Dipole Moments of Some Styrene Copolymers

Zühal Küçükyavuz*

Department of Chemistry, Middle East Technical University, Ankara, Turkey

Bahattin M. Baysal

Department of Chemistry, Istanbul Technical University, Istanbul, Turkey.

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ABSTRACT: Dipole moments of poly(styrene-*co*-*p*-chlorostyrene), poly(styrene-*co*-*p*-methoxystyrene), poly(styrene-*co*-4-vinylpyridine), and poly(styrene-*co*-*N*-vinylcarbazole) copolymers were determined in toluene solutions at different temperatures. The samples were synthesized by using free-radical initiators. The effects of the nature of the polar group, composition, and temperature on the dipole moment ratio were investigated. The mean-square dipole moment per structural unit shows a positive deviation from linearity, in agreement with calculations by Mark based on rotational isomeric state theory. The results are compared with other experimental and theoretical studies.

Introduction

The mean-square dipole moment of a chain $\langle\mu^2\rangle$ is an important configuration-dependent property that can be determined experimentally in dilute solutions or in bulk, over the entire range of molecular weight.[1-3] It can be used to provide information on the configuration of chain molecules.

Rotational isomeric state theory has been used[4,5] to calculate the dipole moments, as well as other configuration-dependent properties of various types of homopolymers such as vinyl chains,[6-10] polyoxides,[11,12] polymethacrylates,[13] and others.[14] The temperature coefficients $d \ln \langle\mu^2\rangle/dT$ have also been calculated and compared with those of experimental studies.[15,16]

Relatively less work has been undertaken on the dipole moments of copolymers. Mark[17-20] pioneered the theoretical studies on the configuration-dependent properties of synthetic copolymers. With rotational isomeric state theory, values of $\langle\mu^2\rangle$ and the unperturbed dimension $\langle r^2\rangle_0$ were calculated as a function of chain length, temperature, chemical sequence distribution, and stereochemical composition. His results were compared with a limited number of experimental studies on the dipole moments of copolymers.

Work and collaborators published a series of articles on the dipole moments of styrene–*p*-chlorostyrene[21] and *p*-methylstyrene–*p*-chlorostyrene copolymers in bulk[22] and in solution.[23,24] Their results on the temperature coefficient did not agree with the calculations by Saiz, Mark, and Flory.[8]

More experimental studies are needed on the dipole moments of copolymers to see the feasibility of rotational isomeric state calculations for determining the values of the reactivity ratios (r_1, r_2) or copolymer sequence distribution.

For the present study we synthesized copolymers of styrene (S), with four different polar monomers, namely, *p*-chlorostyrene (PCS), *p*-methoxystyrene (PMS), 4-vinylpyridine (4VP), and *N*-vinylcarbazole (NVC), and measured their dipole moments in dilute toluene solutions at 1, 25, and 50 °C.

Experimental Section

Copolymer Preparation. Copolymers of S-PCS and S-PMS were prepared by standard methods. Monomers were freshly distilled under reduced pressure before use. They were mixed in proper molar ratios so that the whole composition range could be covered. Benzoyl peroxide was used as an initiator. Polymerizations were carried out in a vacuum at constant temperature. Percent conversions were kept low. The copolymers were dissolved in toluene, reprecipitated with methanol, and dried in a vacuum oven.

Styrene–4-vinylpyridine (S-4VP) copolymers were prepared and analyzed in the manner of Fuoss and Cathers,[25] and S-NVC copolymers were prepared by thermal polymerization in bulk at 100 °C under reduced pressure. The molecular weights of the samples that were used in this work were all above 10^4. Essentially atactic chains are obtained by free-radical or thermal polymerizations.

To determine the nitrogen content of S-4VP and S-NVC copolymers, we used the Winkler modification of the Kjeldahl method.[26] All nitrogen determinations were made in duplicate.

