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NEW OUTLOOK ON POLYMER "CATALYSIS"

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The small angle X-ray scattering was carried out on sodium polyacrylate aqueous solution [1]. Distinct peaks were obtained for the scattering intensity. The peak disappeared when simple salt was added or when the degree of neutralization was lowered to zero. This result provides another direct evidence of the existence of the ordered distribution of macroions in solution, which was inferred on the basis of the experimental findings previously reported such as (i) the extremely low intensity of scattered light from salt-free polyelectrolyte solutions [2], (ii) the cube-root dependence of the mean activity coefficient of polyelectrolytes in solution [3], (iii) the catastrophical drop of the apparent diffusion coefficient of polylysine measured by dynamic light scattering [4], and (iv) the presence of a peak in the small angle neutron scattering of solutions of sodium polyglutamate [5] and sodium polymethacrylate [6]. The intermacroion distance ($2D_{\mathrm{exp}}$) calculated by the Bragg equation from the observed peak decreased with increasing concentration of polyelectrolyte. Recent study shows that $2D_{\mathrm{exp}}$ decreased with decreasing concentration of simple salt, with increasing degree of neutralization, and also with decreasing degree of polymerization [7]. These results, in particular the dependence of $2D_{\mathrm{exp}}$ with the degree of neutralization, support our previous assertion [13] that the regular lattice-like distribution of macroions is due to the intermacroion linkage formed through the intermediary of gegenions. This kind of ionic distribution is a source of profound non-ideality of the solutions as testified by unusually low values of the single-ion activity coefficients of the gegenions (simple ions in general) [8] and also by other conventional thermodynamic measurements. When these activity coefficient data are coupled with the Brönsted-Bjerrum equation, we may expect pronounced influence of macroions on rates of reactions taking place between simple ions in polyelectrolyte systems. As a matter of fact, interionic reactions between similarly charged species were catalysed drastically by oppositely charged macroions [9] and those between oppositely charged species were decelerated largely by cationic and anionic polyelectrolytes [10]. More critical scrutiny indicated, however, that forward and backward processes were influenced independently by polyelectrolytes [11], indicating that polyelectrolytes should not be regarded as catalysts, contrary to the usually accepted view. These polyelectrolyte influence on reaction rates was summarized and discussed in terms of the Brönsted-Bjerrum-Manning theory in recent review articles [12,13]. The theory was found to be fairly satisfactory as far as low polyelectrolyte concentrations and relatively small polyelectrolyte accelerations are concerned. A most recent study [14–16] shows that, in addition to the electrostatic factor, desolvations of reactants and/or activated complexes by macroions are key factors in determining the catalytic influence of polyelectrolytes. The pressure dependence of polyelectrolyte accelerated reaction gave a large positive volume of activation ($\Delta V^{\neq}$), in contrast with a negative $\Delta V^{\neq}$ in the absence of the polyelectrolyte [15]. This implies that the activated complex was dehydrated by macroions to a much larger extent than the reactants, giving rise to stabilization of the complex through increase in the entropy of activation. On the other hand, polyelectrolyte-decelerated reactions were found to be associated with decrease in (positive) $\Delta V^{\neq}$, reflecting that desolvation of reactant caused its stabilization and hence deceleration.

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