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Enhanced Low-Angle Scattering from Moderately Concentrated Solutions of Atactic Polystyrene and Its Relation to Physical Gelation

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ABSTRACT: The enhanced low-angle scattering (ELAS) observed in moderately concentrated solutions of atactic polystyrene is examined in the light of its possible correlation with physical gelation. This paper deals with several points: (i) This correlation is again tested by means of light scattering with solvents of very low freezing points ($T_m \simeq -100$ °C). Results show that ELAS is observable in THF (gelation solvent) but absent in methylene chloride (nongelation solvent). (ii) The vanishing of ELAS is studied as a function of temperature and solution preparation (centrifugation). It is shown that the ELAS disappears at a well-defined temperature on heating and then reappears on cooling. Identical intensity patterns recorded after a heating and cooling cycle attest to the perfect reversibility of the phenomenon. Concerning centrifugation, it is pointed out that for solvents wherein ELAS is evidenced, a gradient of concentration is created unlike for solvents wherein ELAS is absent. (iii) The thermal properties (melting enthalpy and melting point) of the solvents in polymer solutions are examined by differential scanning calorimetry. These investigations reveal that paradoxically the more solvating diluents give rise to ELAS. In addition, it is found that the solvent melting temperature does not vary significantly for solvents wherein ELAS is observed, while it exhibits a rapid falloff in the other ones. These results suggest the existence of a kind of solvent–polymer complex. Light scattering results are further analyzed. It is shown that in all the systems investigated the larger angle data are consistent with $I \sim (q^2 + \xi^{-2})^{-1}$. Determination of ξ^{-1} gives $\xi \sim C^{-3/4}$ in all cases. In solvents where ELAS is observed, the smaller angles are analyzed in terms of the Debye–Bueche scattering function $I \sim (q^2 + a^{-2})^{-2}$. The correlation length a varies as C^{-1}, which suggests that long-range fluctuations are determined by three-body interactions. Finally, all these results are discussed in the light of the different views expressed hitherto on physical gelation of atactic polymers.

Introduction

Solution properties of amorphous polymers have received a renewal of attention the past few years thanks to the theoretical breakthrough of scaling laws.[1] Different studies by scattering techniques have shown that such a theoretical approach accounts for chain behavior in a wide range of concentration and temperature. Yet for semidilute or moderately concentrated solutions, the theory pertains only as long as dimensions smaller than chain dimensions are dealt with. For distances of the order of the chain radius of gyration, light scattering experiments surprisingly reveal in some systems an enhanced low-angle effect that all the theories have failed to predict.[2-8] The appearance of this effect seems to depend on the method used for preparation of the solutions[5] and on the nature of the solvent.[9] Until recently, two major explanations have been put forward. On one hand, it has been claimed that this abnormal scattering could be due to the presence of islands of pure polymer in solution. This explanation is in conflict with the fact that the effect exists in very good solvents.[2] On the other hand, density fluctuations due to chain reptation have been taken into consideration. This statement cannot account for the total absence of effect in some solvents.[9]

While heterogeneities undoubtedly exist and are solvent-dependent, their origin is still puzzling when only considering a completely disordered polymer.

In the light of the discovery by Tan el al.[10] of atactic polystyrene's (aPS) ability to form physical gels, Guenet et al.[9] have suggested that enhanced low-angle scattering and gelation would be different manifestations of the same phenomenon. They have in particular shown that when a polymer–solvent couple can physically gel, the enhanced low-angle scattering is observable at room temperature and

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vice versa. Their interpretation considers the possible "crystallization"[24] of some stereoregular portions of the chain promoting the gelation process as well as the enhanced scattering at higher temperatures.

As physical gelation of aPS has now been definitely confirmed,[11,12] such a correlation between both effects need be investigated more deeply, with special emphasis on the role played by the solvent. In a recent work, Boyer et al.[13] suggest that gelation arises from segment–segment interaction, which could be hindered in very good solvents and promoted in poor solvents. Such an assumption does not seem consistent with the experimental results of Guenet et al.[9] Nevertheless, the main criticism against the correlation between gelation and enhanced low-angle scattering is that gelation cannot be observed in solvents of too high melting points such as benzene, wherein ELAS exists; it then appears crucial to compare solvents with nearly identical thermal properties.

