses of the complexes were reported and the size of the polymer complex was found to be time dependent. The pH effect on complexation was observed but not investigated in detail. The complexation and aggregation in aqueous PMAA–PEO solutions have also been studied by Ohno *et al.* [9] using the light scattering technique as well as by Hemker and Frank [10]. In the report by Ohno *et al.*, some measurements on a PMAA–PVP system have been described and used as an example of a stable complex. DLS studies on a system closely similar to the present one, i.e. an aqueous solution of PVP and poly(monomethyl itaconate, have recently been reported by Leiva *et al.* [11].

It seems evident that the complexation of PMAA with PEO, as well as with PVP, occurs instantaneously after the mixing of the solutions, and that this process is too fast to be studied by light scattering. However, the fast complexation is followed by the aggregation of the complexes, the rate of which is strongly dependent on conditions like temperature, concentration and pH. Hemker and Frank [10] observed that the increase in size of the PMAA–PEO aggregates with time may be described by a power law relationship, and showed this behaviour to be consistent with a model of a diffusion limited cluster–cluster aggregation of the polymer complexes.

The purpose of this study is to find out the pH dependence of the rate of aggregation in PMAA–PVP solutions, as well as to determine the size and the size distribution of the aggregate particles.

EXPERIMENTAL

Materials

PMAA (BDH Chemicals) was purified before use. The polymer was precipitated from a 20 wt% aqueous solution with diethyl ether containing a small amount of hydrochloric acid. The precipitate was washed with diethyl ether, dissolved in methanol, reprecipitated with ethyl acetate and dried under reduced pressure. PVP (K 30, Fluka) was used without further purification. M_w of the polymers were measured by light scattering, using methanol as a solvent for PMAA and water for PVP. The values obtained were 4×10^4 for both polymers.

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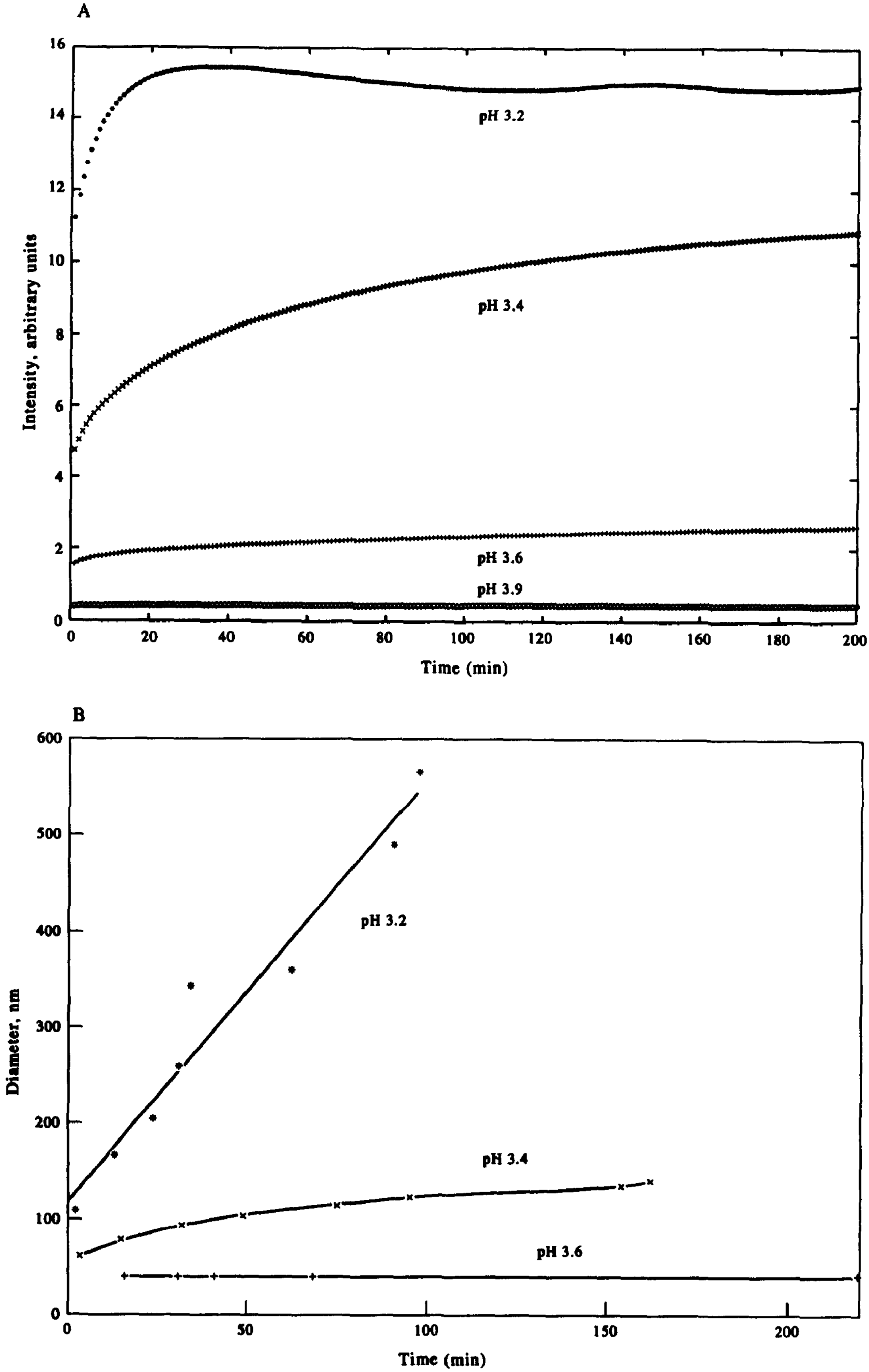

