reflects directly the dynamic process of the replacement of the molecules around the merocyanine and is also considered to correspond to the shrinkage of the polymer conformation. The time necessary for the shrinkage of the polymer chain is less than 1 μs in this system.

The dynamic process of the shift of the peak position followed by laser photolysis as well as a static absorption measurement demonstrates that the decrease of the viscosity during photoirradiation is consistent with the solvation by the ester side groups of the polymer of the strong dipole of the merocyanine molecules. Intermolecular solvation of the polymer chains and association of polymer chains make minor contributions to the effect because the effect was clearly observed even in very dilute solutions. The increase of polymer concentration suppressed the effect.

The time necessary for self-solvation corresponds to the relaxation time of the conformational change of the polymer chain. Although the direct measurement of the conformational change of poly(methyl methacrylate) has not yet been carried out, it is worthwhile to compare the self-solvation time with the relaxation times of helix–coil transitions of poly(α-amino acid)[15] as well as of the compact form–coil transition of the copolymer of maleic acid and styrene.[16] The relaxation time of the helix–coil transition of poly(α-L-glutamic acid) is reported to be less than 10 μs, while the value of the compact form–coil transition of the above vinyl copolymer increases to around 100 ms. The relaxation time reflects the cooperative nature of the transition as well as the flexibility of the polymer system. A factor in favor of the fast transformation of the polymer conformation of poly(methyl methacrylate) in our system is that the conformational change we observed can be reached by relatively small displacement of the polymer segments.

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Micellar Solutions Obtained with Amphiphilic Block Copolymers in the Presence of Water, Oil, and Alcohol. 1. Small Angle Neutron Scattering Structure Investigation in the Case of Poly(2-vinylpyridine-*b*-ethylene oxide) Block Copolymers

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ABSTRACT: Micellar solutions obtained with amphiphilic block copolymers in the presence of water, oil, and alcohol have been studied by the small angle neutron coherent scattering. The investigation of such systems in the Guinier range has shown that the scattering particles are micelles whose radius of gyration, molecular weight, and association number have been determined using the "contrast adjustment method". The examination of the variation of the scattered intensity in the submolecular range has given information on the chain's conformation within micelles. A model taking into account both SANS results and respective affinities of each copolymer block for the solvent medium has been proposed.

It is well known that transparent oil–water systems can be obtained in the presence of surface active materials. These systems have been called microemulsions, micellar emulsions, micellar solutions, or swollen micellar solutions by different authors.[1]

In several previous papers,[2,3] we have shown that amphiphilic block or graft copolymers can lead, in the presence of oil, water, and alcohol, to the formation of transparent phases. These stable four-component systems consist of a dispersed phase containing the copolymer molecules surrounded by a continuous phase. More precisely, the copolymer chains in the dispersed phase present a micellar structure such that the hydrophobic and hydrophilic parts are solvated preferentially by oil and water, respectively. As for the continuous phase, it is constituted of a mixture of the three solvents considered, whose composition corresponds to that of a solvent mixture located on the mutual solubility curve. In this work, the term "micellar solution" will be used for such transparent polymeric systems.

In a preceding paper,[3] we have studied the solubilization of poly(2-vinylpyridine-*b*-ethylene oxide) copolymer molecules by water–toluene–2-propanol mixtures. In particular, we have established the domain of existence of the micellar solutions obtained and determined the composition of the continuous and dispersed phases.

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The purpose of this paper is to use the small angle neutron scattering (SANS) technique—which, as it is well known, is a very suitable method for the determination of molecular shape and size of dispersed particles[4-6] in a continuous medium—to obtain further information on the structure of the transparent micellar phases observed with poly(2-vinylpyridine-*b*-ethylene oxide) copolymers in the presence of toluene, water, and 2-propanol.

Theoretical Section

The neutron scattering technique is a powerful method for all studies of conformations and correlations in polymer solutions. The uniqueness of neutron scattering applied to polymers arises from the contrast which can be established between the polymer and solvent molecules. From measurements of the scattering intensity as a function of the scattering angle, the excess intensity resulting from the polymer can be obtained. At sufficiently low concentrations, the excess intensity may be attributed to intramolecular interferences alone, and thereby the shape and size parameters of the polymer molecules can be determined.

If one considers a block copolymer[7,8] obtained from two different monomers 1 and 2 and takes into account the hypothesis of incompressibility, the coherent scattered intensity $I(q)$ can be written in the form:

$$\frac{\phi \nu^2 c}{I(q)} = \frac{1}{M_{\text{app}} P_{\text{app}}(q)} + 2A_2 c + O(c^2) \qquad (1)$$

ϕ is a constant depending on neutron flux and spectrometer geometry, c is the polymer concentration, and A_2 is the second viriel coefficient. ν is the average contrast factor; $\nu = x\nu_1 + (1-x)\nu_2$ with $\nu_1 = \bar{V}_1(b_1' - b_s')$ and $\nu_2 = \bar{V}_2(b_2' - b_s')$, x being the weight fraction of sequence 1 in the copolymer, b_1', b_2', and b_s' being the coherent scattering lengths per unit volume of monomers and solvent, respectively, and $\bar{V}_1$ and $\bar{V}_2$ being the specific volumes of monomers 1 and 2. M_{app} is the apparent molecular weight of the scattering particles, which according to Leng and Benoit[9] can be given by the expression:

$$M_{\text{app}} = M_{\text{w}} + 2P\left(\frac{\nu_1 - \nu_2}{\nu}\right) + Q\left(\frac{\nu_1 - \nu_2}{\nu}\right)^2 \qquad (2)$$