Dielectric Measurements. Capacitance measurements were performed at low frequencies (1–10 kHz) by using a General Radio Company Type 1620 A capacitance measuring assembly. It was connected to a Balsbaugh Laboratories Model 350-G three-terminal cell, which consists of two coaxial cylinders and requires about 55 mL of solution. Solvent escape was prohibited, and the temperature of the cell was controlled to ±0.1 °C during capacitance measurements. Toluene was used as the solvent in all measurements. It was distilled over sodium wire, and middle fractions were used.

A Brice–Phoenix differential refractometer was used to obtain refractive index increments at a wavelength of 546 nm.

Results

The compositions of S-PCS, S-PMS, and S-4VP copolymers were calculated from the copolymerization equation:[27-29]

$$F_2 = \frac{r_2 f_2^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{1}$$

where F_2 is the mole fraction of polar monomer in the copolymer, r_1 and r_2 are the reactivity ratios, and f_1 and f_2 are the mole fractions of nonpolar (1) and polar (2) monomers, respectively, in the monomer mixture undergoing polymerization. Results are given in Tables I and II. Values of f_1 and f_2 were assumed to be constant throughout the copolymerization since percent conversions were all kept low. Compositions of S-4VP copolymers were also determined from their nitrogen content. The two methods are in good agreement with each other (Table II). Since precise r_1 and r_2 values were not available for the styrene–*N*-vinylcarbazole pair, compositions of these copolymers were determined only from nitrogen analysis.

Low-frequency dielectric increments were measured at several concentrations in the range 0.8–1.5% in toluene solutions at 1, 25, and 50 °C.

The mean-square dipole moments per polar unit in the copolymer chain, $\langle\mu^2\rangle/X_2$, were calculated from the appropriate form of the Guggenheim–Smith equation[30,31]

$$\frac{\langle\mu^2\rangle}{X_2} = \frac{27kTM}{4\pi N_A d_0}\left[\frac{(d\epsilon/dw)_0}{(\epsilon_0 + 2)^2} - \frac{2n_0(dn/dw)_0}{(n_0^2 + 2)^2}\right] \tag{2}$$

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Table I
Data for the Polymerization and Composition of Poly(styrene-*co*-*p*-chlorostyrene),[a] Poly(styrene-*co*-*p*-methoxystyrene),[b] and Poly(styrene-*co*-*N*-vinylcarbazole)[c] Samples

sample	f_2[d]	F_2[e]
S-PCS-1	0.2055	0.249
S-PCS-2	0.7892	0.802
PPCS	1.0000	1.000
S-PMS-1	0.1678	0.157
S-PMS-2	0.3523	0.328
S-PMS-3	0.5141	0.480
S-PMS-4	0.7567	0.721
PPMS	1.0000	1.000
S-NVC-1	0.3020	0.074
S-NVC-1	0.4929	0.368
S-NVC-3	0.4925	0.398
S-NVC-4	0.7934	0.665
PNVC	1.0000	1.000

[a] For S-PCS copolymers, polymerization temperature is 60 °C; r_1(styrene) = 0.74, r_2(*p*-chlorostyrene) = 1.25.[41] [b] For S-PMS copolymers, polymerization temperature is 60 °C; r_1(styrene) = 1.05, r_2(*p*-methoxystyrene) = 0.79.[29] [c] For S-NVC copolymers polymerization temperature is 100 °C. [d] Mole fraction of polar monomer in the monomer feed. [e] Mole fraction of polar unit in the copolymer calculated from eq 1 for S-PCS and S-MPS copolymers. For S-NVC copolymer F_2 is calculated from nitrogen determination.