Fig. 1. Total scattered intensity vs time (A) and average particle diameter vs time (B) for PMAA–PVP samples at different pH.

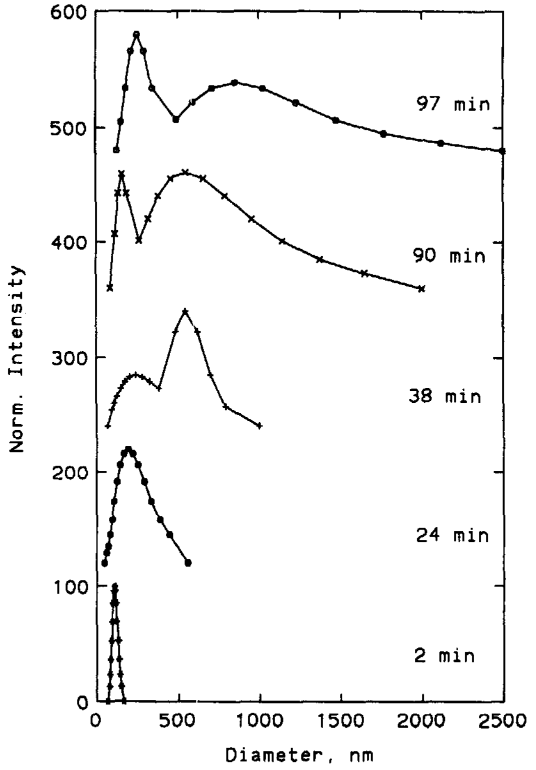

Fig. 2. Particle size distribution curves of PMAA–PVP at pH 3.2.

Preparation of the solutions

The solutions used in the DLS measurements and in the measurements of the scattered light intensity with time were prepared by dissolving the polymers in ultra-pure water. The polymer concentration was 5×10^{-3} moles of the repeating unit per litre (m.r.u.). The pH of the pure solutions were 3.7 for PMAA and 4.6 for PVP and the pH was adjusted with hydrochloric acid for measurements. The concentration of the polymer solutions used in the static light scattering (SLS) measurements varied in the range 0.5–2×10^{-3} m.r.u. For the SLS, the polymers were dissolved in methanol (PMAA) or in water (PVP), with no addition of hydrochloric acid.

Polymer solutions were purified by repeated filtering through 0.22 μm millipore membranes. Prior to the DLS measurements on the aggregating PMAA–PVP solutions, equal amounts of the two polymer solutions of desired pH were mixed in the light scattering cell by adding the PVP solution into the solution of PMAA.

Light scattering measurements

A Brookhaven light scattering instrument with a 136 channel BI2030 correlator and a 35 mW HeNe laser was used. All the measurements were conducted at 25°C.

The molar masses of the polymers and their complex were determined in normal static measurements, using the Zimm method. The scattering angle was varied from 45 to 135° in 15° steps.

