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Association Between Acidic and Basic Copolymers by Low Angle Laser Light Scattering Photometry

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SUMMARY

Measurements of both apparent molecular weight and second virial coefficient of solutions of styrene-4-vinylpyridine copolymer in ethyl benzoate containing varying concentrations of methyl methacrylate-methacrylic acid copolymer isorefractive with ethyl benzoate were carried out by low angle laser light scattering. The apparent molecular weight depended very little on the acidic copolymer concentration. The second virial coefficient first decreased rapidly, then increased and finally tends to level off as the acidic copolymer concentration was raised. Great association is observed when the visible polymer is in excess.

INTRODUCTION

It is well known that solutions of high molecular weight polystyrene (PS) and poly(methyl methacrylate) (PMMA) are incompatible (DOBRY and BOYER-KAWENOKI 1947, KERN and SLOCOMBE 1955, KRAUSE 1972). We have previously (DJADOUN et al. 1977) studied systems of these two incompatible polymers and have shown that depending on the solvent used, compatible pairs of random copolymers of styrene-4-vinylpyridine (SB) and of methyl methacrylate-methacrylic acid (MA) containing only small amount of interacting groups were obtained. Systems of higher content of interacting groups led to the formation of a concentrated phase which was in equilibrium with a phase containing mostly solvent.

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Light scattering is one of several techniques that can be used to study associations. The therory of light scattering from ternary systems (STOCKMAYER 1950, FLORY and KRIGBAUM 1952), has been used by a number of authors (HYDE and TANNER 1968, KUHN et al. 1968, KUHN and CANTOW 1969) to study interactions between two different polymer chains. Using a solvent isorefractive with one of the polymers, KUHN et al. carried out experiments of ternary systems of PS and PMMA in benzene isorefractive with PMMA and found that the apparent second virial coefficient of the PS depended strongly on both the concentration and the molecular weight of the PMMA. They showed that for polymers of high molecular weight, the second virial coefficient of the PS decreased rapidly with an increasing concentration of the invisible PMMA and then levelled off. Similarly VAN DER ESKER et al. found that the second virial coefficient of PS decreases as the polyisobutylene (isorefractive with toluene) concentration increases.

The purpose of this work was to study the association between the acidic and basic copolymers by low angle laser light scattering measurements of the apparent molecular weight and second virial coefficient of a basic styrene copolymer in ethyl benzoate solutions containing varying concentrations of an acidic methyl methacrylate copolymer whose refractive index matched that of the solvent.

EXPERIMENTAL

Homopolymers and copolymers of styrene and of methyl methacrylate were obtained by free radical polymerization at 60°C with azo-bis isobutyronitrile(AIBN) as the initiator and at conversions below 15 %. The copolymers of styrene-4-vinylpyridine and of methyl methacrylate methacrylic acid were characterized spectroscopically and by titration (DJADOUN 1979).

Prior to light scattering measurements, qualitative tests were carried out on the ternary phase equilibria. As expected, we found that, while PS and PMMA in ethyl benzoate exhibited phase separation with two dilute phases, each containing mostly one of the two polymers; copolymers MA-5.10 (methyl methacrylate-methacrylic acid copolymer containing 5.10 mole % of methacrylic acid) and SB-5.80 (copolymer of styrene-4-vinylpyridine with 5.80 mole % of 4-vinylpyridine) in the same solvent led to homogenous solutions up to a polymer concentration of 10 % by weight.

Rayleigh Ratios :

Solutions of various concentrations of the acidic copolymer MA-5.10 in ethyl benzoate were prepared and each solution was used as the solvent for a series of solutions of the basic copolymer SB-5.80 of different concentrations 10^{-3}- 6×10^{-3} g/ml . All measurements of the Rayleigh factors for copolymers and their mixtures were carried out with the low angle laser light scattering photometer KMX-6 manufactured by CHROMATIX at a wavelength of 633 nm.

Refractive index increment measurements:

Since the Rayleigh factors were determined at $\lambda = 633$ nm, it would have been appropriate to measure the (dn/dc) at the same wavelength. With the Brice-Phoenix Differential Refractometer, this could not be carried out directly; however, the refractive index is known to vary with the wavelength according to (HUGLIN 1972):

$$n = a + a'/\lambda^{2} + a''/\lambda^{4}$$

A similar relation should then be valid for (dn/dc). We therefore determined the (dn/dc) at $\lambda = 436$ nm and $\lambda = 546$ nm and by interpolation of a plot of (dn/dc) against $1/\lambda^{2}$ we estimated the values of (dn/dc) at $\lambda = 633$ nm.

