Active Center Aggregation in Lithium-Based Anionic Polymerization. Are Very Large Aggregates Present?

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ABSTRACT: Active chain association is the dominant feature of lithium-based anionic polymerization in nonpolar solvents. This must have an influence on reaction rates. The dissociation mechanism maintains that under normal conditions, chain propagation is carried out by the dissociated species that are present as only a very small fraction of the whole. This requires that the kinetic order be the reciprocal of the association number. A recent paper in this journal has mounted a vigorous attack on the dissociation hypothesis, maintaining that the kinetic order is variable and not constant in each system and hence there can be no relation between association number and kinetic order. Moreover, the claim is made that besides dimers very large active center aggregates are present in all the solutions in large amounts. It seems obvious, however, that variability in kinetic order can only be caused by differences in the rigor of experimental procedures carried out on highly moisture and air sensitive systems at high dilutions. The evidence for the presence of very large aggregates of active centers is totally unconvincing and contrary to existing data previously obtained by the authors themselves and others.

Introduction

The dissociative mechanism for lithium-based polymerization of vinyl and diene monomers in nonpolar solvents has received wide acceptance. It claims that under normal conditions (active chain concentrations less than $\sim 5 \times 10^{-2}$ M), the dissociation products carry out the chain propagation and in some cases initiation also.[1,2] The contribution of other species is negligible. Since all lithium compounds are associated in these solvents and the degree of dissociation is very small, this requires that the kinetic order in active center concentration for dimeric association should be 0.5, and for tetrameric association it should be 0.25, etc. An independent determination of association number should confirm the kinetic data. It has been generally agreed that polystyryllithium is dimeric in nonpolar solvents and that the kinetic order is 0.5,[2−6] in agreement with expectations. Differences have always been present in the case of polydienyl compounds, even as to kinetic orders,[7] since some authors found 0.5[4,5,8] and others found lower values.[9−11] The higher value, however, was later stated to be in error caused by the increased loss of active centers as dilution was increased.[12,13] This always increases the apparent kinetic order. Improvement in techniques to give a lower kinetic order was, however, not accompanied by a change in the association number, which remained at 2, creating a discrepancy between association number and kinetic order in *their* results. This has led to a criticism of the dissociation mechanism,[14−17] despite the fact that the real problem is a difference in experimental results on association numbers in diene polymerization.

More recently, it is claimed that not only are the kinetic orders in the propagation step not 0.25 or 0.5, but they are also variable[17−19] and hence cannot be related to association numbers. Comments have been made on these claims elsewhere[20] on the basis that the variability is simply caused by experimental errors of the type noted above. More surprising is a recent claim that the solutions contain, besides the normal small aggregates, much larger ones composed of 100 or more active chains. Since no one else has found evidence for aggregates of this size, it seems worthwhile to examine the data.

What Are the Large Aggregates?

The evidence for the species present in typical growing polymer solutions was obtained from scattering studies[18] (both neutron and light). Deuteriobenzene solutions of polystyryllithium alone and capped with a few units of diene were prepared, and the data from them were compared with those from deactivation by CD_3OD and $SiCl_4$. The latter two provide models for unassociated and 4-fold associated chains. Two samples were studied with base molecular weights of 8600 (s9) and 15 000 (s15). Neutron scattering studies on the former were used to support previous claims that the diene-tipped chains were associated to dimers. The low molecular weights necessitated the use of rather high concentrations, 0.041 g cm^{-3} in this case. This causes a problem, since intermolecular interference is not negligible under these conditions. This is best illustrated by the neutron scattering data on series s9, which was analyzed in terms of small aggregates since no rapid upswing of scattering was present at low Q. The scattered intensity intercept I_0 at zero angle, (zero Q, where $Q = (4\pi/\lambda)\sin(\theta/2)$ will follow the form[21a,b]

$$KcM = I_0(1 + 2A_2cM) \qquad (1)$$

where the contrast factor K should be $\sim 2.5 \times 10^{-3}$ cm^2 g^{-2} mol for polystyrene in deuteriobenzene.[21a] A_2 should be 1.1×10^{-3}, 9×10^{-4}, and 7×10^{-4} cm^3 g^{-2} mol for the base polymer of $M = 8600$, its dimer, and its tetramer, respectively.[22,23] From the data in Figure 1 of ref 18 it was found that "the respective intercepts demonstrate that a 2-fold difference in molecular weight holds for the terminated product and the active butadiene-capped sample and that a 4-fold difference exists when the 4-arm star is compared with the parent arm".[18] When a correction is made for a concentration of 0.041 g cm^{-3} via eq 1, however, the ratios should be

