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Light scattering study of salt-free 'polyelectrolyte behaviour' of monotelechelic ionomers in a polar solvent

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Salt-free polyelectrolyte behaviour which is typically observed at low polymer concentrations for polyelectrolyte aqueous solutions and random ionomer non-aqueous solutions (in polar solvents) (i.e., negative angular dependence of the reciprocal scattering in static light scattering and an appearance of the fast mode in dynamic light scattering) has been observed for *monotelechelic ionomer* solutions in a polar solvent. This indicates that *only single charge* (per chain) is sufficient to produce *intermolecular electrostatic interactions*, which are responsible for such characteristic behaviour. However, the 'characteristic' behaviour, which is typically observed at higher concentrations for polyelectrolyte and random ionomer solutions (i.e., large positive apparent radius of gyration in static scattering and appearance of the slow mode in addition to the fast mode in dynamic scattering) has not been observed to date for monotelechelic ionomer solutions. The absence of high-concentration characteristics for the monotelechelic ionomer solutions gives additional insight as to the nature and structure of 'heterogeneities' in salt-free polyelectrolyte solutions, which is still controversial. Copyright © 1996 Elsevier Science Ltd.

Introduction

The interest in polyelectrolyte solutions continues to be strong as witnessed by the recent publication of several books on polyelectrolytes[1–3]. Polyelectrolyte solutions are considered to be one of the least-understood categories of condensed matter[3]. For example, the behaviour of *salt-free* solutions of conventional polyelectrolytes made of flexible backbone chains, such as sodium poly(styrenesulfonate) and sodium polyacrylate, is still not well understood in terms of the structure of the solution and the essential factors causing the characteristic behaviour[4]. Mandel points out that 'the origin of the phenomena observed remains partly obscure, indicating that the present treatment of polyelectrolyte behaviour is incomplete and that some fundamental new views are needed to gain a full understanding[2].

It has been demonstrated that random ionomers that contain a relatively small number of ionic groups (up to 10–15 mol%), randomly distributed along non-ionic backbone chains, can be used as a good model system to investigate the characteristic behaviour of salt-free polyelectrolyte solutions[2,5]. A typical example is partially sulfonated polystyrene (SPS) dissolved in an aprotic, polar solvent, dimethylformamide (DMF). All the observations made on random ionomers in polar solvents, including conductimetry, viscometry, osmometry, light scattering (both static and dynamic), and small-angle X-ray and small-angle neutron scattering,

in general parallel those from salt-free polyelectrolytes in water[2].

A further reduction in number of charges can be achieved in telechelic ionomers, whose ionic groups are located only at the chain ends. Some *salt-free 'polyelectrolyte behaviour'* has been observed for telechelic ionomers, dissolved in a polar solvent: a marked upturn in reduced viscosity with decreasing polymer concentration and a significant reduction in scattered intensity with increasing polymer concentration[6,7]. Especially interesting is the fact that similar behaviour has also been obtained on monotelechelic ionomers, which have only one ionic group per chain. Since no intramolecular electrostatic interactions are available for this polymer, the behaviour must be explained by *intermolecular electrostatic interactions*. One of the complexities of polyelectrolyte solutions arises from the fact that both *intramolecular* and *intermolecular* electrostatic interactions are heavily involved. The intramolecular interactions may cause reduction in chain flexibility and chain expansion[4]. The intermolecular interactions may cause ordering of polymer molecules and even formation of higher order structures (e.g., 'domain' and 'temporal aggregates'), which are currently controversial[8–11]. Since these two effects are usually inseparable, the interpretation of the data is not straightforward. One useful approach to investigate the effect of *intermolecular* electrostatic interactions in flexible polyelectrolytes may be use of ionic polymers having a single charge (i.e., monotelechelic ionomers)[6,7]. Since no intramolecular electrostatic interactions are available for this type of

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ionomer, the effects of intermolecular electrostatic interactions can directly be observed.

In this paper, we report results on 'polyelectrolyte behaviour' of monotelechelic ionomers in a polar solvent, DMF, which are investigated by static (angular) light scattering and dynamic light scattering, analysed by CONTIN. Dynamic scattering data are of particular interest, since the interpretation of the dynamic light scattering data on salt-free polyelectrolyte solutions has led to recent controversies over their structures[10,11]. The system (monotelechelic[12] ionomer) is considered to be the extreme case, in which the number of ionic groups is reduced to one per chain. Unlike random ionomers in which there is a distribution of ion content even for monodisperse (in terms of molecular weight) samples, the ion content distribution is very sharp.

