The Influence of Solvents on Unperturbed Dimensions of Polymer in Solution

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ABSTRACT: In this paper we review the unperturbed dimensions of polymers measured in different solvents. It is shown that this quantity, especially in the case of polar polymers and polar solvents, can vary considerably. Depending on the nature of solvent and polymer, K_Θ can be smaller or larger than the value which would be expected in the absence of specific interactions. Some tentative explanations are given involving hydrogen bond formation. In the case of mixed solvents, we have found a linear relation between G^E, the excess free enthalpy of mixing of the solvents, and the difference between the observed value of K_Θ and the average calculated from data in the pure solvents.

One of the principal approximations often made in order to give a thermodynamic interpretation of configurational properties of polymers in solution is to assume that the unperturbed dimensions of polymer molecules do not depend on the solvent in which the molecule is imbedded. In other words, one assumes that the relative energies of rotational isomeric states do not depend on the solvent. As has been pointed by Hearst[1] reviewing a recent book of Flory,[2] this hypothesis, in spite of some evidence in its favor, has not yet been proved correct experimentally.

In this paper we would like to discuss some experimental results obtained in our laboratory and in other laboratories which show that the domain of validity of this hypothesis is much more limited than is usually believed. This is not new and has already been shown by Kurata and Stockmayer.[3] In a recent paper we have given some experimental results showing some examples where unperturbed dimensions depend on solvent, but no systematic review about these effects has yet been published.

Experimental Section

One of the first points to be discussed is the availability of experimental methods for the determination of unperturbed dimensions. If the solvent to be studied is a Θ solvent following Flory's definition, *i.e.*, a solvent in which the second virial coefficient is zero and the limiting viscosity number is proportional to the square root of M, then one knows that the dimensions of the chain are the unperturbed dimensions. It is sufficient, therefore, to determine dimensions and molecular weight in order to get the needed quantity. For this purpose the two best methods available are light scattering and viscosity.

The former is limited to rather high molecular weight and is very sensitive to polydispersity. Its precision therefore is not very great and the validity of the results is always open to question.

As for viscosity, its measurement is much simpler and much more precise. It can be used for any value of molecular weight and, taking into account the fact that the viscosity average is not too far from the weight average, the influence of polydispersity is much less severe on its results. The only difficulty is that its theoretical basis is weaker than that for light scattering, but so many results show the validity of the use of Flory's formula for viscosity in Θ solvents that it seems difficult not to agree with its use.

The problem is much more difficult in a good solvent, where one has to eliminate long-distance interactions to obtain the correct unperturbed dimensions. This elimination is a rather difficult operation and many formulas have been proposed to justify a graphic procedure for obtaining unperturbed dimensions either from light-scatering results or from the limiting viscosity number.[4–6] They are all based on the idea that when molecular weight decreases long-distance interactions also decrease and can be eliminated by a correct extrapolation to zero molecular weight. All these methods are subject to the following difficulty: when the molecular weight is too small, the chains do not obey Gaussian statistics and the viscosity theory is no longer valid; and, when the molecular weight is high and the expansion factor is too large, it is difficult or even impossible to obtain points lying on a straight line.[7,8]

The procedure which at this moment has the favor of many experimentalists has been proposed first by Burchard,[9] and later by Stockmayer and Fixman,[6] who give a theoretical justification for it. If one plots $[\eta]M^{-1/2}$ as a function of $M^{1/2}$ the points lie on a straight line. Its extrapolation to zero molecular weight gives the value of $[\eta]_\Theta M^{-1/2}$, where $[\eta]_\Theta M^{-1/2}$ is the ratio one would get if there were no long-distance interaction. On the other hand, the slope is a measure of long-distance interaction and can be related to the second virial coefficient or to the interaction parameter. The limitations of this method have been studied by different authors who have shown that it is reliable only if expansion factors are smaller than a certain value[8] and the molecular weight larger than about 10,000. A useful recent assessment of the method is found in the article by Tanaka, Imai, and Yamakawa.[8c]

In the case of solvent mixtures, since preferential adsorption can depend on molecular weight[10] in bad solvents, it can sometimes happen that in the low molecular weight range the curve departs from a straight line. This can be explained on the basis that the composition of the solvent in the neighborhood of the chain changes with molecular weight, and with it the quality of the solvent. It happens especially when one is working with mixtures which are very near Θ conditions and are limited to low molecular weights (<30,000). It has never been observed for molecular weights larger than 30,000.