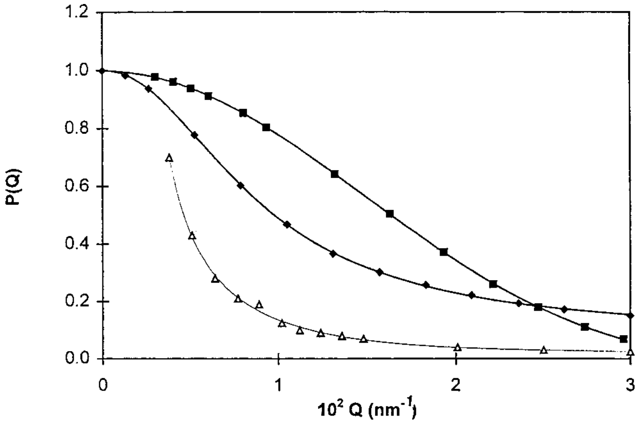

Figure 1. P_θ for various particle shapes of hydrodynamic radius 111 nm: (■) sphere; (◆) prolate ellipsoid of axial ratio 15; (△) experimental results from ref 18. P_θ of the sphere reaches 0.05 at $Q = 0.03$; the ellipsoid only at $Q \sim 0.06$, since its curve is flatter.

much lower, i.e. ~1.6 and ~2.5. Data from the polystyryllithium intermediate presented only in a preliminary communication[24] also present a problem since they show an intensity ratio to dead polymer of ~1.4, closer to that expected of a dimer according to eq 1 and less than that of its butadiene-capped product (~2). Since it is generally agreed that polystyryllithium is a dimer in benzene, this means that the butadiene-capped product is more highly associated, as suggested by others (see ref 40). The association number calculated for the coupled tetramer (2.5) is also much lower than that observed. A similar problem will exist with the measured radii of gyration.[21b] The lack of extrapolation to zero concentration in the neutron scattering data on this sample therefore prevents a definitive answer to the problem of the association number of dienyllithium compounds.

The situation is more complex in the case of neutron scattering experiments on s15, since unlike series s9, scattering increases rapidly at $Q < 0.15$ nm^{-1}. The attempts made[18] to separate the contributions of the "normal" species from those attributed to large aggregates and hence validate the presence of dimers from radii of gyration determined from Guinier plots must be regarded with suspicion since the separation must be somewhat arbitrary, leading to estimates with large uncertainties. Nor can a good estimate of the size of the very large aggregates be obtained, the results being described as "apparent" radii of gyration, on the order of 15−20 nm.

All the quantitative interpretation on the size of the large aggregates depends, therefore, on the light scattering measurements only, where the ability to reach lower Q values exists. Data are only available for series s15. The static light scattering measurements suffer, of course, from the same problems as in neutron scattering, namely, no extrapolation of the data to zero concentration to remove the effect of intermolecular scattering. The dynamic light scattering measurements on the butadiene-capped active polymer show the presence of two species of widely different diffusion constants (9.9×10^{-7} and 3.2×10^{-8} cm^2 s^{-1}). The terminated (inactive) polymer, however, only showed the existence of a species of high diffusion constant (1.05×10^{-6} cm^2 s^{-1}). These diffusion constants can be related to the size of a sphere, which has an equivalent diffusion constant, the so-called hydrodynamic radius, R_h. Analysis in this way shows that the two species of high diffusion constant correspond to R_h values that would be expected of species such as monomers or dimers, but the slow moving species must be much larger, with $R_h = 111$ nm. The authors of ref 18 consider that these species are aggregates of the living polymers containing over 100 units.