P and Q are parameters characterizing the heterogeneity in composition of the particles. It is interesting to note that in the particular case where $\nu_1 = \nu_2 = \nu$ (as it will be seen later, this situation corresponds to the experimental systems investigated), M_{app} is equal to M_{w} (weight average molecular weight of the scattering particles).

$P_{\text{app}}(q)$ is the apparent scattering factor normalized to unity for $q = 0$. $P_{\text{app}}(q)$ is related to the apparent scattering function $S_{\text{app}}(q)$: $P_{\text{app}} = 1/N^2 S_{\text{app}}(q)$, where N is the total number of monomer units per copolymer chain and $S_{\text{app}}(q)$ is given by the relationship

$$S_{\text{app}}(q) = \sum_{\substack{i,j\\1,2}}\sum \langle \mathrm{e}^{i\bar{q}(\bar{r}_1{}^i - \bar{r}_2{}^j)} \rangle = \int e^{i\bar{q}\bar{r}}\, P_{i,j}^{1,2}(\bar{r})\, \mathrm{d}_3 r$$

The brackets correspond to thermal and angular averages and $P_{ij}^{12}(\bar{r})$ is the probability of having at a distance r monomers i and j of sequences 1 and 2. $P_{\text{app}}(q)$ can be expressed as a function of the form factor $P_1(q)$ and $P_2(q)$ of sequences 1 and 2 by the relation:[10]

$$P_{\text{app}}(q) = \frac{1}{\nu^2}[x^2\nu_1{}^2 P_1(q) + (1-x)^2\nu_2{}^2 P_2(q) + 2x(1-x)\nu_1\nu_2 P_{12}(q)] \qquad (3)$$

$P_{12}(q)$ correspond to the diffusion arising from interferences between monomers 1 and 2. If $\nu_1 = \nu_2$

$$P(q) = x^2 P_1(q) + (1-x)^2 P_2(q) + 2x(1-x)P_{12}(q) \qquad (4)$$

In other words, $P_{\text{app}}(q)$ can be assimilated to the real form factor $P(q)$ and therefore, concerning the average contrast factor, the copolymer behaves in the same manner as a homopolymer.

As far as $P(q)$ is concerned and depending upon the q values with respect to the molecular parameters of the polymer chains, one can discern two regions: the low q and the intermediate.

(1) The low q region (Guinier range $qR_{\text{G}} < 1$) provides information on the dimensions of the scattering particles. Then according to the Guinier approximation,[11] $P_{\text{app}}(q)$ can be written as:

$$P_{\text{app}}(q) \simeq e^{-\frac{q^2 R_{\text{app}}{}^2}{3}}$$

or for $q \rightarrow O$:

$$R_{\text{app}}(q) \simeq 1 - \frac{q^2 R_{\text{app}}{}^2}{3} + O(q^4)$$

Under these conditions:

$$\frac{\phi \nu^2 c}{I(q)} = \frac{1}{M_{\text{app}}}\left[1 - \frac{q^2 R_{\text{app}}{}^2}{3}\right] + 2A_2 c$$

with

$$\bar{R}_{\text{app}}{}^2 = \frac{x\nu_1}{\nu}\bar{R}_1{}^2 + \frac{(1-x)\nu_2}{\nu}\bar{R}_2{}^2 + \frac{x(1-x)\nu_1\nu_2}{\nu^2}\bar{L}^2 \qquad (5)$$

where $\bar{R}_1{}^2$ and $\bar{R}_2{}^2$ are the mean-square radii of gyration of blocks 1 and 2, respectively, and $\bar{L}^2$ is the mean square distance between the centers of mass of blocks 1 and 2. When $\nu_1 = \nu_2$, $\bar{R}^2 = x\bar{R}_1{}^2 + (1-x)\bar{R}_2{}^2 + x\,(1-x)\bar{L}^2$, and one does determine the real value of the radius of gyration.

In the general case where ν_1 is different from ν_2, for a given polymer concentration plots of $c/I(q)$ or log $I(q)$ vs. q^2 lead to an apparent radius of gyration. Moreover, the Zimm method allows us to obtain, by extrapolation to both zero concentration and zero scattering vector, the radius of gyration, the molecular weight, and the second viriel coefficient A_2.

(2) In the intermediate range (submolecular range) $R_{\text{G}}^{-1} < q < b^{-1}$, where b is the length of the statistical unit, the measurements of the scattered intensity give information about the shape of the particles and the short distance conformation of polymer chains.

In the intermediate domain, $P(q)$ is given by the general expression $P(q) \sim 1/q^n$ (ref 12), where n is the exponent which characterizes the structure of the scattering particles.

