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Differences in association behavior of isotactic and atactic poly(methacrylic acid)

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ABSTRACT

In this paper we show by light scattering techniques that polymer tacticity introduces an opposite association behavior in the case of aqueous solution of poly(methacrylic acid) in the presence of 0.1 M NaCl. Aggregates of highly stereoregular isotactic poly(methacrylic acid), iPMA, are disrupted by shear and gradually reform in solution at rest, whereas those of the usual atactic form, aPMA, multiply as a result of mechanical stress (phenomenon of negative thixotropy) and gradually decrease in number after its cessation. The aggregates have characteristics of microgel particles and may act as precursors for temperature induced gelation at higher concentrations. According to the shape parameter ρ ($\sim$0.6 and $\sim$0.70 for iPMA and aPMA, respectively) iPMA aggregates have a denser core than aPMA ones. Additional differences between both isomers are demonstrated at higher degrees of neutralization, α_N, through the analysis of the polyelectrolyte slow mode, which was identified for all $\alpha_N > 0.25$ with iPMA but only for $\alpha_N = 1$ with aPMA.

1. Introduction

The ability of polyelectrolytes, synthetic and natural, to associate in solution is exploited in daily life and in various technological fields. Simple triggers for intermolecular association are the change in temperature or solvent, the reduction of the polyion charge, the addition of appropriate cosolutes, and less frequently mechanical stress [1,2]. Especially suitable to study the effect of polyion charge on intermolecular association are weak synthetic polyelectrolytes like poly(methacrylic acid), PMA, where polyion charge can easily be varied by changing the degree of neutralization, α_N, of carboxyl groups. Moreover, PMA offers an additional possibility to control association by varying its stereoregular structure or polymer tacticity. While the irregular atactic PMA, aPMA, was reported to associate and form gels in concentrated aqueous solutions at low polyion charge ($\alpha_N = 0$), either by heating [3] or by shearing [4], these possibilities have been indicated only recently for the highly regular isotactic PMA, iPMA. iPMA is, in contrast to aPMA, not soluble in water below a certain critical α_N value ($\alpha_N \approx 0.2$) [5–7]. van den Bosch et al. [5] demonstrated that a 10 w/w% iPMA solution with $\alpha_N = 0.28$ (polymer with mass average molar mass $M_w = 10$ kg/mol and 92% isotactic and 8% atactic triads) very rapidly forms an elastic gel when cooled below about 0 °C. Contrary, a concentrated aPMA solution with $\alpha_N = 0$ (polymer of a very high molar mass, no stereoregular composition given, but presumably a typical atactic or conventional polymer) was reported to form a gel network when heated above 47 °C [3]. Furthermore, anomalous rheological behavior was reported for aPMA, known as negative thixotropy or also antithixotropy [4,8]. This phenomenon refers to a reversible [4], or possibly irreversible [8], shear-induced viscosity increase, which was ascribed to a possibility that more intermolecular bonds between PMA chains are formed in the field of flow than in a system at rest [4]. Until today, to the best of our knowledge, no report on the effect of shear on solution behavior of iPMA is available. Nevertheless, these few investigations suggest that intermolecular association of PMA depends significantly on polymer tacticity. This issue was never investigated in detail and, in view of broad range of PMA applications, it is important to fill this gap.

In this Paper we therefore present a comparative static, SLS, and dynamic light scattering, DLS, study of both PMA isomers in dilute aqueous solution at 25 °C in the presence of 0.1 M NaCl by varying the polyion charge. Light scattering, LS, is known to be very sensitive for following intermolecular association in solution. As indicated above, at low charge it may be expected that PMA chains are intermolecularly associated, which should be clearly demonstrated

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in LS experiments by a low diffusion coefficient related to aggregates and by very strong scattering. At high charge, on the other hand, repulsion between likely charged polyions prevents chains to associate, but causes that they cannot orient and move freely in solution. This leads to so called anomalous diffusive mode that is in LS studies classified by various descriptions, e.g. as an extraordinary mode [9], slow mode [10,11], polyelectrolyte effect [12] or as multimacroion/interchain domain (or cluster) formation [13–15]. This mode is also associated with a low diffusion coefficient, but in contrast to the case of aggregates contributes considerably less to the total scattering intensity as a result of osmotic stiffness of polyelectrolyte solutions and consecutive small fluctuations. At sufficiently high salt concentrations, when the interchain repulsions are efficiently screened, the slow polyelectrolyte mode should disappear [10,14,16,17]. Both phenomena, aggregation and the slow mode, manifest themselves in the LS measurements by contributing a low diffusion coefficient [3,4,6,8,18–20]. The aim of our study is to address these issues in dilute iPMA and aPMA solutions.

2. Experimental section

2.1. Materials

aPMA (Polymer Source Inc.; sample no. P14096-MAA; the weight and number average molar mass values are $M_w = 189{,}000$ g/mol, $M_n = 165{,}000$ g/mol, respectively) was used as received. The tacticity of aPMA was determined from the ^{1}H NMR spectrum of the methylated polyacid, the poly(methyl methacrylate), PMMA, in deuterated chloroform and is reported in Table S1 (Supplementary data). The aPMA sample is rich in syndiotactic triads; it contains around 70% syndiotactic triads. Two iPMA samples were used. One, designated as iPMA-l, was a gift from Prof. Hugo Berghmans (Catholic University of Leuven) and had $M_w = 32{,}000$ g/mol and $M_n = 11{,}000$ g/mol and its stereoregular composition was 93% of isotactic, 3% of syndiotactic, and 4% of atactic triads. The other one, designated as iPMA-h, was from Polymer Source Inc. (sample no. P6628A-MAA), had a higher molar mass and lower polydispersity ($M_w = 56{,}250$ g/mol and $M_n = 37{,}500$ g/mol), and was highly isotactic with more than 98% of isotactic triads.