Accordingly in this paper, where we report results of light scattering and differential scanning calorimetry experiments, our purpose is manifold: (i) to examine again the relevancy of the correlation proposed by Guenet et al.[9] between the enhanced low-angle scattering and the physical gelation, taking into account the melting temperature of the solvents; (ii) to investigate the influence of temperature on low-angle scattering in order to test the concept of "crystallization" even in the sol phase; (iii) to understand how the preparation method of solutions can modify their scattering properties by investigating more precisely the effects of centrifugation;[5] (iv) to show that Flory's interaction parameter χ cannot be regarded as the main factor of these phenomena; (v) to see if local effects of chain solvation (through the number of solvent molecules bound per monomer unit, as measured by DSC) could be correlated to the existence of abnormal scattering and introduce the idea that gelation could be due to the formation of a kind of "crystalline complex" between solvent and polymer.

Experimental Section

A. Materials. We used three atactic polystyrene samples synthesized by anionic polymerization. Their weight-average molecular weights, (M_w) are 5.6×10^6 (aPS1), 1.7×10^6 (aPS2), and 1.8×10^5 (aPS3), and their polydispersity indices measured by gel chromatography are lower than 1.3. Their ^{13}C NMR spectra reveal the usual stereoregularity of anionic polystyrene.[12] All the solvents were of high-purity grade.

B. Light Scattering Experiments. Measurements of light scattering intensity were recorded with a Wippler-Scheibling type photogoniodiffusometer[14] operating with a red laser beam (λ = 6320 Å). The temperature was controlled within 0.5 °C. Moderately concentrated solutions were prepared from dilute stock solutions (approximately 10^{-3} g·cm^{-3}) that had been homogenized for 48 h and carefully cleaned by successive filtrations on no. 4 and no. 5 sintered funnels. These dilute solutions were then collected in the appropriate apparatus represented in Figure 1, and the solutions were concentrated by freeze-drying. The apparatus was rinsed several times beforehand by filtered solvent until a symmetrical angular dependence of the scattered intensity was obtained. The advantage of this device lies in the possibility of concentrating solutions under study in a system totally sealed from the atmosphere and of preventing the introduction of dust. In solvents whose refractive index is too different from that of glass, very precise studies on moderately concentrated solutions require the use of high-quality light scattering cells made of optical glass.

In order to check the reproducibility of the results gained from moderately concentrated solutions, some measurements were repeated 1 week later.

Light scattering measurements have been first carried out on dilute solutions for all the solvents. The actual value of the weight-average molecular weight was obtained (within 5%) which confirms the absence of dust. In addition the values of the radii of gyration R_g and second virial coefficient A_2 provide information on the solvent quality. Flory's interaction parameter can be determined from values of A_2 according to

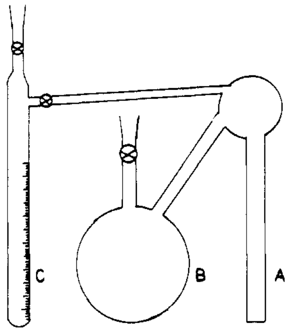

Figure 1. Sketch of the apparatus used for concentrating solutions: (A) light scattering cell; (b) dilute solution reservoir; (C) graduated reservoir used to measure the volume of freeze-dried solvent.

$$A_2 = (v_2/M_w)^2(1/v_1)\,(1/2 - \chi) \qquad (1)$$

where v_2 and v_1 are the partial specific volumes of the polymer and solvent, respectively.

C. UV Spectroscopy. For some experiments (see part C of Results) we have determined the concentration of solutions after dilution by using a Shimadzu UV240 spectrophotometer. A calibration curve was previously established, and the accuracy on concentration is 1%.

D. Differential Scanning Calorimetry. This technique enables one to determine the melting temperature T_m and melting enthalpy ΔH_{sol} of the solvent in concentrated aPS solutions.