If the system is homogeneous, $n = 1/\nu$, ν being a characteristic critical exponent:[28] $n = 1$, $\nu = 1$ for a rigid rod; $n = 2$, $\nu = 1/2$ for a Gaussian chain; and $n = 5/3$, $\nu = 3/5$ for a swollen chain in the presence of excluded volume effects.[13,14] It is worth noting that, for statistical chains with finite persistence length l,[15] a $1/q$ scattered intensity variation appears for values of q corresponding to $ql \gg 1$, where the chain behaves like a rod: $n = 3$ for collapsed chains under the Θ point; and $n = 4$ for a two-density model.

All of these results are valid in the dilute regime defined by $c < c^*$ [16,17] with $c^* = M/NR^3$, where M is the molecular weight of the particles and N the Avogadro's number.

In the semidilute regime defined by $c > c^*$, the coils interpenetrate each other, and Edwards has introduced a screening length ξ [18] to characterize the pair interaction between segments (ξ can be considered as the distance beyond which there is no excluded volume effect between

Table I
Coherent Scattering Lengths per Unit Volume of Polymers and Solvents

	water	toluene	2-propanol	PEO	PV2P	P2VP-PEO block copolymers
$b'_D \times 10^{-10}$, cm cm^{-3}	6.4	5.685	6.3	7.7		
$b'_H \times 10^{-10}$, cm cm^{-3}	−0.562	0.94	−0.327	0.685	1.474	0.895

Table II
Characteristics of Micellar Solutions Investigated

	system W (water-rich side)	system T (toluene-rich side)
micellar solutions (wt %)		
copolymer	4.10	5.3
water	38.51	6.64
toluene	12.83	59.62
2-propanol	44.56	28.44
continuous phase (wt %)		
water	32.0	3.6
toluene	17.5	68.3
2-propanol	50.5	28.1

any two segments in the solution or as the mean distance between two successive contacts of a chain with any other chain).

It should be emphasized that the determination of the form factor for block copolymers is rather complicated, each block interacting differently with the solvent medium. Moreover, in the particular case of the systems investigated in our study, a further difficulty arises from the fact that the solvent is a ternary solvent mixture. In order to reduce our systems to the case of a copolymer in a unique solvent, using the "contrast adjustment method",[10] we have kept the scattering length of the solvent mixture constant regardless of its composition. This result has been obtained by adjusting the scattering length per unit volume of the water–toluene–2-propanol mixtures to that of deuteriated toluene (Table I), which corresponds to the following compositions (% w/w): water H9.5/D90.5; 2-propanol H 8.3/D91.7; toluene H0/D100.

On the other hand, in the case of the systems P2VP–PEO block copolymer and water–toluene–2-propanol considered, $\nu_{PEO} = -4.15 \times 10^{10}$ cm g^{-1} and $\nu_{P2VP} = -4.01 \times 10^{10}$ cm g^{-1}. These parameters have been calculated from the scattering lengths given by neutron tables[20] and the values of the specific volumes of PEO[21] and P2VP:[22]

$$\bar{V}_{PEO} = 0.83 \text{ cm}^3 \text{ g}^{-1};\ b'_{PEO} = 0.685 \times 10^{10} \text{ cm cm}^{-3}$$

$$\bar{V}_{P2VP} = 0.952 \text{ cm}^3 \times \text{g}^{-1};\ b'_{P2VP} = 1.474 \times 10^{10} \text{ cm cm}^{-3}$$

Consequently, $\nu_{PEO} \simeq \nu_{P2VP} \simeq \nu_{copolymer}$ (-4.12×10^{10} cm g^{-1}), and it can be concluded that the real values of the radius of gyration and molecular weight of the scattering particles are obtained.

Experimental Section

P2VP/PEO block copolymers were prepared via anionic polymerization.[23] The sample considered in this paper is homogeneous in composition and has a narrow molecular weight distribution. Its molecular characteristics are: M_w(P2VP) = 11 000; M_w(copolymer) = 46 000; 2VP(wt %) = 24.0.

In this study, we have investigated two systems located in the pseudoternary phase diagram on the transition line emulsion-transparent system which are toluene-rich and water-rich, respectively, and whose composition is given in Table II.

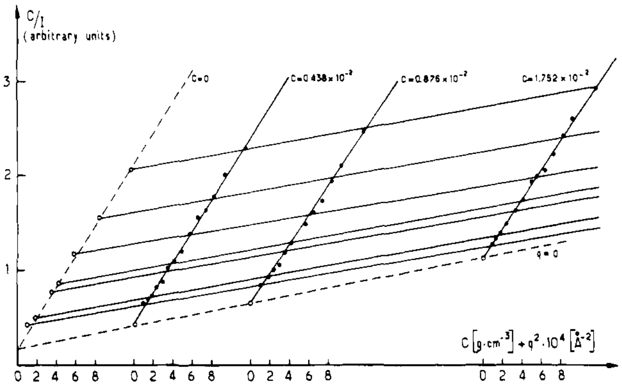

Figure 1. Zimm plot for the system W.