Table II
Data for the Polymerization and Composition of Poly(styrene-*co*-4-vinylpyridine) Samples[a]

sample	f_1[b]	f_2[c]	F_2[d]	F_2[e]
S-4VP-1	0.8728	0.0151	0.027	0.028
S-4VP-2	0.8273	0.0277	0.050	0.051
S-4VP-3	0.7589	0.440	0.081	0.082
S-4VP-4	0.7163	0.0712	0.127	0.118
S-4VP-5	0.6555	0.0951	0.169	0.154
S-4VP-6	0.6421	0.1142	0.196	0.183
S-4VP-7	0.5970	0.1810	0.275	0.259
S-4VP-8	0.6021	0.2225	0.308	0.301
S-4VP-9	0.5527	0.2563	0.347	0.347
S-4VP-10[f]	0.3151	0.5177	0.484	0.429

[a] Polymerization temperature 80 °C; reactivity ratios r_1(styrene) = 0.62, r_2(4-vinylpyridine) = 0.52.[41] [b] Mole fraction of styrene in the toluene solution of monomer feed. [c] Mole fraction of 4-vinylpyridine in the toluene solution of monomer feed. [d] Calculated from eq 1. [e] Calculated from nitrogen determination. [f] Insoluble in toluene.

In the above equation X_2 is the number of polar units in the chain, d_0, ϵ_0, and n_0 are the density, dielectric constant, and refractive index, respectively, of the solvent, w is the weight fraction of solute, and increments $(\mathrm{d}\epsilon/\mathrm{d}w)_0$ and $(\mathrm{d}n/\mathrm{d}w)_0$ are at infinite dilution. M is the molecular weight per polar unit and calculated as

$$M = \frac{M_{\text{polymer}}}{X_2} = \frac{X_1M_1 + X_2M_2}{X_2} = M_2 + \frac{F_1}{F_2}M_1 \qquad (3)$$

where M is the molecular weight, F_1 and F_2 are the mole fractions, and X_1 and X_2 are the number of nonpolar (1) and polar (2) units in the copolymer. Results of the dipole moment measurements are given in Table III.

In Figures 1 and 2, $\langle\mu^2\rangle/X_2$ values calculated from eq 2 are plotted against the mole fraction of polar component for S-PCS, S-PMS, S-NVC, and S-4VP copolymers at 1, 25, and 50 °C.

The dipole moment ratios for sufficiently long chains, D_∞, were calculated at 25 °C by using

$$D_\infty = \frac{\langle\mu^2\rangle}{X_2\mu_0^2} \qquad (4)$$

in which μ_0 is the dipole moment of the repeat unit in the chain. The D_∞ values are plotted against the mole fraction of polar component in the chain (F_2) in Figure 3. Appropriate μ_0 values were chosen from McClellan's tables[32] and are given in Table III. For S-NVC copolymers the

Table III
Dipole Moment Determination

sample	$(\mathrm{d}\epsilon/\mathrm{d}w)_0$ (25 °C)	$(\mathrm{d}n/\mathrm{d}w)_0$ (25 °C)	$\langle\mu^2\rangle/x_2$, D^2 1 °C	25 °C	50 °C	D_∞ (25 °C)
S-PCS1	0.8170	0.097	2.93	2.67	2.73	0.67[a]
S-PCS2	1.5175	0.096	1.90	1.76	2.11	0.44
PPCS	1.6207	0.094	1.68	1.65	1.94	0.41
S-PMS-1	0.5390	0.090	1.89	1.56	1.41	1.07[b]
S-PMS-2	0.6853	0.090	1.37	1.23	1.23	0.84
S-PMS-3	0.7864	0.090	1.14	1.08	1.08	0.74
S-PMS-4	0.9363	0.090	0.99	1.00	0.99	0.69
PPMS	0.9399	0.090	0.79	0.78	0.80	0.54
S-4VP-1	0.3482	0.089	2.44	2.15	1.59	0.31[c]
S-4VP-2	0.3973	0.090	2.14	2.01	1.67	0.29
S-4VP-3	0.4704	0.094	2.31	1.91	1.48	0.23
S-4VP-4	0.5750	0.098	2.21	2.04	1.51	0.29
S-4VP-5	0.7115	0.098	2.70	2.42	1.99	0.34
S-4VP-6	0.9493	0.098	3.64	3.49	2.73	0.50
S-4VP-7	1.3175	0.098	4.33	3.79	3.35	0.54
S-4VP-8	1.6865	0.098	4.67	4.39	4.20	0.62
S-4VP-9	1.9526	0.103	4.40	4.27	4.25	0.61
S-NVC-1	2.3170	0.178	6.04	5.48	4.97	0.53[d]
S-NVC-2	2.0514	0.178	5.74	5.44	4.39	0.53
S-NVC-3	2.4120	0.179	4.44	4.02	3.82	0.39
PNVC	2.7858	0.195	4.22	3.71	3.59	0.36