A DSC II Perkin-Elmer microcalorimeter was employed. Cooling rates of 2.5–5 °C/min were used to make the solvent crystallize. Thermal analysis was performed with heating rates ranging from 5 to 20 °C/min.

A desired quantity of aPS was introduced into a weighed "volatile sample" pan. An estimated volume of solvent was pipeted into the pan, which was then tightly sealed. The pans were set aside at room temperature for at least 2 months so as to ensure a thorough homogenization. The weight of each pan was measured prior to use in order to determine the concentration of the solution. Some DSC measurements were repeated a month later to test for possible incomplete homogenization. It has been checked that cooling just below $T_{freezing}$ (temperature at which the solvent crystallizes) or 30–40 °C below $T_{freezing}$ does not significantly alter the results.

The variation of ΔH_{sol} with polymer concentration is generally linear (see Figure 4), and the extrapolation to $\Delta H_{sol} = 0$ gives a polymer concentration c_p' (grams of polymer per gram of solution) for which all the solvent is adsorbed (no longer free molecules able to freeze). From the c_p' value, the ratio R of the number of solvent molecules adsorbed per monomer unit can easily be deduced from relation

$$R = \frac{(1 - c_p')/m_{sol}}{c_p'/m_p} \qquad (2)$$

where m_{sol} and m_p are the molecular weights of the solvent and of the monomer unit, respectively. This technique has already been widely applied to water-soluble systems.[15,16] Correspondingly, if the variation is linear, R gives a measure of adsorbed solvent molecules per monomer, even in dilute solution.

Results

A. Correlation between Gelation Ability and Enhanced Low-Angle Scattering. Guenet et al.[9] used chloroform and 1,2-dichloroethane in their experimental investigation. The correlation found between gelation ability and enhanced low-angle scattering might be called into question on account of the relatively high melting points of these solvents (see Table I). As a result, the

Table I
Parameters of Different Solvents and Behavior of Their aPS Solutions

solvent	T_m, °C	χ	existence of gelation[a]	ELAS	solvation ratio (R)	$T_m = f(c_p)$	exponent α
benzene	5.5	0.45[b]	no	yes	0.93	constant	
p-dioxane	11.8	0.46[c]	no	yes	0.97	constant	0.82
p-chlorotoluene	7.5	0.47[c]	no	no	0.5	decrease	0.77
p-xylene	13	0.47[c]	no	no	0.46	decrease	0.70
THF	−65	0.46[b]	yes	yes	3.22		0.75
methylene chloride	−95	0.48[c]	no	no			0.70
carbon disulfide	−111	0.4[b]	yes	yes	2.56		
chloroform	−65		no	no			
1,2-dichloroethane	−35		no	no			

[a] From ref 10, ELAS is enhanced low-angle scattering. [b] Values taken from literature data. [c] Values determined in this work.

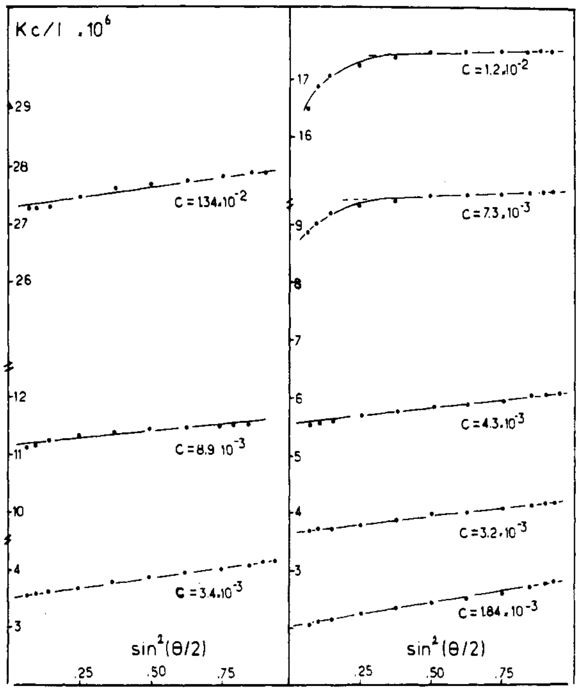

Figure 2. Zimm plots for aPS2 in THF (right) and methylene chloride (left) T = 19.5 °C, polymer concentration in g·cm^{-3}.