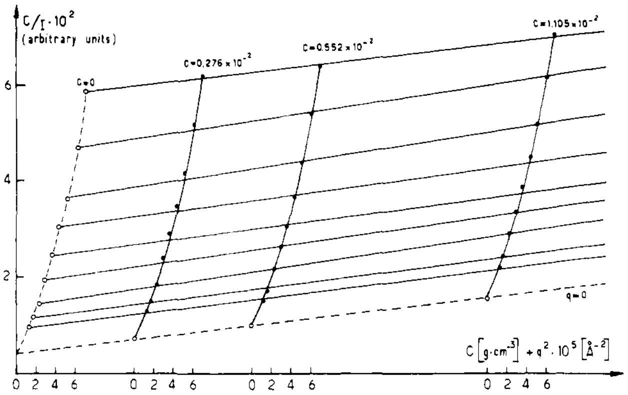

Figure 2. Zimm plot for the system T.

Low angle neutron scattering experiments were carried out on the Von Laue Langevin Institute instrument, using procedures described elsewhere.[24,25]

All measurements in the Guinier range were made at room temperature, using the D11 small angle neutron scattering camera at momentum transfers between 5×10^{-3} Å^{-1} and 2×10^{-2} Å.

The investigations of the asymptotic behavior ($qR_G \gg 1$) were carried out on the D17 apparatus for which the scattering vector ranges from 10^{-2} to 10^{-1} Å^{-1}.

It should be emphasized that the concentration of the polymer solutions studied was always lower than c^*.

Results and Discussion

1. Dimensions and Molecular Weight of Micelles. The results concerning the two systems investigated are summarized in Table III. The radius of gyration for the water-rich system, for which a typical Zimm plot is shown in Figure 1, was determined from the initial slope at $c = 0$ of the C/I against q^2 dependence. In the case of the toluene-rich system, the angular dependence of C/I plots exhibits a slightly upwards curvature (Figure 2). There-

Table III
Characteristics of Micelles Obtained from SANS Experiments

	R_G, Å, extrapolated at $c = 0$	$M_w \times 10^{-4}$	no. of aggregation
system W (water-rich side)	170	10	2
system T (toluene-rich side)	250	250	54

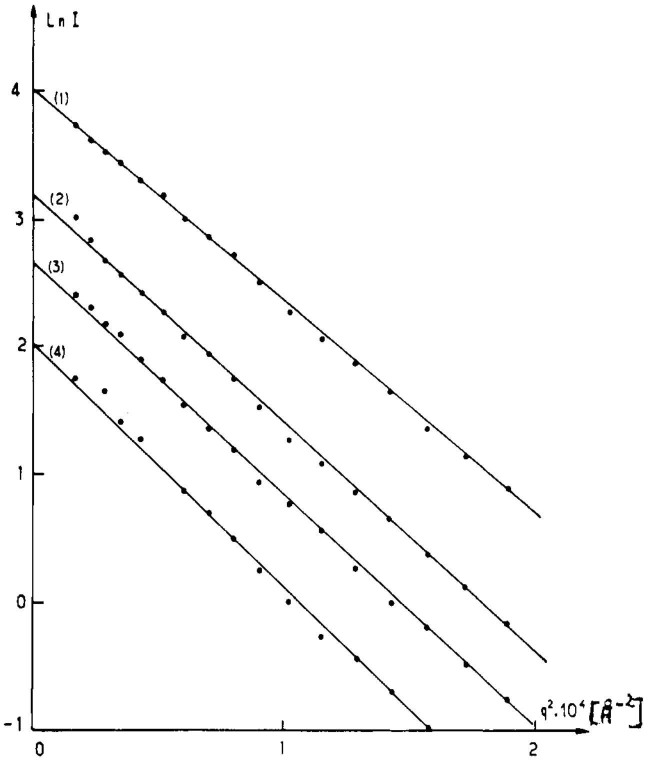

Figure 3. Guinier representation for the system T for different concentrations: (1) $C = 1.1 \times 10^{-2}$ g cm^{-3}; (2) $C = 0.55 \times 10^{-2}$ g cm^{-3}; (3) $C = 0.28 \times 10^{-2}$ g cm^{-3}; and (4) $C = 0.14 \times 10^{-2}$ g cm^{-3}.

fore, it was difficult to obtain the accurate value of the mean square radius of gyration from the representation $C/I = f(q^2)$. This difficulty was overcome by using the Guignier's method which led to a linear variation of ln I vs. q^2 in the small q range (Figure 3). Moreover, it can be observed that the slope of c/I or ln I does not practically depend on polymer concentration, which means that the dimensions of particles are very little affected by the dilution process employed[26] (the systems were diluted with a ternary solvent having the same composition as the continuous phase[3]).

The molecular weight of particles was determined from the intercept at $c = 0$ and $q = 0$ of $c/I = f(q^2)$ plots (Zimm method). The apparatus constant ϕ was calculated from the absolute measurement of the incoherent diffusion of water.