Experimental

In a previous study, a polystyrene-based ionomer with dimethylamino end groups was used[6,7]. In this work, a polystyrene-based ionomer with lithium sulfonate end groups is used. The polystyrene-based telechelic polymers were synthesized by anionic polymerization of styrene. Living chains were deactivated with 1,3-propanesultone to obtain lithium sulfonate end groups[13]. A small amount of sample was separated from the same batch to obtain polystyrene as a reference polymer. The number-average molecular weight, M_n, was 50 000 with a narrow molecular weight distribution ($M_w/M_n = 1.05$), as determined by g.p.c. The telechelic functionality was higher than 0.95, as determined by potentiometric titration of the acid end groups, where acid samples were obtained by precipitating lithium salt polymer into methanol containing excess amount of perchloric acid. The final ionomer samples were prepared by freeze-drying in benzene/methanol (90/10, v/v), followed by drying for 1 week at room temperature. Polymer solutions were prepared by dissolving the dried sample in DMF under stirring overnight at room temperature. Low-angle light scattering experiments were conducted with a KMX-6 low-angle laser light scattering photometer (Chromatix) at $25 \pm 0.5°C$. The specific refractive index increment, dn/dc, was measured at $25 \pm 0.1°C$ by using a KMX-16 differential refractometer (Chromatix). Angular measurements and dynamic scattering measurements were conducted with a BI-200SM photogoniometer (Brookhaven) with a 35 mW He–Ne laser and a BI-2030 digital correlator (Brookhaven). All light scattering measurements were conducted at a wavelength of 632.8 nm. The optical clarification of the solution was carried out by passing the solution through two membranes (PTFE Membrane Filter: Whatman), whose pore sizes were 0.45 and 0.1 μm (or 0.2 μm), in succession. Experimental details concerning low-angle light scattering[14], angular light scattering[15], and dynamic light scattering analysed by CONTIN[16] are described elsewhere.

Results and discussion

Figure 1 shows static light scattering results: both low-angle data and angular data are plotted in the same figure. Two major points are noted: first, the characteristic behaviour of low-angle light scattering results is seen[17–19]: the Kc/R_0 value rises steeply from the intercept, bends over, and levels off at higher concen-
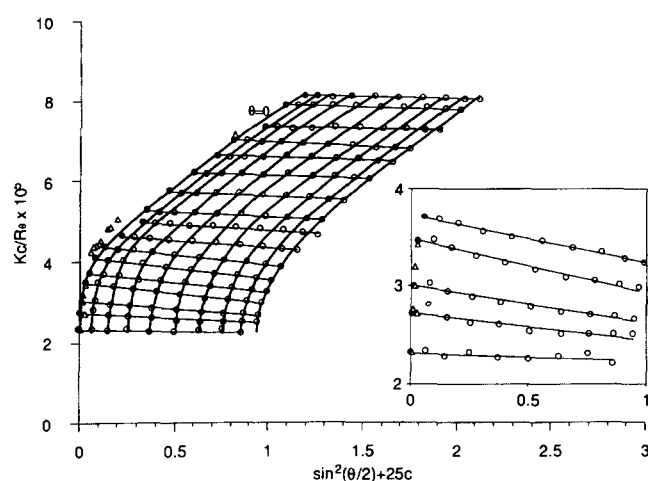

Figure 1 A Zimm plot for monotelechelic ionomer in DMF as well as low-angle light scattering data: circles represent angular data and triangles represent low-angle data. The concentration range covered is 5.0×10^{-5}–4.8×10^{-2} (g cm^{-3}). The inset is magnification of low concentration data

tration. Here, K is the optical constant, c is the polymer concentration (g cm^{-3}), and R_0 is the excess reduced scattered intensity (R_θ) extrapolated to zero angle. The behaviour can be explained in terms of the reduced scattered intensity due to low osmotic compressibility, $\partial c/\partial\Pi$, arising from *intermolecular* electrostatic interactions between polyions. Second, the angular data of a Zimm plot at low concentrations shows *negative slopes*, which are typically observed for random ionomers in a polar solvent[15] and polyelectrolytes in water[20,21]. Again, negative angular dependence of the reciprocal reduced scattered intensity, Kc/R_θ, is explained as arising from *intermolecular* interactions; intermolecular electrostatic interactions cause non-random arrangement of polyions, which is reflected in the intermolecular interference term in scattering equations, leading to a negative contribution in angular dependence[15]. An important conclusion to be drawn from these observations on monotelechelic ionomers is that one ionic group (per chain) is enough to cause non-random arrangement of polymer molecules due to strong *intermolecular* electrostatic interactions. This is consistent with our previous conclusions inferred from viscosity and low-angle light scattering measurements of monotelechelic ionomers[6,7].