Dynamic measurements were performed as follows. The scattering angle was kept constant, at 90°. The number of samples was 10^7 or higher and thus, the number of counts in each channel was not less than 10^6, which corresponds to a statistical error of less than 0.1% [12]. The intensity autocorrelation function was collected in 136 channels and 6 delay channels were used to estimate the measured baseline. Only the data where the difference between the measured and the calculated baselines was less than 0.2% were used for further analysis. An average particle size was obtained from the correlation function by fitting the data in a single exponential. The particle size distribution was calculated using the program CONTIN (B.I.C. version 3.0).

RESULTS AND DISCUSSION

The PMAA–PVP complex is formed by hydrogen bonding and further stabilised by the hydrophobic interaction [13, 14]. To be able to study the aggregation processes occurring after the fast initial complexation, one has to find experimental conditions (pH, temperature, concentration) where the process is detectable but not too fast to be followed accurately by light scattering. Further, the optimal concentration regime is very much determined by the method of investigation: in the present case, where the wavelength and the intensity of the incident light are fixed, the intensity of the scattered light depends critically on concentration.

To find out the best possible experimental conditions, the intensity of the scattered light was measured as a function of time starting from the moment of mixing the two polymer solutions. The increase of intensity with time has also been used, for example, when studying the pH dependence of the thermally induced phase transition of poly(*N*-isopropyl acrylamide) derivatives [15]. In the present case, considerable differences in the rate and extent of the increase in intensity were detected when the pH of the solution was gradually increased from 3.2 to 3.9. The scattered light intensity versus time is shown in Fig. 1(A). As can be seen from the figure, the increase of intensity is fastest and most pronounced at the lowest pH, whereas only very small changes can be observed at pH 3.6. At pH 3.9, no increase of the scattered light intensity could be detected.

At pH 3.2 the scattered light intensity reached a constant level in about 30 min. However, the average particle size measured by DLS increased continuously up to at least 90 min, as is shown in Fig. 1(B). With increasing size of the scatterers, the intensity of the light should also increase; it is obvious that at pH 3.2 the polymer complex starts to precipitate. The constancy of the scattered light intensity would then be a result of two simultaneous processes: aggregation and precipitation. In aggregation, the size of the scatterers increases while their number decreases; precipitation greatly decreases the number of large scattering particles.

The particle size distribution is shown in Fig. 2 for the system at pH 3.2. The distribution turned out to change from the initially unimodal one to bimodal with aggregation times longer than 34 min, i.e. at about the same time as the maximum plateau value of the scattered light intensity is reached. As is evident in Fig. 1(B), the dependence of the average diameter of the particles on time may be expressed as a straight line better than by exponential or power law expressions at pH 3.2. The aggregation process in this case is more complex than in the samples with higher pH.

At pH 3.4, the intensity of the scattered light [Fig. 1(A)], as well as the average particle size [Fig. 1(B)], increases continuously during the time measured. The particle size distribution is unimodal but broadens with time [Fig. 3(A)]. The time dependence of the average particle size may be well described by a power law expression. Plotting the logarithmic average particle size vs logarithmic time gives a straight line from which it is possible to obtain an