From the data collected in Table III, it can be seen that the molecular weight of the particles, on one hand, is higher than the molecular weight of the individual copolymer molecules and, on the other hand, increases with toluene content. This result means that whatever the relative proportions of water and toluene, several copolymer molecules associate to form a micelle, the degree of association decreasing when the medium becomes richer in water (the number of copolymer molecules within a micelle being respectively 54 and 2 for systems T and W). It must also be noted that the dimensions of the micelles are greater in the toluene-rich domain than in the water-rich solvent, whereas the behavior of a PEO homopolymer, whose molecular weight ($M_w = 27\,000$) is equivalent to that of the PEO block of the copolymer, in a ternary solvent corresponding to the continuous phase of W and T systems (Table II) is quite opposite. The large discrepancy between the values of the radii of gyration of the PEO for the two water/toluene ratios considered implies that the solvent medium relative to the W system is a better solvent for the PEO sequences, which constitute the major part of the copolymer chains, than for the solvent medium corresponding to the T system. Furthermore, it can be reasonably assumed that, whatever the water or toluene content, the quality of the solvent is worse for P2VP than for PEO blocks. As a consequence, in order to maintain the copolymer molecules in solution, a much greater number of polymer chains must associate in the T region than in the W region.

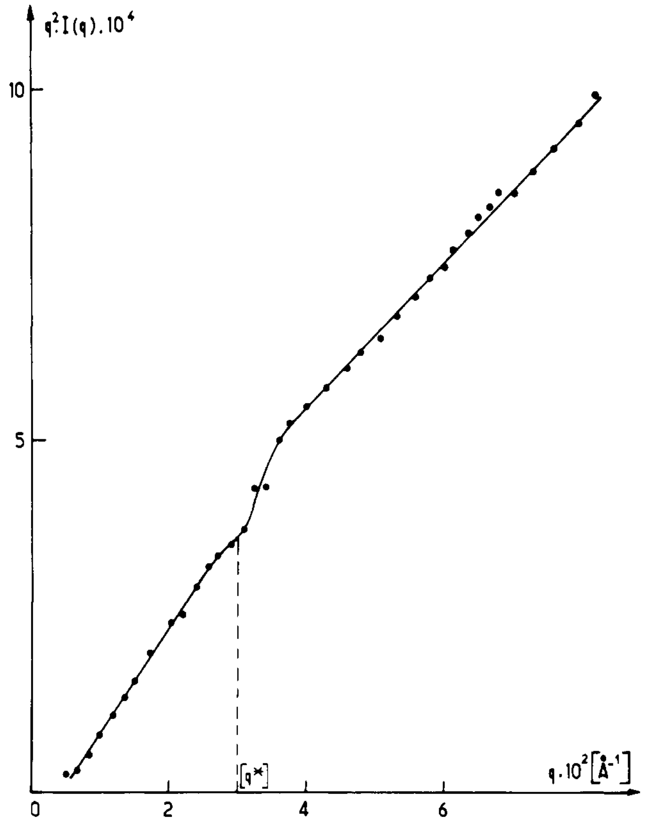

Figure 4. Kratky representation: $q^2I(q)$ in arbitrary units vs. q for the system W (polymer concentration: 1.75×10^{-2} g cm^{-3}).

Our data have been analyzed by considering monodisperse scattering particles. This hypothesis seems to be reasonable according to electron microscopy observations on similar systems.[2] Anyway, the effect of polydispersity would not modify the qualitative conclusions concerning the relative dimensions and association number.

2. Internal Structure of Micelles. As mentioned above, when $qR_G \gg 1$, the scattering law provides information on the internal structure of the scattering particles. A classical representation for getting information on the submolecular structure of flexible chains is to use the Kratky representation, i.e., to plot Iq^2 vs. q, which allows us to characterize deviation from Gaussian behavior.

The scattering data of our experiments are shown in Figures 4 and 5 in the form of $q^2I(q) = f(q)$ plots. We have observed that the behavior of each system is independent of the polymer concentration in all the investigated domain of q (the greater dispersion of experimental points for the more dilute system (Figure 5) is due to the lower scattered intensity). As can be noticed, the scattering functions exhibit different behaviors depending on the range of q investigated. In order to obtain more information about these behaviors and the q^* values which characterize the crossover between the different scattering regimes, the results have been plotted according to a log–log representation (Figures 6 and 7); such a plot leads to the evaluation of the exponent n of $P(q) \simeq 1/q^n$.

We see that the value of the crossover scattering vector q^* does not practically depend on the location of the