[a] μ_0 = 2.00 D (for *p*-chloroethylbenzene in benzene).[32] [b] μ_0 = 1.21 D (for *p*-methoxytoluene in benzene).[32] [c] μ_0 = 2.655 D (for 4-ethylpyridine in benzene).[32] [d] μ_0 = 3.21 D (for *N*-vinylcarbazole in toluene, determined in this work).

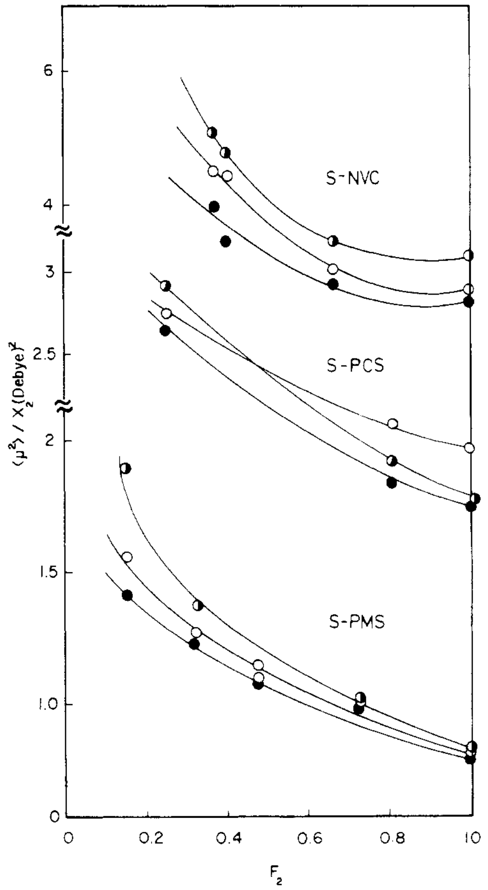

Figure 1. Mean-square dipole moments of S-PCS, S-PMS, and S-NVC copolymers in toluene solutions at (◐) 1, (○) 25, and (●) 50 °C.

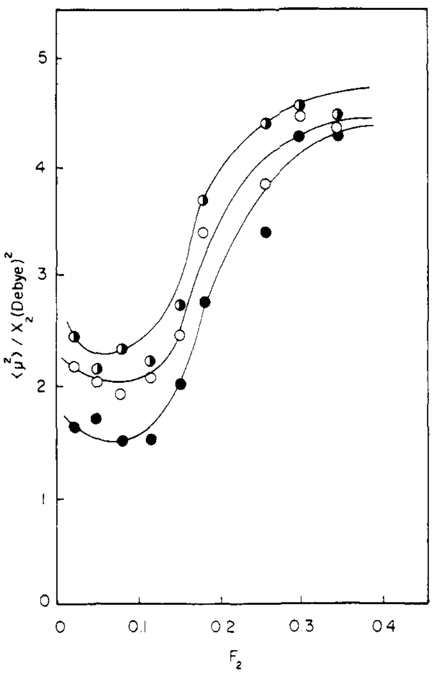

Figure 2. Mean-square dipole moments of S-4VP copolymers in toluene solutions at (◑) 1, (○) 25, and (●) 50 °C.