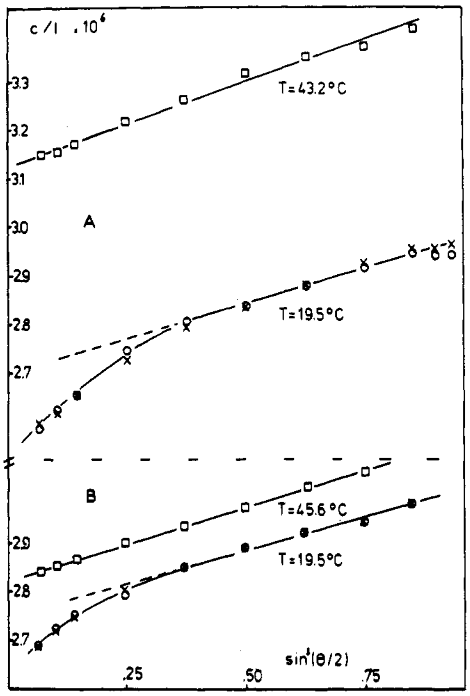

Figure 3. Zimm plots for aPS2 in p-dioxane (A), c = 5.7 × 10^{-3} g·cm^{-3}, and THF (B), c = 5.6 × 10^{-3} g·cm^{-3} at different temperatures. (□) before and (×): after heating and cooling cycle.

absence of enhanced low-angle scattering could be merely fortuitous. It then appears necessary to compare two solvents of very low melting points (Table I) wherein aPS gelation takes place in one of them only. According to Tan et al.[10] methylene chloride (no gelation) and THF (gelation) are good candidates for such a comparison.

Light scattering results obtained with these solvents (see Figure 2) show that only THF solutions exhibit the low-angle effect. This result therefore provides further support to the hypothesis which attributes the same origin to gelation and abnormal scattering. In addition these results can be examined with respect to the solvent quality toward polystyrene. The χ values gathered in Table I show that THF is a better solvent than methylene chloride. According to the recent suggestion of Boyer et al.[13] one could expect that methylene chloride solutions present the characteristics of "aggregation". Our experiments reveal the inverse behavior. From Table I is also appears that among the solvents benzene, p-dioxane, p-xylene, and p-chlorotoluene, with very similar χ parameters and freezing points, only two exhibit an abnormal scattering.

B. Effect of Temperature. Reversibility of the Enhanced Low-Angle Scattering. Guenet et al.[9] suggest that some kind of "crystallization" could be responsible for the abnormal scattering in solutions at higher temperatures. They thereby consider that T_m^{gel} (melting temperature of the gel) does not correspond to the complete disappearance of the "crystals" but simply to the loss of three-dimensionality. If this view is correct there should exist a temperature at which the abnormal scattering vanishes, this effect being reversible.

Experiments (see Figure 3) performed in THF and p-dioxane solutions show that the enhanced low-angle scattering disappears at $T \sim 43$ °C, in a relatively narrow temperature range. The results obtained after a heating and cooling cycle are reproducible within experimental accuracy, which ascertains the reversibility of the phenomenon.

In addition, THF and p-dioxane have been purposefully chosen for this study on account of their very different freezing points. The present results, which show a vanishing temperature of the abnormal scattering nearly the same in both solvents, suggest that gelation would also occur at temperatures close to each other had p-dioxane had a lower freezing point. Yet the knowledge of physical gelation at low temperature in THF suggests that the same "crystalline" origin be attributed to the scattering behavior in solvents like benzene and p-dioxane.