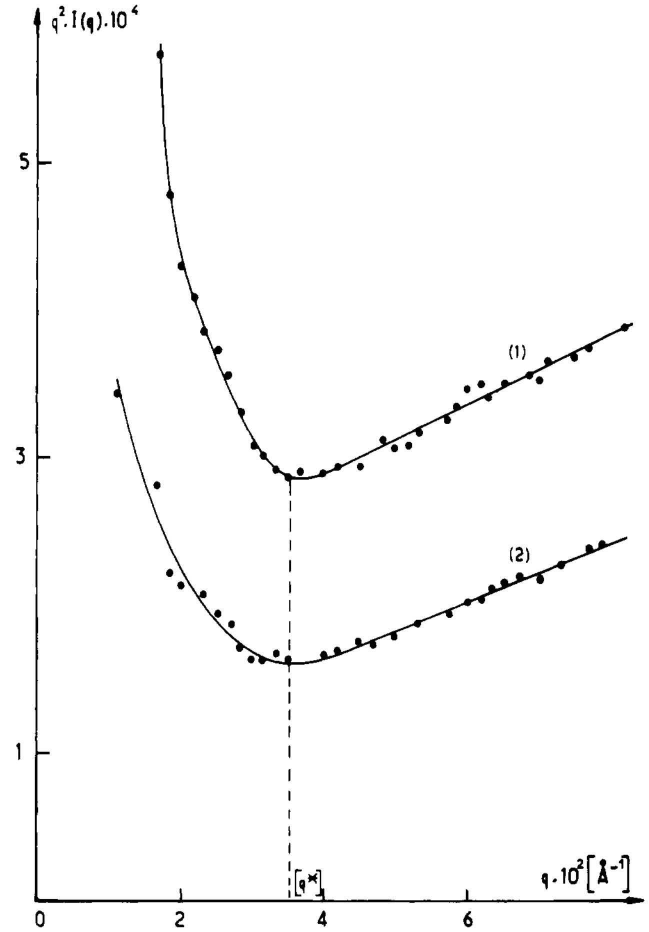

Figure 5. Kratky representation: $q^2I(q)$ in arbitrary units vs. q for the system T for different concentrations: (1) $C = 1.1 \times 10^{-2}$ g cm^{-3}; and (2) $C = 0.55 \times 10^{-2}$ g cm^{-3}.

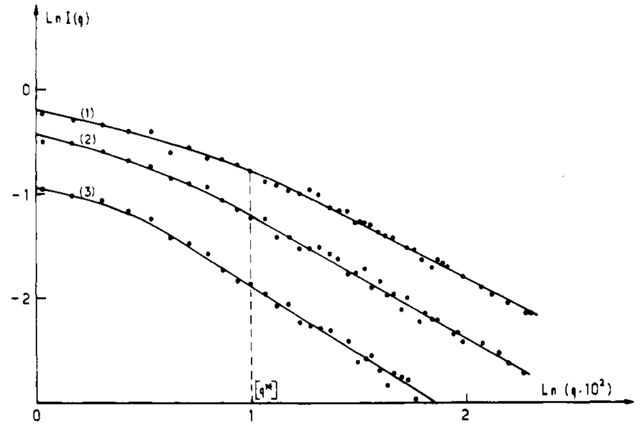

Figure 6. Log-log representation of the scattered intensity vs. q for the system W for different concentrations: (1) $C = 1.75 \times 10^{-2}$ g cm^{-3}; (2) $C = 0.88 \times 10^{-2}$ g cm^{-3}; and (3) $C = 0.44 \times 10^{-2}$ g cm^{-3}.

Table IV
Values of the Exponent n and of the Crossover Scattering Vector q^* in the Intermediate Range

	n ($1.8 \times 10^{-2} < q < q^*$)	q^*, Å^{-1} (crossover)	n ($q > q^*$)
system W (water-rich side)	3	3.2×10^{-2}	1
system T (toluene-rich side)		3.5×10^{-2}	1.66

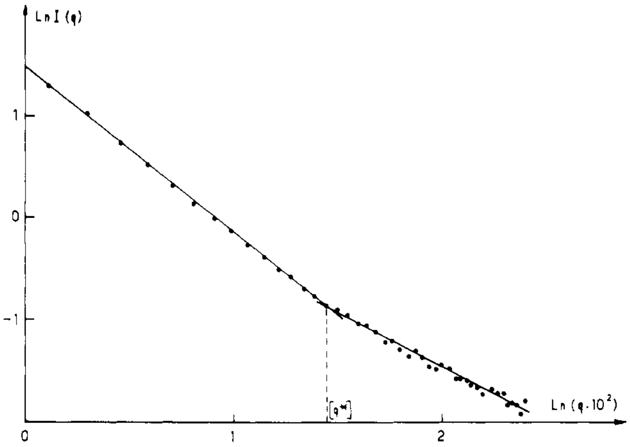

Figure 7. Log-log representation of the scattered intensity vs. q for a PEO sample in the water-rich side (polymer concentration: $C = 2.8 \times 10^{-2}$ g cm^{-3}).

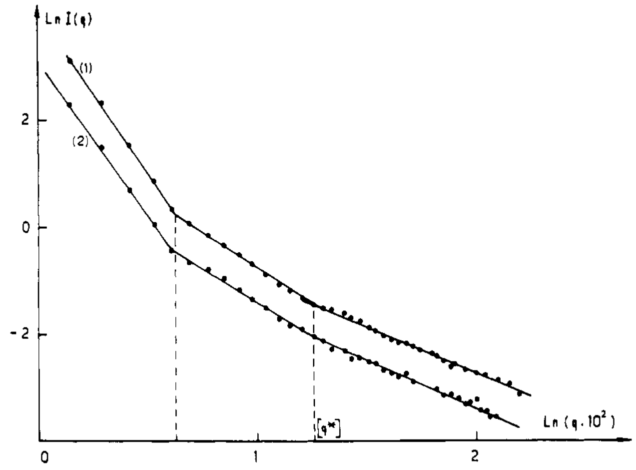

Figure 8. Log-log representation of the scattered intensity vs. q for the system T for different concentrations: (1) $C = 1.1 \times 10^{-2}$ g cm^{-3}; and (2) $C = 0.55 \times 10^{-2}$ g cm^{-3}.