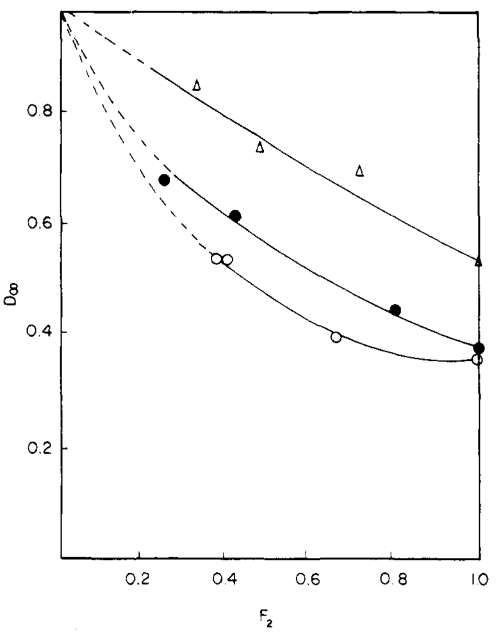

Figure 3. Dipole moment ratios for various copolymer systems as a function of mole fraction of polar component (at 25 °C): (Δ) poly(styrene-*co*-*p*-methoxystyrene); (●) poly(styrene-*co*-*p*-chlorostyrene); (○) poly(styrene-*co*-*N*-vinylcarbazole).

dipole moment of *N*-vinylcarbazole monomer measured in toluene at 25 °C was used as μ_0.

Discussion

Figure 1 shows that in S-PCS, S-PMS, and S-NVC copolymers, as the fraction F_2 of polar component in the chain decreases, the mean-square dipole moment per polar unit in the chain increases at each temperature. Because as F_2 gets smaller, the dipoles are located farther from each other, the interaction between them (and the inhibition of internal rotation due to the dipole–dipole interaction) is reduced. In the limiting case of infinite internal dilution, the effective dipole moment per polar unit approaches the value μ_0. Accordingly, the dipole moment ratios approach unity as F_2 approaches zero. This effect is seen in Figure 3 for each copolymer system. The internal dilution effect was first pointed out by Burshtein and Mikhailov[33] and has also been observed in studies of styrene–methyl methacrylate,[34] styrene–methyl acrylate,[35] and styrene–*p*-chlorostyrene[36] copolymers in dilute solutions.

From Figure 3 one can see that for different copolymers having the same mole fraction of polar component, the dipole moment ratios are all different. This reflects the difference in the flexibility of the chains: S-PMS copolymers are more flexible than S-PCS, and S-NVC copolymers are the most rigid ones. The higher flexibility of S-PMS copolymers might be attributed to the existence of the C–O bond in the side chain, whereas the bulky side groups in S-NVC copolymers can cause the lower D_∞ values for these copolymers.

One can also read the $\langle\mu^2\rangle/X_2$ and D_∞ values for pure polar homopolymers ($F_2 = 1$) from Figures 1–3. They are also tabulated in Table III. Our result for PPCS is rather close to the value obtained by Yamaguchi et al.[37] (They obtained $\langle\mu^2\rangle/X_2 = 1.80\ D^2$ in toluene at 30 °C.) Other values of $\langle\mu^2\rangle/X_2$ or D_∞ obtained for PPCS in different studies in a variety of solvents are far from our result. This was discussed in detail in another article.[16]

The ratio D_∞ obtained in this work for PPMS in toluene at 25 °C is much lower than the value reported in benzene ($D_\infty = 0.94$) in the previous work,[16] although the same μ_0 value was used. This may possibly indicate a specific solvent effect. Although it has been widely accepted that D_∞ is not influenced by changes in long-range interactions if the dipole moment vector is perpendicular to the chain backbone,[2,38] a Monte Carlo study by Mattice et al. disputes this idea.[39] See, however, the more recent discussion by Mansfield.[40]

For S-4VP copolymers the internal dilution effect was not observed. For this system, when $F_2 > 0.40$ the copolymer does not dissolve in any nonpolar solvent, including toluene. For that reason the composition range covered was $0 < F_2 < 0.40$. As seen in Figure 2, $\langle\mu^2\rangle/X_2$ increases with F_2 in this composition range. Actually the product of reactivity ratios[25] ($r_1r_2 = 0.32$) suggests that the alternating tendency of this copolymer system is greater than for S-PCS and S-PMS although all of them are nearly random copolymers ($r_1r_2 = 0.76$ for S-PCS, $r_1r_2 = 0.83$ for S-PMS, and $r_1r_2 \approx 0.20$ for S-NVC copolymers at the polymerization temperatures[41]). The average sequence length of 4VP units never exceeds one,[37] and therefore $\langle\mu^2\rangle/X_2$ is expected to remain constant in this composition range.