A static light scattering study is required to obtain information on the shape of these aggregates. As in neutron scattering, this technique shows a rapid upswing in scattering at low values of Q, attributed to large particles. Scattered intensity in all scattering techniques, neutron, light, and X-ray, can be described as the product of two terms, a contrast factor K independent of Q, but dependent on the scattering technique, and a form factor P_θ dependent on Q only. P_θ is sensitive to the shape of the scatterer. Form factors of many types of particles have been available for many years, originally derived for X-ray scattering experiments but equally valid for all scattering methods.[21a,25]

The authors of ref 18, therefore, examined the form factors of spheres and ellipsoids having the same hydrodynamic radius (111 nm), suggested by the dynamic light scattering results. Prolate and oblate ellipsoids of large axial ratio approximate rodlike and disklike structures, respectively, either being possible structures for the large scale aggregates. The P_θ function of the observed data was compared with the calculated curves shown in Figure 8 of ref 18. These were based on the presumption that the smallest dimension should be commensurate with the size of the basic polymer unit. This was taken as between 5 and 25 nm and used for the semiminor axis of an ellipsoid whose semimajor axis was then determined to retain a hydrodynamic radius of 111 nm.[26] They concluded that the experimental data were consistent with large extended particles, roughly prolate ellipsoids of axial ratio between 15 and about 100, most likely at the lower end of the range.

Unfortunately, the P_θ factor calculated in ref 18 for the prolate ellipsoid is not correct. It is intuitively obvious that a spherical particle has the most compact form and with first-order interference it must have the most compact P_θ vs Q relation. (P_θ goes to zero at the lowest Q.) This is also clear from examining the figures in many publications.[27−30] Use of the classical series development of Porod[28] for P_θ of a prolate ellipsoid of axial ratio 15 ($a = 25$, $b = 382$ nm, Table 2, ref 18) shows this is indeed the case, as shown in Figure 1.[31] The P_θ function changes little for higher axial ratios. The experimental data presented in ref 18, Figure 8, cannot agree with the form factor of any particular shape since it is more compact than that of a sphere (correctly reported in the figure). This may have been due to the difficulty in converting the raw data of Figure 7 to a P_θ function. Examination of the data in this figure suggests that it would indeed be difficult to normalize the curve to unity at zero Q.

No convincing evidence has, therefore, been presented for the presence of large extended aggregation of the active centers in these systems; all that is clear is that large structures were present in the solutions. An obvious source of such particles, particularly since the static light scattering data appear to have been extended down to 15°,[32] is contamination of the solutions by extraneous particulate matter commonly referred to as “dust”, a phenomenon well-known to experienced workers in the field, particularly before good fine filters were commercially available. Its presence causes a large downward curvature in Zimm plots (increase in scattering) at low angles together with a normal angular dependence at higher scattering angles and is well described in the literature to the point where tabulation of properties (density and refractive index) of likely components was done.[33] A typical example can be found[14] in a scattering study made by the lead author on solutions of a styrene−butadiene−styrene block copolymer having a very short center block. A sharp increase in scattered light at low angles due to contamination is visible in its Figure 5 and is probably the source of the claim that such polymers associate in cyclohexane. A properly filtered solution shows no excess low-angle scattering or excess association.[34] This material is normally easily removed by 0.2-μm pore size commercial filters, but it is obvious that they cannot be used on a living polymer solution. Nor can they be used in the high-vacuum systems required for rigorous preparations. Only coarse-fritted glass filters, which are inadequate for the purpose, are possible. Extraneous low-angle scattering is inevitable under these conditions. The same material will cause, in dynamic light scattering, the broad peak in the G vs Γ plots (Figure 6, ref 18) corresponding to large slowly diffusing particles. Indeed, Pecora[35] has reported, in a dynamic light scattering study of plasmids in aqueous solutions, the presence of slowly diffusing particles of hydrodynamic radius 250 nm. These were attributed to “dust”, and it was noted that these artifacts were present in all samples studied despite prior centrifugation of the solutions. This source was rejected in the present case since the terminated (inactive) polymer solution showed no increased scattering at low angles (at least down to $Q = 8 \times 10^{-3}$ nm^{-1}), although it was “captured” from the active (living) solution. Since any practitioner of the art of light scattering knows that filtration is essential to obtain good data at low angles, this presents a problem in interpretation of the data, if as claimed no filtration was used even to remove the inorganic lithium salts precipitated in the termination process. The alternative, microgel, which gives the same effect,[33] might be plausible for the diene-capped samples if stored too long, but is unlikely for the polystyryllithium samples.