RESULTS

The low angle capability permits simple, rapid and more accurate measurements of molecular weight ($\bar{M}_w$) and second virial coefficient (A_2), calculated by linear regression analysis from the intercept and the slope of $Kc/\Delta R_\theta$ versus concentrations . ΔR_θ is the difference between the Rayleigh ratio of the solution and that of the solvent. The constant K is given by

$$K = (2\pi^2 n_o^2 / N\lambda^4).(dn/dc)^2.(1 + \cos^2\theta)$$

where N is Avogadro's number, λ the wavelength, n_o the refractive index of the solvent and θ the average scattering angle. The refractive indices of ethyl benzoate and dioxane used in the calculations of the K values are 1.500 and 1.420 respectively. The estimated value of the (dn/dc) in ethyl benzoate of the SB-5.80 was found to be much larger than that of the acidic copolymer for which the (dn/dc) was very close to zero.

The molecular weight for the SB-5.80 and MA-5.10 copolymers in dioxane are obtained as 3.7×10^5 and 8.10×10^5 repectively; their second virial coefficients are found to be 7.6×10^{-6} and 12.6×10^{-6} respectively.

To study the association between the acidic and basic copolymers, we determined the apparent weight average molecular weight for the SB-5.80 in solutions of the acidic copolymer in ethyl benzoate for which (dn/dc) is sufficiently small (0.005) to neglect its contribution to light scattering. Apparent weight average molecular weights and second virial coefficients are summarized in Table (1); their plots as a function of the acidic copolymer concentration are shown in figures (1,2) . Fig.(3) exhibits the variation of $Kc/\Delta R_\theta$ for each concentration of the SB-5.80 at the different concentrations of the MA-5.10.

TABLE 1

Weight Average Molecular Weight and Apparent Second Virial Coefficient for SB-5.80 in ethyl benzoate solutions of MA-5.10 copolymer.

$c\times10^4$ (g/ml)	$1/\bar{M}_w$	$10^{-5}\bar{M}_w$	$10^6 A_2$
0.00	2.80	3.57	6.87
4.00	2.70	3.70	6.13
10.00	2.60	3.84	2.20
20.00	2.20	4.54	5.28
40.00	2.18	4.58	5.76

DISCUSSION

In order to characterize the effect of the invisible polymer on the extension of the other species, light scattering from solutions containing two homopolymers incompatible with each other in a medium isorefractive with one of the polymeric species has been carried out by a number of authors [HYDE and TANNER 1968, KUHN et al. 1968]. Let us now consider the results to be expected in light scattering from solutions containing two polymers carrying small amounts of strongly interacting groups, compatible with each other and with one of the polymeric species isorefractive with the medium. The principles governing the behavior of such systems can be most easily understood by considering a model system containing two trifunctional species.

Let us assume for simplicity that the association of the interacting groups goes to completion ; then, if the invisible species [A] is in large excess, each molecule of the visible polymer [B] will associate with three molecules of [A] . If f is the weight fraction of visible polymer in the complex

$$[dn/dc]_{complex} = f.[dn/dc]_{visible}$$

$$c_{complex} = c_{visible} / f \quad \text{and} \quad M_{complex} = M_{vis.} / f$$

$$\text{so that} \quad K_{vis.}\, c_{vis.} / \Delta R_{\theta} = 1 / M_{vis.}$$

Since these species are invisible, the presence of MA-5.10 will have no effect on the observed molecular weight. Conversely when SB-5.80 is in large excess, these molecules will associate with one [A] and the molecular weight will be three times that of an isolated [B]. Of course this model is unrealistic in that associations of interacting groups do not go to completion, depend on the solvent used, on the nature of the species and tend to decrease with increasing dilution.

Figure (1)

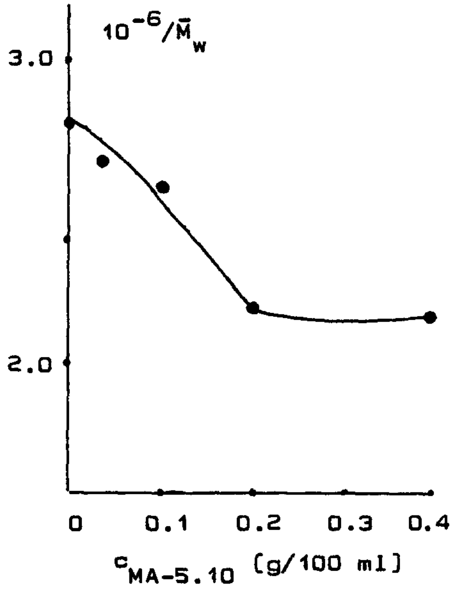

Figure (2)

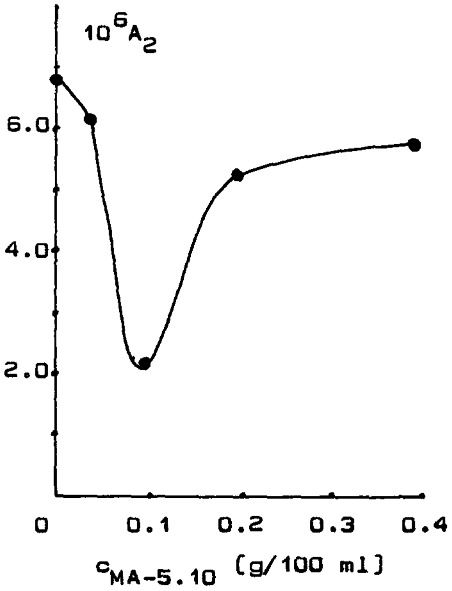

Figure (1) : Reciprocal of the weight average molecular weight of SB-5.80 versus concentration of the MA-5.10 copolymer.