The increase in the effective dipole moment per polar unit with increasing F_2 in S-4VP copolymers might be attributed to the change in solvent efficiency accompanied by the variation of composition. Toluene is a good solvent for polystyrene as well as for the copolymers in which the mole fraction of polar component is low. However, it becomes a nonsolvent if the mole fraction of polar component exceeds 0.40. For other copolymer systems studied in this work, toluene is a good solvent for both polar and nonpolar components.

To compare the experimental results with calculations of the dipole moments of vinyl copolymers based on the rotational isomeric state theory,[17] we evaluated $\langle\mu^2\rangle/x$ for each copolymer system, x being the degree of polymerization ($x = X_1 + X_2$). Calculated values of $\langle\mu^2\rangle/x$ for S-PCS copolymer by Mark are lower than our experimental values, although they also belong to stereochemically random copolymers[43] (replication probability $P_r = 0.5$). In this early study, the calculation was based on the dipole moment of the *p*-chlorostyrene unit, which had been reported by Burshtein and Stepanova[44] as 1.68 D. This

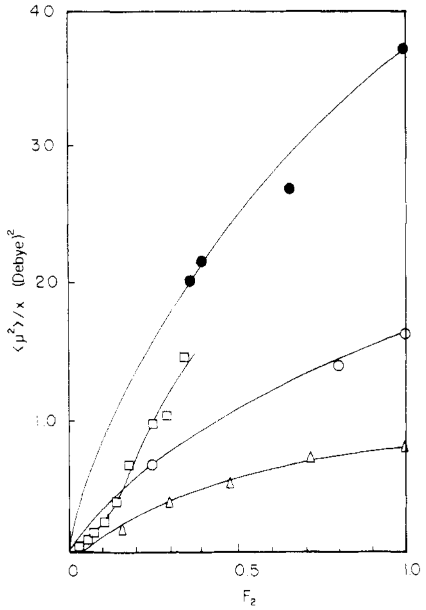

Figure 4. Values of $\langle\mu^2\rangle/x$ of various copolymers as a function of the mole fraction of polar component (at 25 °C): (●) poly(styrene-*co*-*N*-vinylcarbazole); (○) poly(styrene-*co*-*p*-chlorostyrene); (□) poly(styrene-*co*-4-vinylpyridine); (△) poly(styrene-*co*-*p*-methoxystyrene).

value is lower than other experimental values.[32] As a matter of fact, 1.68 D is replaced by μ_0 = 1.90 D in the later study of the dipole moments of PPCS chains by Mark et al.[8] It should be mentioned that our measurements were carried out at lower temperatures than that used in the calculations of Mark,[17] but there is a good qualitative agreement between the theoretical predictions and our experimental results: $\langle\mu^2\rangle/x$ changes linearly with composition for the block copolymers ($r_1r_2 = \infty$), and there is a positive deviation from linearity for random atactic copolymers.[43] For smaller values of the product r_1r_2 the deviation from linearity is enhanced.

Positive deviation from linearity is observed in all our copolymer systems. In the case of S-4VP copolymers, in which the reactivity ratio product is smaller (r_1r_2 = 0.32), this deviation is more pronounced, as seen in Figure 4.