How plausible generally is the attribution of the presence of large particles in solution to large active polymer aggregates? First of all, the statement that a lower limit to the number of chains per aggregate is 100 leaves a large gap between them and the dimers, which does not seem plausible. The difference between the results obtained from s9 and s15 suggests that the results vary between preparations, as might be expected from the “dust” explanation. More importantly, the data are totally incompatible with all previously reported data on association numbers in these systems, which give no evidence for such large aggregates. This would apply to the concentrated solution viscosity measurements of the lead author who is noted for many exact association numbers of 2[4,5,14] in all active polymer solutions. Concentrated viscosity determinations would be highly influenced by the presence of so much high molecular weight material. Neither are the present results compatible with previous light scattering data on polyisoprenyllithium in hexane,[14] which were carried out at Q values as low as 10^{-2} nm^{-1} without any trace of large aggregates. These results would be less sensitive to “dust” since the molecular weights used were much higher. Part of the problem with these later studies is that the molecular weights are very low, and hence “dust” will be much more evident because of the polymers much lower scattering power. Similarly, all other authors reports are not compatible with the presence of very large aggregates.[3,6,11,36a,b]

The discussion and implications of the experimental results are a repetition of criticisms of the dissociation theory,[15,16] which have been answered.[37−40] Their contents make it clear that the experimental results are designed to criticize this theory. An extensive compilation of power laws in active center concentration taken from the literature is also presented. In it deviations occur from exact values of 0.25 or 0.5, as would be expected for systems that are extremely sensitive to traces of moisture and other polar impurities. The effects of experimental error are never considered, which is surprising since the lead author’s own kinetic results[4,8] showed the classic increase in apparent order expected from loss of active centers on dilution. The variation has even been made to look worse by a little “revisionist” editing.[41] Other attempts to discredit the dissociation theory involve misinformation. In note 51, Burchard’s association studies[42] on amino group terminated polystyrenes are described as due to hydrogen bonding. In reality, the experiments describe dimerization via salt formation between the amine ends and a dinitrophenol derivative. The enthalpy change (42 ± 5 kJ/mol in dioxane, ~46 kJ/mol in benzene[43]) is not in disagreement with the enthalpy reported (38 kJ/mol)[44] for a polyisoprenyllithium *dimer to tetramer* association in benzene. The implication that a polyisoprenyllithium dimerization was involved is incorrect, and the enthalpy presented for the latter process of ~150 kJ/mol is unbelievable,[37] as are similar ones calculated for allyllithium in the gas phase.[20] In note 73, the second virial coefficient in a light scattering experiment on association numbers[6] is claimed to be 4.9×10^{-3} cm^3 g^{-2} mol and hence too high, implying unreliability in the data. It is in fact 1.9×10^{-3} cm^3 g^{-2} mol, well within the expected range.[22] The authors have calculated A_2 from the slope of the c/I plot vs c given, forgetting the required constant K, which can easily be obtained from the molecular weight given in the text.

Finally, it is necessary to make some remarks about the statement that it is usually possible to suggest several mechanisms that will lead to the same experimental kinetic orders as does the dissociation theory. This statement has been frequently made,[14,15,18] quoting in support a review by Brown,[45] which presents no evidence at all on the subject. This discrepancy has been noted elsewhere,[37] and a tentative alternative mechanism has been suggested albeit with reservations. References 17 and 18, on the other hand, offer no alternative. It is surprising also to read that there is no good reason aggregates should be less reactive than dissociation products, the latter have terminals that have high dipole moments effectively canceled in dimers and which in higher aggregates become buried inside a hydrocarbon shell. Both effects should decrease reactivity.

Conclusions

A set of experiments has been described that do not even solve the problem of the association number of dienyllithium compounds, 2 or 4? The claim of the presence of very large active center aggregates is totally unbelievable from the evidence provided and incompatible with all previous experiments.

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(32) Reference 18 claims an argon ion laser was used for both static and dynamic light scattering experiments at λ 632.8 nm, but this is the wavelength of a helium−neon laser. From the context it seems likely that the wavelength used for dynamic measurements was 488 nm (Argon ion) and 632.8 nm for the static measurements.
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