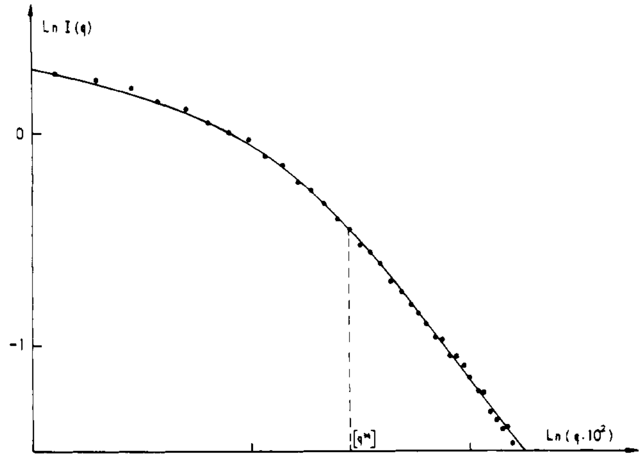

Figure 9. Log-log representation of the scattered intensity vs. q for a PEO sample in the toluene-rich side (polymer concentration: $C = 2.9 \times 10^{-2}$ g cm^{-3}).

system on the pseudoternary phase diagram. As a consequence, there must exist a correlation between q^* and the conformation of the block copolymer molecules within the micelles in spite of the great difference between the particle dimensions and solvent quality for T and W systems which will be successively examined. We have also studied the behavior of a PEO homopolymer (Figures 8 and 9) whose characteristics have already been mentioned.

System W (Water-Rich Side). Examination of Table IV and Figure 6 shows for copolymer micelles a transition between the behavior of $I(q)$: a wide angle behavior characterized by a $1/q$ dependence and a smaller q domain with a weaker decay of the scattered intensity. This behavior can be compared with the scattering variation of a corresponding homoPEO ($M_w = 27\,000$) in an identical solvent. Figure 7, which shows the log-log representation of $I(q)$, exhibits a crossover at $q = q^*$ between the behavior characterized by two different q exponents n (in the general representation $I(q) = 1/q^n$). For $q > q^*$, $n = 1$, while for $q < q^*$, $n \simeq 5/3$. This scattering response can be interpreted in terms of a chain with excluded volume effects at a distance scale greater than $l = A/q^*$ defining a persistence length of the chain; at distances smaller than l, the chain is seen as a rigid rod. Since the correct value of A is a question which does not seem fully settled in theory, we have restricted our analysis to semiquantitative considerations by taking $A = 1$, leading in this case of PEO homopolymer to $l = 28$ Å which is quite reasonable in comparison with the measured radius of gyration, $R_G = 120$ Å. This result shows that the PEO homopolymer in a water-rich solvent behaves like a semirigid coil with persistence length l.

Returning to the case of the copolymer, it can be noticed that the rodlike behavior limit corresponding to the high q range is shifted toward smaller q, which would lead to a higher value of persistence length ($l \sim 40$ Å). Consequently, it can be deduced that the PEO sequences within the micelle exhibit a local rigidity even more pronounced than that in the case of PEO homopolymer. This local rigidity can be asserted from the following reasons: the neutrons "see" mainly the PEO blocks because they constitute the major part of the copolymer (76%); the water-rich medium is a good solvent for PEO chains, which is not the case for P2VP blocks; above all, the PEO homopolymer exhibits a similar behavior, whose rigid character can be enhanced in the case of copolymer by a segregation effect due to the presence of the P2VP sequence.

Concerning the scattering variation of smaller q, the excluded volume behavior observed for homoPEO cannot be detected on the copolymer. It is difficult to give an unambiguous interpretation of this difference. Moreover, it could be explained by the fact that by increasing the stiffness of the chains, the range of q between the asymptotic and Guinier ranges is strongly restricted and cannot be observed experimentally.

System T (Toluene-Rich Side). The situation in the toluene-rich domain is different (Table IV, Figure 8).

For $q > q^*$, $P(q)$ varies like $q^{-5/3}$. Such a behavior which characterizes a short range excluded volume regime has also been observed with the PEO homopolymer in the same solvent (Figure 9). The latter result means that the excluded volume is ascribable to the PEO blocks.

For $q < q^*$, the form factor is proportional to $1/q^3$. Such a value for the exponent n of q suggests for the PEO blocks a more compact structure at higher distances which is not in opposition, on one hand, to the value of the radius of gyration of the PEO homopolymer in the same solvent mixture ($R_G = 45$ Å) and, on the other hand, to the high aggregation number (54) which provides an efficient protection of P2VP blocks. It can be noted that for the small q values, the exponent n relative to the PEO sample (Figure 9) is not clearly defined. This result is probably due to the fact that the corresponding qR values are only slightly greater than 1.