However, another characteristic angular dependence, typically observed at higher concentrations for random ionomer solutions in a polar solvent[15] and polyelectrolytes in water[20,21], has not been observed for the monotelechelic ionomer solutions; i.e., positive angular dependence resulting in larger particle size (or apparent radius of gyration, R_g) than that of the unmodified polymer. This will be discussed when dynamic light scattering results are presented.

Figure 2 shows dynamic light scattering results analysed by CONTIN. A single peak appears in the spectrum of the decay rate, Γ (normalized by the square of the scattering vector, q). It is seen that the diffusion coefficient ($D = \langle\Gamma\rangle/q^2$, which is obtained from the average value of abscissa) is greater than that of unmodified PS; therefore, this corresponds to a fast mode. The appearance of the fast mode is typically
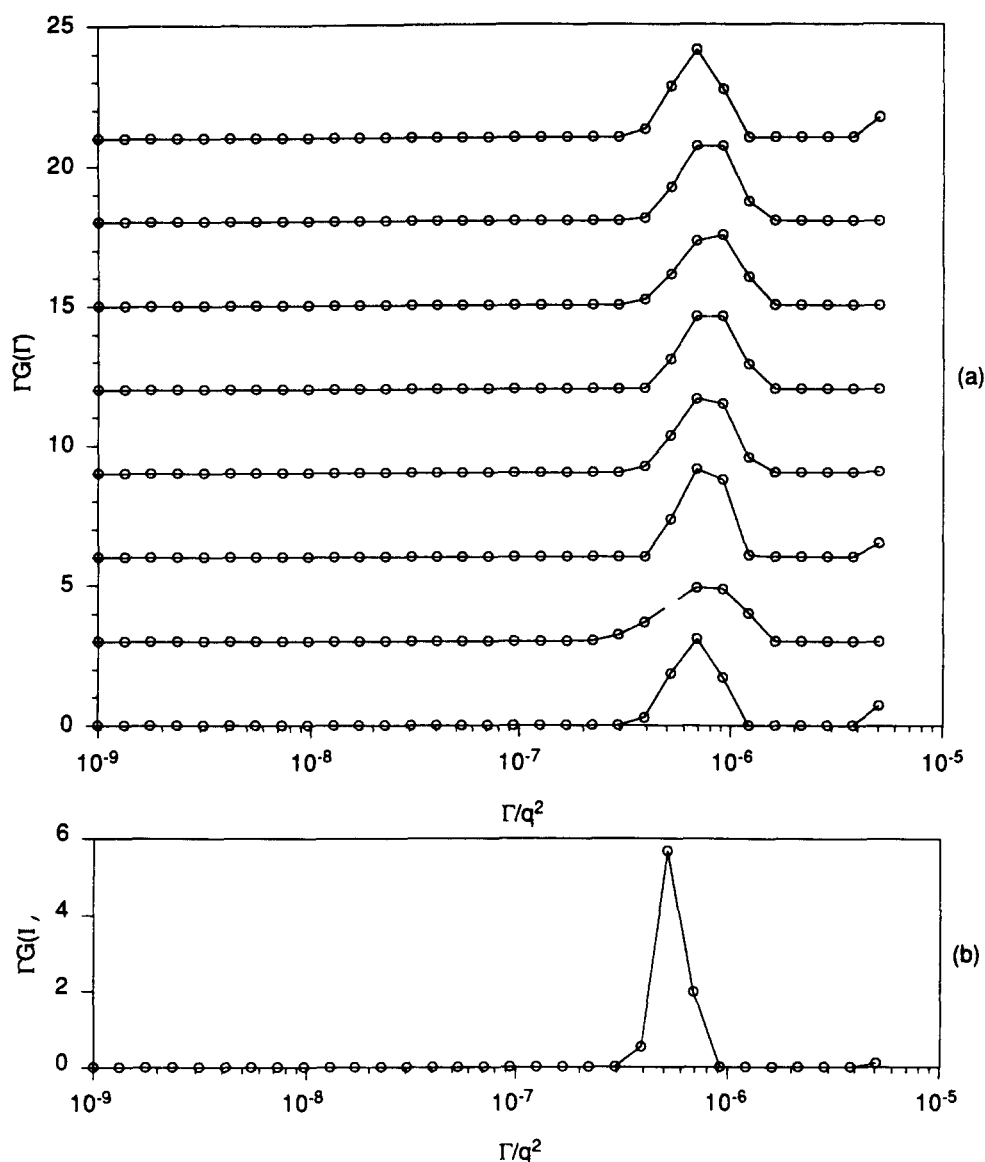
Figure 2   (a) A spectrum of decay rate, Γ normalized by the square of the scattering vector, q, which is obtained by CONTIN analysis for monotelechelic ionomer in DMF. Data at 60° are shown and each curve is shifted along the ordinate. The concentration range covered is 1.5×10^{-3} (bottom curve)–1.8×10^{-2} (top curve) (g cm^{-3}). (b) A spectrum of decay rate for polystyrene in DMF