Solutions of iPMA and aPMA were prepared in 0.1 M aqueous NaCl at α_N values ranging from 0 to 1 for aPMA and from 0.25 to 1 for iPMA. PMA concentration was 0.023 M (given in moles of carboxyl groups per liter, which corresponds to polymer concentration, c_p, of 2 g/L at $\alpha_N = 0$). The concentration dependency was measured for $\alpha_N = 0$ (aPMA) or 0.23 (iPMA-h) and 1 (both PMAs). For this purpose, c_p values were in the range from 1 to 5.5 g/L.

aPMA is soluble in water at any α_N. The stock solution of aPMA at $\alpha_N = 0$ was prepared by dissolving dry polymer (acid form) in 0.1 M NaCl. After one day of stirring, when the polymer was visually dissolved, the solution was filtered through hydrophilic Sartorius-Minisart filters with pore size 0.45 μm and diameter 28 mm. The polymer concentration was determined after filtration by potentiometric titration with a standardized aqueous 0.1 M NaOH solution. Higher α_N values ($\alpha_N = 0.25$, 0.50, 0.75, and 1) were prepared by adding a calculated amount of 1 M NaOH solution to this stock solution.

In contrast to aPMA, iPMA is insoluble in pure water at $\alpha_N < 0.2$ [5–7], therefore a stock solution of iPMA with $\alpha_N \sim 0.5$ was first prepared and used for the preparation of other α_N values. Dry polymer was suspended in an appropriate amount of water. A calculated amount of 1 M NaOH was added slowly. The solution was stirred for ∼2 days, with intermediate heating to around 50 °C for a few hours, and then filtered through 0.45 μm Sartorius filter. The exact α_N and c_p of this stock solution were determined after filtration by potentiometric titration as described for aPMA. Solutions with other α_N were prepared by adding a calculated amount of either 1 M NaOH (for $\alpha_N > 0.5$) or 1 M HCl (for $\alpha_N < 0.5$). In the case of HCl addition, salt (NaCl) that resulted in solution was removed by dialysis against triple distilled water. The concentration of NaCl in stock solutions was set to 0.1 M by adding a 1 M NaCl solution.

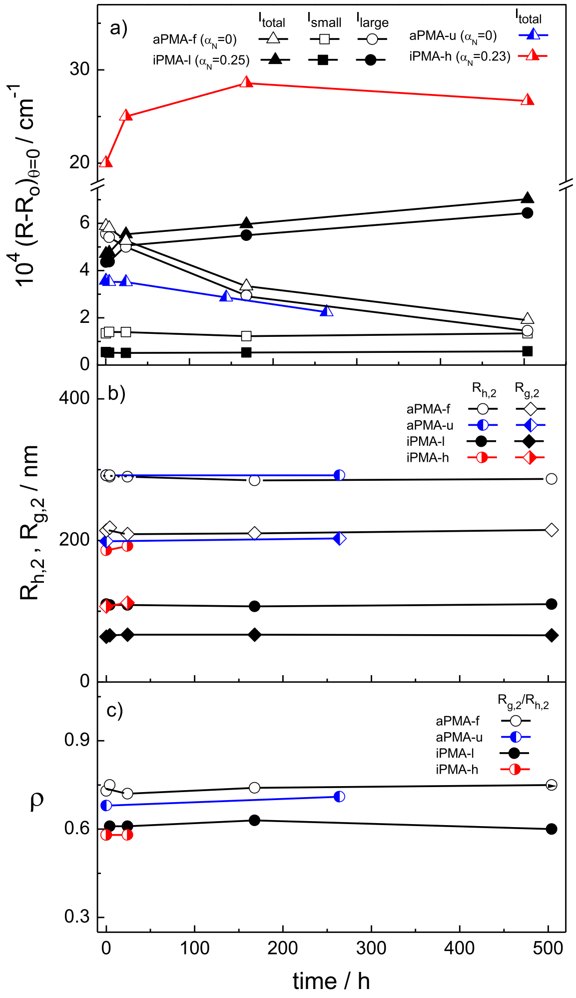

Fig. 1. Time dependence of absolute intensities (a), $R_{h,2}$ and $R_{g,2}$ (b), and shape parameter ρ (c) for intermolecular aggregates of aPMA ($\alpha_N = 0$) and iPMA ($\alpha_N \sim 0.25$) in aqueous 0.1 M NaCl.

2.2. Methods

Dynamic, DLS, and static light scattering, SLS, experiments were conducted using a 3D cross-correlation spectrometer from LS Instruments GmbH (Fribourg, Switzerland) [21,22] operating at a wavelength $\lambda_o = 632.8$ nm. Intensity of scattered light was collected in the angular range from 40° to 150°. All LS studies were performed at 25 °C. Other experimental procedures are presented in Supplementary data. Prior to LS measurements, solutions were filtered through 0.22 μm Millex HV filters directly into LS cells. aPMA ($\alpha_N = 0$) solution was studied also without being filtered. In this case, an aliquot of the stock aPMA solution (filtered through 0.45 μm Millex HV filter well before LS measurement) was measured into the cell and diluted with the solvent that was filtered through 0.22 μm filters directly into the cell. Correlation functions of the intensity of scattered light, $G_2(t)$, were recorded simultaneously with the integral time averaged intensities, $I_\theta \equiv I_q$, where q