In this paper we shall show some results obtained by the Burchard–Stockmayer–Fixman method used only to confirm and complete data obtained in pure Θ solvents. Since in every case the data obtained in this way were in good agreement with data obtained directly, we feel that its use for comparative purposes is justified, at least under our experimental conditions.

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[1] J. E. Hearst, *J. Polym. Sci., Part A-2*, **8**, 487 (1970).

[2] P. J. Flory, "Statistical Mechanics of Chain Molecules," Wiley, New York, N. Y., 1969.

[3] M. Kurata and W. H. Stockmayer, *Advan. Polym. Sci.*, **3**, 196 (1963).

[4] P. J. Flory and T. G. Fox, *J. Amer. Chem. Soc.*, **73**, 1904 (1951).

[5] M. Kurata, W. H. Stockmayer, and A. Roig, *J. Chem. Phys.*, **33**, 151 (1960).

[6] W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **No. 1**, 137 (1963).

[7] J. M. G. Cowie, *Polymer*, **7**, 487 (1966).

[8] (a) H. Inagaki, T. Miyamoto, and S. Ohta, *J. Phys. Chem.*, **70**, 3420 (1966); (b) G. C. Berry, *J. Chem. Phys.*, **46**, 1338 (1967); (c) G. Tanaka, S. Imai, and H. Yamakawa, *ibid.*, **52**, 2639 (1970).

[9] W. Burchard, *Makromol. Chem.*, **50**, 20 (1961).

[10] A. Dondos and H. Benoit, *ibid.*, **133**, 119 (1970).