Conclusion

The small angle neutron scattering results reported in this paper have allowed us to obtain a better knowledge of the conformation of the P2VP-PEO copolymer molecules in the presence of water, toluene, and alcohol. The experiments carried out, in the Guinier range, have shown that copolymer molecules associate to form micelles whatever the composition of the ternary solvent medium, the association degree being higher in the toluene-rich side than in the water-rich side. Moreover, solubilization studies indicate that the ternary solvents considered are better solvents for PEO chains than for P2VP chains. As a consequence, and since the PEO blocks form the major part of copolymer molecules, it is reasonable to assert that the core of the micelles is constituted by the P2VP chains and is surrounded by the PEO chains.

On the other hand, the results obtained in the submolecular range give additional information on the conformation of copolymer molecules within the micelles. In the water-rich domain, the PEO blocks exhibit a local stiffness which means that the PEO chains are in a good solvent medium. Under these conditions, the P2VP content in the copolymer being low, a small number of PEO blocks are sufficient to protect the P2VP blocks. In the toluene-rich region, the PEO blocks present a short-range excluded-volume behavior which shows that the dimensions of PEO chains are smaller. Furthermore, the form factor behavior relative to the low q range implies for the micelles a compact structure which is in good agreement with the high value of the association number.

It can be noticed that a study, carried out simultaneously with this work by Candau et al.[27] on the structure of colloidal particles in water-oil mixtures stabilized by poly(styrene-*g*-ethylene oxide) graft copolymers, has led to different results due mainly to the more pronounced hydrophobic character of the polystyrene backbone of the graft copolymers.

In order to obtain more precise information on the structure of micellar solutions found with block copolymers, further investigation along this line is in progress, concerning more particularly: the influence of the weight fraction of hydrophobic or hydrophilic blocks; the influence of the temperature on the systems investigated; and a more accurate description of the conformation of copolymer molecules within the micelles by selectively labeling each block.

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Excess Polarizability and Volume of Mixing and Their Effect on the Partial Specific Volume and the Refractive Increment of Polymers in Mixed Solvents

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ABSTRACT: The phenomenon of excess polarizability of mixing was confirmed experimentally and justified theoretically. A unified phenomenological method of treatment of changes of thermodynamic properties resulting from mixing was developed and applied to the changes of volume and polarizability. Formulas were developed which related partial specific volume and refractive increment of polymers in mixed solvents with the experimentally observable phenomenological parameters of mixing. The introduction of the parameters related to the excess polarizability of mixing proved crucial for the proper interpretation of refractive increments. The minimum observed on the dependence of specific volume of polymer on the composition of a mixed solvent is a result of the volume changes related to mixing the solvents themselves.

During our studies of the preferential adsorption onto polystyrene in mixed solvents,[1,2] we needed the values of the refractive increment and of the partial specific volume as a function of the composition of the solvent. At first, we tried to predict these values from the values measured using pure solvents. We made several predictions based on various mixing rules used in literature: they differed substantially among themselves. Also, the preferential adsorption quantities resulting from these calculations were internally inconsistent. Finally, we decided to obtain the necessary data experimentally; our calculation of the preferential adsorption was based fully on experimental values.[1,2]

During the above studies, we obtained the partial specific volume and the refractive increment of polystyrene in two mixed solvent systems as a function of the solvent composition. We tried to analyze the experimental dependences by traditional means:[3,4] they defied interpretation. Realizing that both the specific volume and the refractive increment are strongly influenced by the changes of volume in mixing the *solvent* components, we decided to expand the study to include mixtures of low molecular weight compounds in the absence of polymer. The changes of volume were not sufficient to explain the dependence of refractive index on composition. It became obvious that the mixing rules for refractive index need to be reformulated. However, there already exists a large amount of literature (cf. ref 5 and 6) about the mixing rules and their merits. When more rigorous standards are applied, none of the formulas reproduce the experimental data satisfactorily. The idea of developing still another mixing rule did not seem inviting. On the other hand, we realized that the older theories had one concept in common. They struggled for the best relation between the external field acting on the macroscopic sample and the internal field acting on an individual molecule. All theories implicitly or explicitly assumed that the polarizability of a molecule is its invariant characteristic. Only Letcher and Bayles[7] recognized that this is not satisfactory, and they introduced a concept of "excess molar refraction".

This study will show that a theory using the concept of excess polarizability of mixing leads to a very satisfactory description of the refractive indices and refractive increments. However, we are still not able to solve the old problem of the internal field. Because the Lorenz–Lorentz formula is known to perform best from the existing theories, we have used it as our starting point and combined it with the concept of excess polarizability of mixing. Of course, the Lorenz–Lorentz internal field is still controversial: our relations must therefore be considered as phenomenological.

While the changes of volume in mixing are well-known and their effect on specific volumes and refractive increments is occasionally considered, there does not seem to exist any comprehensive approach. We are therefore presenting in this paper a useful frame of phenomenological relations, which can be used for unified presentation of all the changes accompanying mixing. The somewhat unexpected form of the dependence of specific volume of polymer on the composition of the mixed solvent becomes

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