In the present study, negative temperature coefficients for the dipole moment ratios were found for S-PMS, S-NVC, and S-4VP copolymers in the temperature interval 1–50 °C (Figures 1 and 2), and $-\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$ lies in the range $(1.5\text{–}8) \times 10^{-3}$ K^{-1}, substantially independent of copolymer composition. But for S-PCS copolymers, $\langle\mu^2\rangle/X_2$ (and D_∞) decreases from 1 to 25 °C, but there is an increase in $\langle\mu^2\rangle/x$ after 25 °C (Figure 1). This behavior has been observed before for PPCS by Baysal and Aras[16] and Burshtein and Stepanova.[44]

Saiz et al.[8] calculated $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$ as -3×10^{-4} K^{-1} for atactic poly(*p*-chlorostyrene) chains over the temperature interval 20–60 °C. A negative temperature coefficient was also indicated for poly(*p*-chlorostyrene-*co*-*p*-methylstyrene), which is similar to S-PCS copolymer, in the calculations by Mark,[17] although an exact value for the temperature coefficient was not given in that study.

Yoshihara and Work[45] give a positive temperature coefficient, $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T = (6\text{–}10) \times 10^{-4}$, for the dipole moment of undiluted PPCS over the temperature interval 406–447 K. Also, they have found positive temperature coefficients for poly(*p*-methylstyrene-*co*-*p*-chlorostyrene) in benzene solutions[24] and in the undiluted state.[22] Our results do not agree with these.

In the analysis of the dipole moments of copolymers, to get rid of the uncertainties that arise in choosing the proper μ_0 value, Work et al. proposed to use the ratio R_x, defined as[21–24]

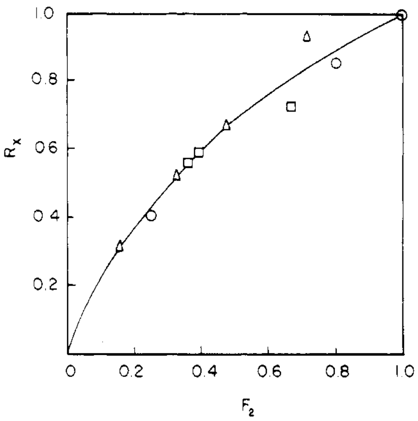

Figure 5. Ratio $R_x = \mu_e^2(F_2)/(\mu_e^2(F = 1))$ as a function of mole fraction of polar component for various copolymers in toluene solutions at 25 °C: (○) poly(styrene-*co*-*p*-chlorostyrene); (△) poly(styrene-*co*-*p*-methoxystyrene); (□) poly(styrene-*co*-*N*-vinylcarbazole).

$$R_x = \frac{\mu_e^2(F_2)}{\mu_e^2(F_2 = 1)} \tag{5}$$

where F_2 is the mole fraction of the polar unit in the chain and μ_e is the effective dipole moment per structural unit:

$$\mu_e^2 = \langle\mu^2\rangle/x \tag{6}$$

We calculated R_x values for S-PCS, S-PMS, and S-NVC copolymers over the whole composition range and plotted them versus F_2 in Figure 5. For S-4VP copolymers, we could not measure $\mu_e(F_2 = 1)$, since the pure polar homopolymer does not dissolve in any nonpolar solvent. Almost the same curve was obtained for all these copolymer systems, which shows that this method of analysis does not give any additional information on the molecular structure, such as the flexibility of the chains or effect of sequence distribution or side groups on the effective dipole moment.

Registry No. S-PCS (copolymer), 62742-92-1; S-PMS (copolymer), 24936-43-4; S-NVC (copolymer), 26710-15-6; S-4VP (copolymer), 26222-40-2.

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Communications to the Editor

Size Distribution of Complexes Formed between Poly(dimethyldiallylammonium chloride) and Bovine Serum Albumin

The formation of complexes between globular proteins and synthetic polyelectrolytes is generally evidenced by phase separation. The polymer-rich phase may be a liquid, i.e., a "complex coacervate",[1] or a solid precipitate. Examples of the latter have been observed for hemoglobin and dextran sulfate,[2] potassium poly(vinyl alcohol sulfate), and carboxyhemoglobin in the presence of poly(dimethyldiallylammonium chloride),[3] lysozyme and poly(acrylic acid),[4] and RNA polymerase and poly(ethylene imine).[5] Systems that exhibit coacervation include gelatin and polyphosphate[6] and serum albumin and poly(dimethyldiallylammonium chloride).[7]