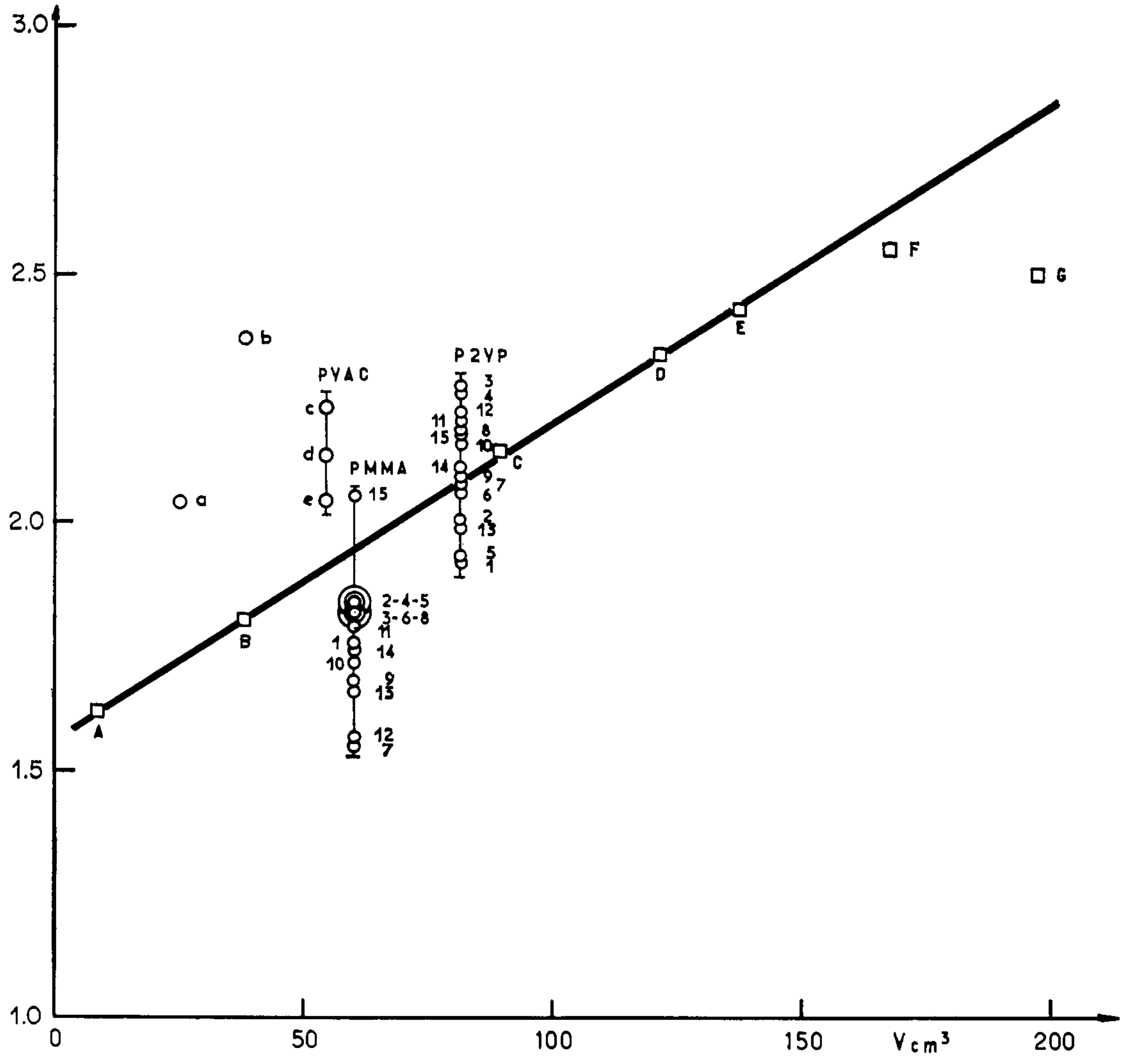

Figure 1. Values of the coefficient of steric hindrance σ as function of the molar volume of the side group for different vinyl polymers. The significance of the letters and the numbers is found in the text and tables.

As was said before, the hypothesis of the independence of unperturbed dimensions on the solvent has been proposed mainly in binary systems—one polymer and one solvent. We shall therefore first show results which are in contradiction to this hypothesis. In a second part we shall give results obtained in solvent mixtures since they show effects which are very similar to those observed in pure solvents, and they provide evidence which is useful in order to give an explanation of the observed facts.

Results

I. Case of Binary Mixtures (Polymer + Solvent). Even if our purpose were to show that unperturbed dimensions depend on solvent it would be unfair not to agree that in many cases the converse is true. If one looks carefully at the examples which have been given to justify these results, one sees that in the majority of cases they have been obtained on nonpolar polymers in nonpolar solvents.

Using these results, Kurata and Stockmayer plotted the steric factor σ, which is defined as the ratio between the actual unperturbed dimensions and the value calculated by neglecting steric hindrance and assuming free rotation, as a function of the volume of the side groups in vinyl polymers.[3] The points A, B, C, D, and E for polyethylene, polypropylene, polystyrene, poly(2,4-dimethylstyrene),[11] and polyvinylnaphthalene[12] lie on a curve but many other vinyl polymers having different side groups like nitrile, pyridine, or alcohol do *not* follow this line (Figure 1). Before discussing these points, we would like to remark that this line is a first approximation and does not take into account the flexibility of the substituent or its shape. It would be expected that a long-chain substituent would not introduce as much steric hindrance as a bulky one. For instance, unperturbed dimensions have been measured for polydiphenylpropene[13] and polyparacyclohexylstyrene[14] (points F and G in Figure 1). These two monomers have larger molar volumes, but the σ values for their polymers do not differ too much from the values obtained for polyvinylnaphthalene. These exceptions are easy to understand since, for these polymers, side groups are free to take a position in which they do not introduce much steric hindrance in the conformations of the backbone.

Points a and b correspond, respectively, to poly(vinyl alcohol) in water,[15,16] and to polyacrylonitrile in dimethylformamide.[17] They are not on the straight line corresponding to nonpolar polymers. We shall now cite some examples

[11] C. S. Hsia Chen and R. F. Stamm, *J. Polym. Sci.*, **58**, 369 (1962).

[12] L. A. Utracki and R. Simha, *Makromol. Chem.*, **117**, 94 (1968).

[13] A. Dondos, *Eur. Polym. J.*, in press.

[14] H. Kuwahara, K. Ogino, M. Konuma, N. Iida, and M. Kaneko, *J. Polym. Sci., Part A-2*, **4**, 173 (1966).

[15] P. J. Flory and F. S. Leutner, *ibid.*, **3**, 880 (1948).