Figure (2) : Apparent second virial coefficient of the SB-5.80 versus concentration of the MA-5.10 copolymer.

Figure (3) shows plots of our light scattering data of given concentrations of the SB-5.80 copolymer as a function of the acidic copolymer; all these graphs exhibit a minimum; for a small concentration of the SB-5.80 (0.1g/100 ml), the $Kc/\Delta R_\theta$ values remained practically the same as the concentration of the acidic copolymer increased (inexcess). On increasing the concentration of the basic copolymer, these values decreased more rapidly for small concentrations, then increased and finally levelled off on further increase of the acidic copolymer concentration. The minimum of these plots is shifted towards smaller concentrations of the acidic copolymer as the concentration of the basic copolymer increases.

This may be an explanation of the expected great association when the visible polymer is in large excess. As the concentrations of both copolymers increase, interactions between molecular chains of MA-S.10 species occur and reduce the acid-base interactions as shown from the increase of the $Kc/\Delta R_\theta$ values in Fig.[3]. That the tendency to level off on increasing the concentration of the visible copolymer occurs at lower values than for the visible copolymer in pure solvent is also evidence of the acid-base interactions. If we characterize the apparent molecular weight by the value obtained by extrapolation of the linear portions of the plots of $Kc/\Delta R_\theta$ against c, then we obtain values increasing very slightly from 3.6×10^5 to 4.6×10^5 as the concentration of the acidic copolymer is increased from zero to 0.2 g/100 ml . The molecular weight levelled off on further increase in the acidic copolymer concentration to 0.4 g/100 ml. With nonassociating particles the second virial coefficient A_2 obtained from the slope of the $Kc/\Delta R_\theta$ plot is a measure of the excluded volume U, i.e. $A_2 = U/M^2$. When we deal with associating particles, the situation is more complicated, since the apparent molecular weight at any concentration is affected both by solution nonideality and the varying mass of the particle, thus an interpretation of A_2 plotted in Fig.[2] as function of the concentration of the acidic copolymer is rather uncertain. HARRINGTON and BURKE have found from both

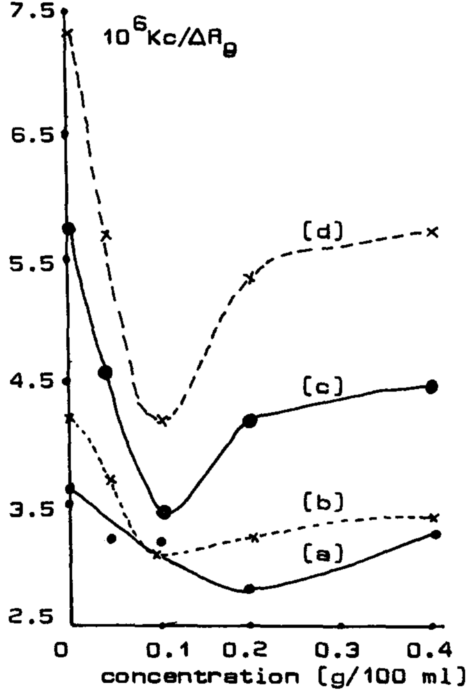

Figure [3] :Plots of $Kc/\Delta R_\theta$ of the SB-5.80 versus the acidic copolymer concentration; [a] 0.1 g/100ml ,[b] 0.2 g/100 ml;[c] 0.4 g/100 ml; [d] 0.6 g/100 ml.

the concentration dependence of the reduced viscosity studies and high speed sedimentation equilibrium studies that myosin molecules are in rapid, reversible equilibrium with a dimeric species at high ionic stength. They observes a minimum in the plots of their apparent molecular weight versus concentration. They concluded that the presence of a minimum is a strong indication of non-ideal associating systems. The highest concentration of the acidic copolymer in the mixture used in our experiments was 0.4 g/100 ml; further increase of the acidic copolymer concentration might lead to similar phenomena as those observed by HARRINGTON and BURKE whose experiments were carried out at much higher concentrations. Tentatively, we assume that the decrease in A_2 observed at low concentrations of the acidic copolymer is due to desolvation following molecular association. At higher concentrations, the acidic copolymer may associate with its own kind by carboxyl dimerization and this would compete with the acid-base association , reducing the desolvation of the basic copolymer.

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