C. Effect of the Centrifugation of the Solutions. Some studies[5,17] have shown that the presence of the scattering anomaly, although reproducible, is dependent on the procedure of solution preparation. More precisely Dautzenberg[5] and Koberstein et al.[17] have found that the low-angle effect present in moderately concentrated solutions of aPS in benzene tends to decrease after centrifu-

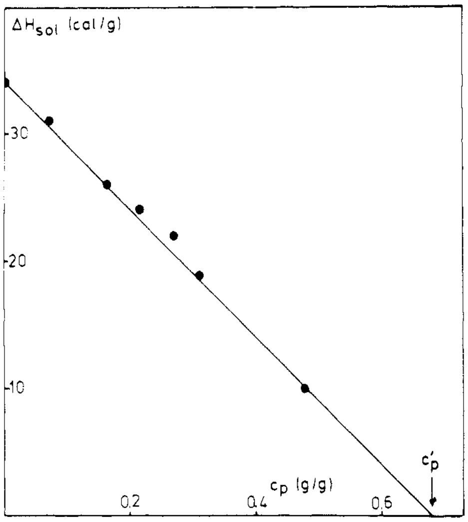

Figure 4. Variation of solvent melting enthalpy, ΔH_{sol}, vs. polymer concentration c_p for the aPS$_3$-p-xylene system.

gation of these solutions. No satisfactory explanation of this effect has been proposed hitherto.

We have prepared solutions of aPS in p-dioxane (low-angle effect) and in 1,2-dichloroethane (no effect)[19] at 1.3 × 10^{-2} and 1.06 × 10^{-2} g·cm^{-3} of polymer, respectively. These solutions have been centrifugated during 4 h at 15000 rpm, and then the concentrations in the supernatant and in the coacervat have been determined by UV spectrscopy. For the p-dioxane solution the supernatant concentration was found to be significantly lower than the initial concentration (1.2 × 10^{-2} g·cm^{-3}), the coacervat being more concentrated. On the contrary the coacervat and supernatant concentrations are exactly the same (1.06 × 10^{-2} g·cm,$^{-3}$) for 1,2-dichloroethane.

This result shows that with solvents wherein the low-angle effect appears, the "crystallization" leads to the formation of large aggregates of high molecular weight which are separated in the centrifugation process. Evidently light scattering experiments which should be performed on the supernatant solutions must show an attenuated low-angle effect since it is strongly dependent on polymer concentration. This may explain the experimental observations of Dautzenberg[5] and Koberstein.[17] Moreover, our experiments give additional support to the difference of behavior in these solvents.

D. Enhanced Low-Angle Scattering and Chain Solvation. All the above results strongly suggest that the solvent plays a prominent role in the existence of enhanced low-angle scattering and correspondingly in the gelation process. As these phenomena are apparently not correlated to the interaction parameter, which is a macroscopic measure of solvent quality, the knowledge of interactions at the molecular level is required. Here, emphasis is put on solvents with nearly identical χ and melting points. From the plots $\Delta H_{sol} = f(c_p)$ (see an example of such a plot in Figure 4 and the experimental part) in different solvents we have deduced the ratio R (number of solvent molecules adsorbed per monomer unit). From Table I, where other properties of the solvents are reported, a relevant comment can be made: the solvents that apparently solvate the polymer the least (p-xylene and p-chlorotoluene of low values of R) do not lead to the low-angle scattering effect. This result could be regarded as a paradox if one infers that the interaction parameter χ plays the main role in these phenomena.

In fact this suggests that the way the solvent molecules and the polymer interact at the molecular level is essential.

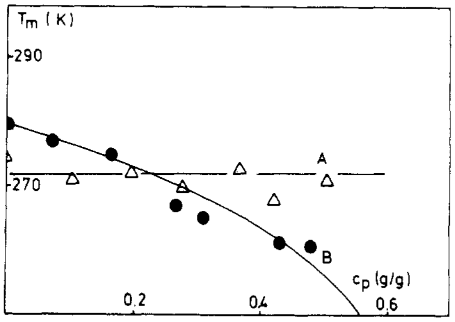

Figure 5. Variation of the solvent melting temperature, T_m, as a function of polymer concentration c_p: (A) p-dioxane; (B) p-xylene.

It may be thought that the organization of the solvent molecules around the chain strongly governs the ability of "crystal" formation.