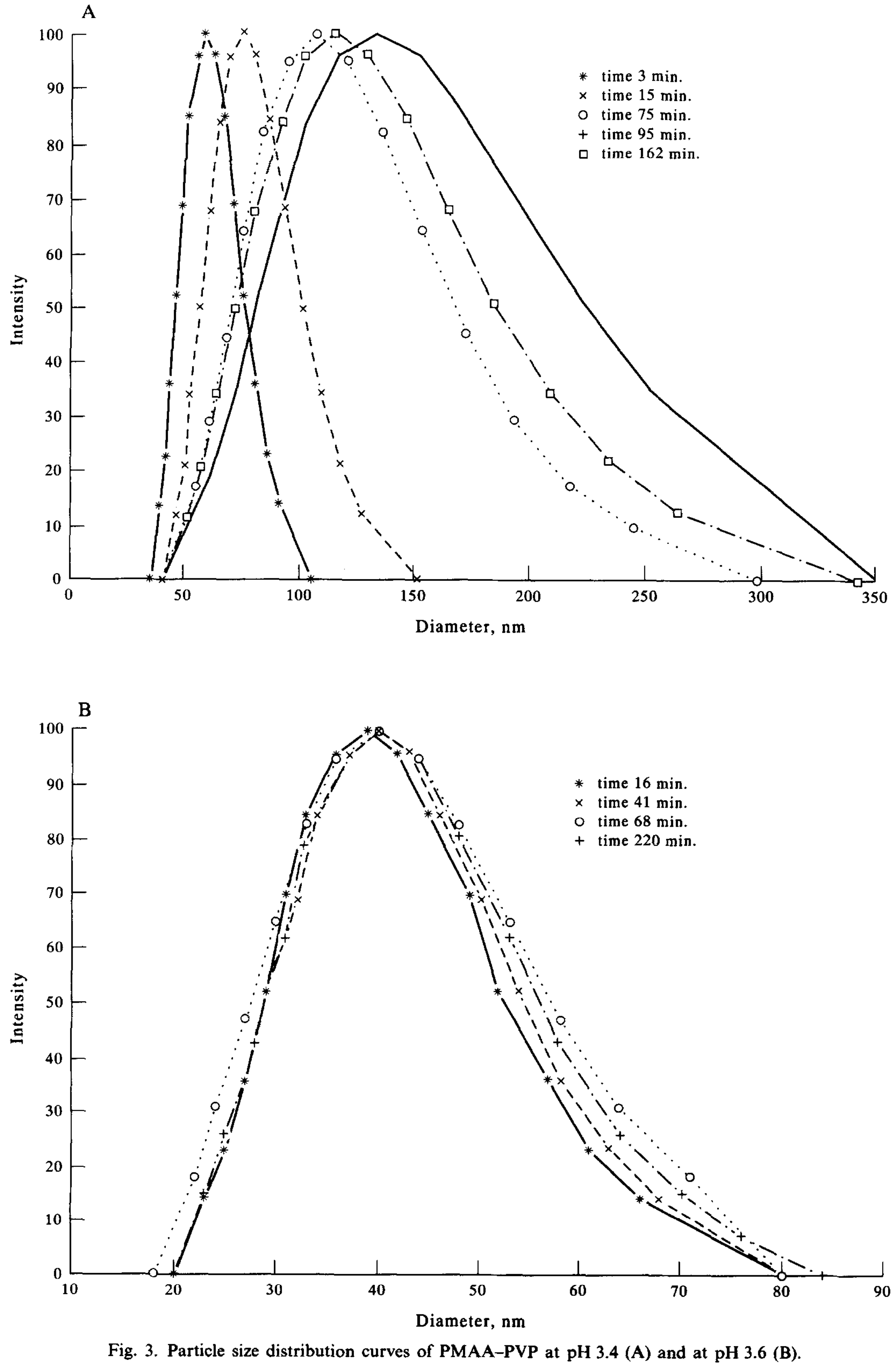

Fig. 3. Particle size distribution curves of PMAA–PVP at pH 3.4 (A) and at pH 3.6 (B).

apparent value for the initial aggregate size by extrapolating to $t = 0$. In this case the initial size was determined as 62 nm. According to the reasoning by Hemker and Frank [10], the power law behaviour indicates the domination of the diffusion limited aggregation over the reaction limited one.

The intensity of scattered light also increases with time at pH 3.6. The shape of the curve representing the intensity with time is equal to that measured at pH 3.4 [Fig. 1(A)]. However, the increase observed at pH 3.6 is much lower than in the more acidic solutions. The average particle size is around 40 nm during the time interval investigated. The size distribution is unimodal and independent of time, as is seen in Fig. 3(B). The increase of the intensity of scattered light is in this case due to the increase in the number of large scattering particles; the particles, once formed, seem to be relatively stable.

At pH 3.9 the intensity of scattered light was observed to be independent of time [Fig. 1(A)]. The intensity measured from this sample was too low to allow the determination of the particle size and the size distribution. Evidently, no aggregate formation is taking place at this pH under the present experimental conditions.

The angular and concentration dependence of the scattered light intensity, the excess Rayleigh ratio, was measured for the PMAA–PVP complex. The pH of the complex solution was 4.1 in the absence of any added HCl which prevents the precipitation of the complex. A usual Zimm plot was obtained, from which M_w was determined as 3×10^5. The second virial coefficient (A_2) was 7×10^{-5} mL mol/g^2, and the radius of gyration (R_g) 26 nm. The measured molar mass of the complex is about an order of magnitude higher than that of the single polymer chains. R_g of the complex is about the same as that of the single chains, indicating a compact structure of the complex. As expected, A_2 has a low value owing to the weak interaction between the complex and the solvent.

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