There are several reasons for investigating such systems. Complexation of enzymes with polyelectrolytes offers a route to immobilized and, possibly, more stable forms of enzymatically active insulin,[8] catalase,[9] and urease and penicillin amidase.[10] Other changes in protein activity that accompany complex formation are also of interest, such as the reduction of oxygen affinity for hemoglobin in complexes with polyanions[11] which could lead to new blood substitutes.[12] The stoichiometry of colloid titrations of proteins with polyelectrolytes may help to shed light on the number and location of ionizable groups on the protein surface.[13,14] Complex formation between proteins and strong synthetic polyelectrolytes may provide useful models for theories about the nonspecific affinity of DNA-binding proteins[15] such as RNA polymerase, which appear to interact with nucleic acids largely through electrostatic effects.[16] Last, on a more practical level, selective coacervation or precipitation of proteins by polyelectrolytes could offer a novel approach to protein separation.[4,7,17]

We have previously studied the coacervation of several globular proteins with poly(dimethyldiallylammonium chloride) (PDMDAAC).[7] Phase separation occurs abruptly upon the addition of base to neutral or acidic mixtures of the two macroions at some well-defined pH. The value of $\mathrm{pH}_{\mathrm{crit}}$ is nearly linear with ionic strength and also increases with protein isoelectric point. In order to apply this phenomenon to protein separation, a clearer understanding of the mechanism of phase separation is needed. The following are among the relevant questions that may be posed: Is phase separation preceded by molecular complex formation? Are such (hypothetical) complexes purely intrapolymer? How many proteins bind per polymer chain, and is the binding highly cooperative?

Most of the foregoing queries hinge on the identification of a soluble, equilibrium polyion–protein complex. Such soluble complexes have been identified for hemoglobin and anionic polyelectrolytes[11,18] and for serum albumin and poly(4-vinyl-*N*-ethylpyridinium bromide).[19] However, despite the great variety of techniques one could apply to these systems, no reports deal with the characterization of polyion–protein complexes in the region of incipient phase separation. We have therefore measured the apparent dimensions of complexes of PDMDAAC with bovine serum albumin (BSA) at pH's below and above $\mathrm{pH}_{\mathrm{crit}}$. Since PDMDAAC is a strong polycation, its dimensions are invariant with respect to pH.

PDMDAAC, a commercial sample "Merquat 100" from Calgon Corp. (Pittsburgh) with nominal molecular weight 2×10^5 and reported polydispersity of $\bar{M}_w/\bar{M}_n \simeq 10$ was dialyzed and freeze-dried before use. Bovine serum albumin was from Sigma Chemical Co. Solutions were prepared by combining one volume of 3.0 g L^{-1} PDMDAAC with two volumes of 10.0 g L^{-1} BSA in 0.010 M 9:1 NaCl/sodium acetate and then adjusting the pH by addition of 0.10 M NaOH. (Multivalent anion buffers, such as phosphate, lead to slight precipitation of PDMDAAC.) Turbidity was measured with a Brinkman PC600 fiber optics probe colorimeter, equipped with a 420-nm filter and a 2-cm path length probe tip. All values are reported as the corrected turbidity, i.e., [ln %*T*(blank) − ln %*T*(solution)], where the blank is a polymer-free sample. Solutions for QELS, 3.0 g L^{-1} in polymer and 10.0 g L^{-1} in protein, were filtered (0.20 μm Milipore), and, in some cases, centrifuged (2000 rpm, 15–20 min) in the 1-cm cylindrical sample cell, which was then placed in the toluene refractive index matching bath (25.0 °C) of a Malvern RR102 spectrometer. The light source was a 20-mW He–Ne laser (Jodon); scattered light was collected at 90° by using a PM frontal aperture of 0.5 mm. The PMT output was analyzed with a Nicomp TC-200 computing autocorrelator. Photon counts were acquired until computed distributions were stable, usually corresponding to a "fit error" of less than 5 and "residual"[20] of less than 5, normally requiring the acquisition of 50 000 counts above base

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