Indirect evidence for the existence of "crystalline" parts may come from the variation of the solvent melting point with polymer concentration. Two cases are possible:

(i) A melting point depression occurs with polymer concentration, this depression being enhanced in the vicinity of c_p'. This stands for the case of a blend of solvent and purely amorphous polymer.

(ii) The melting point remains constant. Such a situation corresponds to several cases, among which is a solid solution or a complex. At any rate it indicates the existence of two phases, one of which has a "crystalline" character.

From Table I and Figure 5, one observes that for low R ratios the first situation occurs whereas for solvents of high R values there is no decrease of melting point. This result may prove to be of importance since it suggests again the existence of a kind of complex between solvent and polymer in systems where gelation and scattering anomaly take place. Conversely, strong segment–segment interactions seem to exist in p-xylene and p-chlorotoluene, where gelation does not occur (T_m decrease), and it is then difficult to believe that such types of interactions are responsible for this phenomenon.

Discussion about Low-Angle Scattering Effect

A. System without Anomaly. For moderately concentrated solutions of flexible chains, the scattering law is of a Lorentzian type, leading to

$$c/I \propto q^2 + \xi^{-2} \quad (3)$$

where q is the scattering vector, c the polymer concentration (g·cm^{-3}), I the scattered intensity, and ξ the screening length defined by Edwards.[18] This relation only applies for $R_g^{-1} < q < b^{-1}$ (if R_g and b are the radius of gyration and the statistical length, respectively), a requirement fulfilled owing to the use of a high wavelength in our light scattering experiments. ξ can be deduced from relation 3 by equating $c/I = 0$ in the appropriate range of q. Scaling laws[1] predict a variation of ξ as a function of polymer concentration

$$\xi \propto c^{-\alpha} \qquad (\alpha = 3/4) \quad (4)$$

in good solvents and for $c > c^*$, c^* being the overlap threshold.[1]

In our experiments the angular dependence of c/I for methylene chloride p-xylene, and p-chlorotoluene is found to be linear (see Figure 2, for instance) in the full experimental range of the scattering vector. This is in agreement with the recent Benoit and Benmouna theory,[19] which predicts that eq 3 holds even well below the value of q =

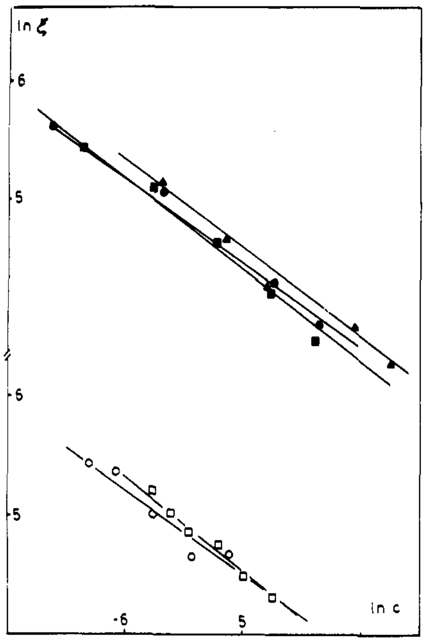

Figure 6. Log ξ vs. log c: upper part, solvents without abnormal scattering (●) methylene chloride, (■) p-chlorotoluene, and (▲) p-xylene; lower part, solvents exhibiting abnormal scattering (□) p-dioxane and (○) THF.

R_g^{-1}. In addition ξ determined from these experimental results varies as a function of polymer concentration with the exponent predicted by the scaling law of eq 4 (see Figure 5 and Table I).

B. Systems with a Low-Angle Anomaly. In some systems and only above c^* increasing concentration leads to an increasing downturn of the curve $c/I = f(q^2)$ in the smaller angle region of the Zimm plots (see Figure 2 and the figures of ref 2 and 5, for instance). Such an anomaly is generally regarded as a manifestation of long-range heterogeneities. The question is now to what extent this behavior differs from theoretical laws and what type of information can be drawn from these differences about the correlation length of these heterogeneities.

