Consequences of linking charged and uncharged monomers to binary copolymers studied in dilute solution. Part I: Viscometric behavior of the homopolymers, the effects of charging, and uncommon salt effects

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ABSTRACT

Intrinsic viscosities, generalized intrinsic viscosities and viscometric interaction parameters were measured for aqueous solutions of poly(ethylene oxide) [**PEO**], poly(*N,N*-dimethyl aminoethyl methacrylate) [**PR**] (uncharged) and for poly{[2-(methacryloyloxy)ethyl] trimethylammonium iodide} [**PR⁺**] (charged) within a wide range of molar masses. In this manner it was possible to establish the information required for the study of non-additivity effects upon the formation of binary copolymers from the monomers specified above. The following additional items were of particular interest: The effects of charging **PR** to **PR⁺** and the composition dependence of the coil overlap in the case of saline (NaCl, CaCl₂ and NaI) solvents. NaCl turned out to be much less efficient in shielding the electrostatic interactions than the other salts due to its large tendency to form ion pairs in solution.

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1. Introduction

Despite the undisputable importance of copolymers – whether block or random – it is presently practically impossible to predict their properties from knowledge on the behavior of the corresponding homopolymers. This lack of information is due to theoretical and practical reasons. On the theoretical side, it is the complexity of the topic, which makes it – for instance – necessary to use three interaction parameters even for copolymer solutions in a single solvent. The problems on the experimental side result above all from the absence of reliable methods for the study of polyelectrolyte solutions.

Bearing this situation in mind, we have initiated the present investigation with the goal of collecting evidence for the simplest possible case of *dilute* copolymer solutions by means of overlookable experimental expenditure. To that end we have employed a comparatively new viscometric approach [1]. It is generally applicable for the modeling of the viscosities of dilute polymer solution. Its main progress – as compared with traditional methods – lies in its aptitude for quantitative description of solutions of polyelectrolytes or globular proteins, irrespective of the presence or absence of extra salt.

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Based on the expectation that copolymers made of charged and uncharged monomers should deviate drastically in their properties from the corresponding homopolymers, we were looking for suitable linear representatives of homo- and copolymers. The combination of the monomers N,N-dimethyl aminoethyl methacrylate and ethylene oxide turned out to be suited best; one reason is that the former has the advantage of being easily quaternized.

This first part of the two papers deals with the uncharged poly(N,N-dimethyl aminoethyl methacrylate) (usually abbreviated as **PDMAEMA** but in the following for simplicity called **PR**), its charged analogue **PR$^+$**, and poly(ethylene oxide) (**PEO**). The required sample of **PR** was kindly provided by Dr. Valérie Jérôme (University of Bayreuth, Germany) from Prof. Dr. Axel H.E. Müller's group (Johannes Gutenberg University, Mainz, Germany). Detailed knowledge on the homopolymers specified above is required for the investigation of copolymers presented in part II [2]. In view of the fact that the viscometric properties of polyelectrolytes depend strongly on the type and the amount of extra salt we have also varied the salinity of the solvents.

It should not remain unmentioned that the viscometric behavior PR$^+$ appears interesting as such because of its ability to form complexes with DNA – so-called nonviral gene vectors [3,4], and because of a number of other interesting properties like sensitivity with respect to temperature, pH and CO_2 [4–7].

2. Theoretical background

Starting point of the present approach [1] is the introduction of a generalized intrinsic viscosity, $\{\eta\}$, according to:

$$\{\eta\} \equiv \left(\frac{\partial \ln \eta}{\partial c}\right)_{c,T,p,\dot{\gamma}} = \left(\frac{\partial \ln \eta_{\text{rel}}}{\partial c}\right)_{c,T,p,\dot{\gamma}} \tag{1}$$

In the above relation, η is the viscosity of the polymer solution at constant temperature, pressure and shear rate, and η_{rel} is η/η_o, where η_o stands for the viscosity of the pure solvent. The *generalized* intrinsic viscosity signifies the specific hydrodynamic volume of the polymer at *arbitrary concentration c* (mass/volume), in contrast to the intrinsic viscosity itself, which is the specific hydrodynamic volume at *infinite dilution*:

$$[\eta] = \lim_{\substack{c \to 0 \\ \dot{\gamma} \to 0}} \{\eta\}_{T,p} \tag{2}$$

The above equations can be applied to any type of polymer. Their great advantage lies, among other things, in the ability to provide access to unadulterated $[\eta]$ values for polyelectrolytes in the absence of extra salt.

The following relation has turned out to be very helpful for the modeling of measured solution viscosities as a function of composition [8]:

$$\ln \eta_{\text{rel}} = \frac{\tilde{c} + \alpha\tilde{c}^2}{1 + \beta\tilde{c} + \gamma\tilde{c}^2} \tag{3}$$

where α quantifies the composition dependence of the friction between the components, β and γ take into account the changes of the free volume of polymer solutions as compared with those of pure solvent.

For simplicity and better comparison of the results, the compositions of the mixtures are in this equation given in terms of reduced concentrations, $\tilde{c}$, defined as follows:

$$\tilde{c} = c[\eta] \tag{4}$$

Eq. (3) is capable of modeling the experimental results for virtually all polymer solutions (including solutions of polyelectrolytes in the absence and in the presence of extra salt) from the pure solvent up to the melt or to the glassy solidification of the system [8]. In most cases two out of the three parameters suffice for that purpose, where it is normally α that can be set zero.

For the composition dependence of the generalized intrinsic viscosity, Eqs. (1) and (3) yield to:

$$\{\eta\} = \frac{[\eta](1 + 2\alpha\tilde{c} + (\alpha\beta - \gamma)\tilde{c}^2)}{(1 + \beta\tilde{c} + \gamma\tilde{c}^2)^2} \tag{5}$$

which enables the calculation of the degree of coil overlap, Ω, according to:

$$\Omega = \{\eta\}c \tag{6}$$

The use of the generalized intrinsic viscosity (instead of $[\eta]$ as in the case of reduced concentrations) accounts for the fact that the coil dimensions change with the polymer concentration in the general case. Eq. (5) yields the following expression for Ω:

$$\Omega = \frac{\tilde{c}(1 + 2\alpha\tilde{c} + (\alpha\beta - \gamma)\tilde{c}^2)}{(1 + \beta\tilde{c} + \gamma\tilde{c}^2)^2} \tag{7}$$

It would of course be gratifying to ascribe a molecular meaning to the parameters α, β and γ. Presently the only successful interpretation is phenomenological only. From Eq. (3) it is obvious that β quantifies the viscometric effects of contacts between the solvent (the concentration of which is practically unity at low $\tilde{c}$ values) and isolated polymer coils; in contrast