observed for random ionomers in a polar solvent[16] as well as polyelectrolytes in water[20,21]. The fast mode may be interpreted in terms of non-equilibrium thermo-dynamics[23,24]: as indicated by the generalized Stokes–Einstein relation, diffusion is caused by the 'thermo-dynamic driving force' for diffusion (i.e., chemical potential gradient), which is proportional to the inverse osmotic compressibility, $(\partial c/\partial \Pi)^{-1}$. Since this term is very large for polyion solutions, arising from large *intermolecular* excluded volume due to repulsive inter-actions[15], the diffusion coefficients of polyions are significantly enhanced. Although the fast mode may also be interpreted as arising from polyion–counterion coupling, in which fast moving counterions 'drag' slow moving polyions, leading to larger diffusion coefficients of polyions[21,22], the first interpretation is more general and consistent with our conclusion that *intermolecular interactions are responsible for much of the characteristic behaviour*. Again, the appearance of the fast mode suggests that one ionic group is enough to produce strong electrostatic interactions, leading to such behaviour.

However, there seems to be no slow mode, which has been observed for both random ionomers in a polar solvent[16] and polyelectrolytes in water[20,21]. The existence of the slow mode is the indication of 'hetero-geneities' in the solution[16,20,21]. The appearance of the two modes in dynamic scattering data is closely related to the angular-dependence of static scattering data: at low polymer concentration, the fast mode dominates and the angular-dependence is negative, and with increasing polymer concentration, the slow mode begins to dominate and the angular-dependence becomes positive[16,21].

Characteristic behaviour of telechelic ionomer solutions observed at low concentrations can be related to *intermolecular interactions*, as explained above. On the other hand, the reason for the absence of the high-concentration characteristics, i.e., positive angular dependence in static scattering data and the slow mode in dynamic scattering data, is more complex. The first factor to be considered is the absence of intramolecular electrostatic interactions. Although how it is related to the slow mode is not immediately

clear, such interactions should be more important in dilute solutions. Usually, high-concentration characteristics are attributed to the existence of 'heterogeneities'. Some models have been proposed to explain the formation of such 'heterogeneities' in salt-free polyelectrolyte solutions. Among them, most widely used are the following ones. One is due to formation of 'aggregates', such as an 'ordered phase' in a two-phase structure, which is formed by polyion–polyion attractions through intermediary counterions[9], and 'temporal aggregates' formed through dipole–dipole type attractions through the distortion of counterion clouds[8]. It should be stressed that these models are explained due to *intermolecular* interactions. Another is due to the existence of aggregate/particles, already existing in dry polyelectrolyte samples[11], which cause strong scattering contribution to salt-free polyion solutions, since scattering from polyions is very small, especially at high concentration, as noted in the higher value of c/R_θ (reciprocal scattered intensity per unit concentration) in *Figure 1*. The absence of the 'heterogeneities' in monotelechelic ionomer solutions may be explained in terms of weaker ionic interactions than that needed for aggregate (or 'domain') formation, since the ion content of our sample is only 0.2 mol% (or one ionic group per 500 repeat units). However, it may also be explained as arising from the 'purer' samples that we used. Since random ionomers and polyelectrolytes most widely used have been made by sulfonation reaction of anionically polymerized (standard) polystyrene in contrast to telechelic ionomers that are made by anionic polymerization only, and since an intermolecular cross-linking side reaction may occur during sulfonation reactions[25], a small amount of cross-linked polystyrene may exist and works as 'aggregates' whose sizes are sufficiently small to pass through filters, but large enough to contribute to overall scattering. More studies are needed to clarify these points.

In summary, for the monotelechelic ionomer dissolved in a polar solvent, characteristic behaviour (i.e., negative angular dependence of reciprocal scattered intensity and an appearance of the fast mode), which is typically observed at low polymer concentrations for polyelectrolytes in water or random ionomers in a polar solvent, has been observed. This is explained as arising from intermolecular electrostatic interactions that are caused by only one charge per chain. However, the characteristic behaviour (i.e., large positive apparent R_g and appearance of the slow mode in addition to the fast mode), which is typically observed at higher polymer concentrations for polyelectrolytes in water or random ionomers in a polar solvent, has not been noted. While the cause for the absence of high-concentration characteristics is not yet narrowed down at this time, our results should have important bearing on the nature

and structure of 'heterogeneities' in salt-free polyelectrolyte solutions. Better understanding will be obtained by more detailed study, which is currently conducted in this laboratory and will be reported in the future.

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