We will adopt the analysis procedure proposed by Koberstein et al.[17] It is based on the fact that relation 3 can be applied in the full experimental range of the scattering vector as supported by Benoit and Benmouna theory[19] and confirmed by our experimental results in solvents wherein there is no polymer scattering anomaly. Consequently they assume that the scattered intensity can be simply written as the sum of two terms

$$I(q) = 1/(q^2 + \xi^{-2}) + I_{EX} \qquad (5)$$

where I_{EX} is the low-angle excess intensity due to long-range heterogeneities.

If this analysis is correct, I_{EX} can be determined according to

$$I_{EX} = c\left[\frac{1}{(c/I)} - \frac{1}{(c/I)_T}\right] \qquad (6)$$

where (c/I) is the actual reduced intensity and $(c/I)_T$ is the reduced intensity extrapolated from the linear behavior in the wide-angle region.

The approach of Debye and Bueche[20] can be used to describe these long-range fluctuations. It leads to a scattering law of the form

$$I_{EX} = K\eta^{-2}a^3/(1 + a^2q^2)^2 \qquad (7)$$

where K is the classical optical constant, a is the average correlation length, and η^{-2} is the contrast density. The values of a can be determined from the plot $I_{EX}^{-1/2} = f(q^2)$ by equating $I_{EX}^{-1/2} = 0$.

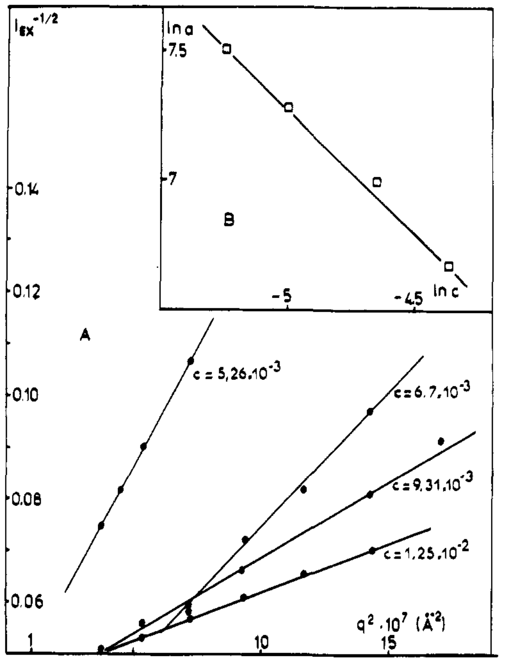

Figure 7. (A) Plot of $I_{EX}^{-1/2}$ vs. q^2 for aPS1 in p-dioxane, polymer concentration c in g·cm^{-3}. (B) log a vs. log c for this system.

Before studying the function $I_{EX}^{-1/2}$, it is necessary to test the hypothesis used by Koberstein et al.,[17] according to which the angular dependence of the scattered intensity at a high angle is given by relation 3. If it is true the ξ values determined from the linear part of the scattering curves should vary as with solvents without anomaly. Figure 6 shows that solvents such as p-dioxane or THF give the expected scaling laws of ξ vs. c ($\alpha \sim {}^3/_4$). Incidentally, it is worth noting that the phenomenon responsible for gelation and low-angle scattering does not modify the screening length.

Since this analysis procedure seems to be well grounded we have plotted in Figure 7 $I_{EX}^{-1/2}$ vs. q^2 for different concentrations of aPS ($M_w = 5.6 \times 10^6$) in p-dioxane. Linear relationships are obtained, indicating good agreement with the random correlation function used in the Debye–Bueche theory. In addition the logarithmic plot of a vs. c leads to the relation

$$a \propto c^{-0.95}$$

This result could easily be accounted for by considering that three-body contacts are involved in the formation of "crystals". In such a case one could expect that the mean distance between such contacts varies as c^{-1}, in good agreement with experimental results.

Concluding Remarks

From the experimental results altogether and from the above discussion several conclusions can be drawn: (i) We give further support to the correlation between the existence of a scattering anomaly at low angle and the capability of gelation, as previously suggested by Guenet et al.[9] (ii) A direct correlation between the appearance of these phenomena and the solvent quality expressed in terms of the interaction parameter χ apparently does not exist. (iii) These effects seem to be more closely related to the local solvation of the chain. (iv) Whatever the solvent used, the screening length varies with the concentration according to scaling-law predictions. (v) The correlation length of the long-range heterogeneities varies as c^{-1}, as expected for three-body contacts.

These conclusions appear to be consistent with the following interpretation: in some highly solvating solvents formation of "microcrystals", including chain segments and solvent molecules, are responsible for the gelation phenomenon at low temperature and long-range heterogeneities in solutions at higher temperature.

This interpretation is in complete contradiction with the hypothesis of Boyer et al.,[13] who propose a segment–segment interaction mechanism. They claim that such a point of view is consistent with the solubility parameters of the solvents. This type of analysis entails that poor solvents must promote gelation. It is then difficult to understand the fact that CS_2, which is well-known to be at room temperature a very good solvent for aPS (parameter $\chi = 0.4$) is precisely the better gelation solvent. In addition, results reported in this paper are hardly accountable by such a mechanism. Our results suggest that the local organization of the solvent molecules around the polymer plays the prominent role. This is not surprising if we consider that the partial specific volume of polymers in solution is strongly dependent on the form and the size of solvent molecules,[21,22] an effect that is never taken into consideration in the thermodynamic theories.

If our hypothesis is correct the existence of these "complex crystals" remains to be confirmed. Yet the possibility of polymer crystallization including solvent molecules has been recently shown by Tadokoro et al.[23] in the case of syndiotactic (methyl methacrylate). This polymer, which is otherwise uncrystallizable from the bulk, can form crystalline structures in the presence of solvent. There is strong evidence that the solvent participates in the crystalline lattice, hence forming a complex. Such a crystallization process might exist for atactic polystyrene as well. Guenet et al.[9] have suggested that the stereoregular sequences (isotactic or syndiotactic) could form "crystals". If one considers the stereoregularity data on aPS it appears that the mean length of such sequences is very low but it is not known so far what is the critical size of such "crystals" to be stable and accordingly to act as junction points.

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(24) In what follows, the words "crystal", "crystallization", "crystalline complex" and the like are bracketed by quotation marks in order to emphasize that the actual structure, if certainly far from amorphous, is not necessarily genuinely crystalline in the usual sense of the word.

Small-Angle Scattering of Polyelectrolyte Solutions

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ABSTRACT: The calculation of the small-angle scattering of polyelectrolyte solutions in previous papers is extended to the case of dilute and low molecular weight polyelectrolyte solutions, using the same assumption that the probability of finding two monomers from different polymers within a distance R_0 is negligible. When the monomer concentration n is sufficiently high, R_0 is very small compared with the polymer length, and the maximum point of the scattering intensity, q_m, is given by the relation $q_m = 7.24n^{1/2}$ (Å^{-1}), where q is the absolute value of the scattering vector. As n decreases, the relation between q_m and n deviates from this relation, and for sufficiently small n it becomes $q_m = 3.97(n/N)^{1/3}$ (Å^{-1}), where N is the degree of polymerization of the polyelectrolyte. The result agrees well with experimental results of small-angle neutron and X-ray scattering and of light scattering of sodium poly(styrenesulfonate) solutions without added salts.

I. Introduction

In previous papers[1] the small-angle scattering of polyelectrolyte solutions was calculated, using a wormlike chain polymer model.[2] With the assumption of a strong electrostatic repulsion between the polymer chains, this theory can explain the results from small-angle neutron and X-ray scattering experiments that the scattering intensity of the polyelectrolyte solutions has a broad maximum in no added salts,[3-9] and that this maximum point q_m is proportional to the square root of the monomer concentration n.[3,6] Although these qualitative results have already been obtained theoretically by Hayter and others,[8] and by the recent paper,[10] this calculation further determined the absolute value of q_m

$$q_m = 8.36n^{1/2} \qquad (\text{Å}^{-1}) \tag{1}$$

which agrees well with the experimental values,[3] where q is the absolute value of the scattering vector $\mathbf{q}$