[16] H. A. Dieu, *ibid.*, **12**, 417 (1954).

[17] K. Kamide, K. Fujii, and H. Kobayashi, *Makromol. Chem.*, **117**, 190 (1968).

TABLE I
UNPERTURBED DIMENSIONS OF PMM IN DIFFERENT PURE SOLVENTS

No.	Solvent	Dielectric constant (ϵ)	T, °C	$K_\Theta \times 10^2$	σ
1	Benzene	2.274	25	4.5	1.76
2	*p*-Xylene	2.400	25	5.1	1.84
3	*p*-Xylene	2.400	75	5.0	1.82
4	$CHCl_3$	4.90	0	5.1	1.84
5	$CHCl_3$	4.90	25	5.1	1.84
6	THF	7.20	25	5.0	1.82
7	Cyclohexanol	15.00	77.6	3.1	1.55[a]
8	Acetone	21.45	20	4.9	1.82
9	Acetonitrile	38.8	30	3.9	1.68[b]
10	Acetonitrile	38.8	45	4.2	1.72[b]
11	Acetonitrile	38.8	65	4.7	1.79[b]
12	Nitromethane	39.4	1.5	3.3	1.56
13	Nitromethane	39.4	25	3.75	1.66
14	Nitromethane	39.4	59	4.3	1.74
15	DMF	36	25	7.0	2.05

[a] See ref 19. [b] See ref 18.

TABLE II
UNPERTURBED DIMENSIONS OF P2VP IN DIFFERENT PURE SOLVENTS

No.	Solvent	ϵ	T, °C	$K_\Theta \times 10^2$	σ
1	Benzene	2.27	31	5.3	1.92
2	Benzene	2.27	60	6.15	2.00
3	$CHCl_3$	4.90	0	8.8	2.27
4	$CHCl_3$	4.90	25	8.75	2.26
5	THF	7.20	30	5.4	1.93
6	THF	7.20	50	6.6	2.06
7	2-Propanol	13.8	25	6.75	2.07
8	2-Propanol	13.8	65	7.9	2.19
9	Cyclohexanol	15.0	40	6.9	2.09
10	Cyclohexanol	15.0	80	7.7	2.16
11	Ethanol	25.7	−1.5	8.1	2.20
12	Ethanol	25.7	25	8.3	2.22
13	Methanol	32.6	0	6.0	1.99
14	Methanol	32.6	25	7.1	2.11
15	Methanol	32.6	40	7.8	2.17

showing that for such polymers which behave irregularly σ depends also on solvent.

Case of Poly(methyl methacrylate). This polymer has been studied in many different solvents and the results are quoted in Table I, where we have shown the temperature of the experiments, the value of $K_\Theta = [\eta]_\Theta M^{-1/2}$, and the parameter σ. We have also given the dielectric constant of the solvent in order to see if there is a correlation between ϵ and σ. Among these solvents, acetonitrile[18] and cyclohexanol[19] are Θ solvents, *p*-xylene is at 25° slightly below the Θ point, and the others are good solvents. If one accepts the validity of these results, one sees that K_Θ has values between 3.1×10^{-2} and 7.0×10^{-2} g/cm^3, a range which lies certainly outside the domain of experimental errors. This family of points has been put on Figure 1. Qualitatively speaking the larger the dielectric constant, the lower is the K_Θ value, but this parameter does not seem to give the key for the explanation of the results.

Case of Poly(2-vinylpyridine). As for poly(methyl methacrylate), we have shown in Table II K_Θ and σ values for different solvents at different temperatures. Since some authors claim[20,21] that there exists a configurational change around 25° we have excluded from this table all values below 25°. Therefore we do not have Θ solvents in this range of temperature. In this case K_Θ varies from 5.3×10^{-2} in benzene to 8.8×10^{-2} in chloroform.

We have also three values for poly(vinyl acetate); they have been obtained in chloroform (point c, Figure 1), methanol (point d, Figure 1),[22] and in two Θ solvents (point e, Figure 1)—ethyl *n*-butyl ketone and ethyl isoamyl ketone.[23] One can also quote results obtained by Koleske and Lundberg[24] for poly(ϵ-caprolactone), who show a K_Θ value in DMF larger than in benzene.

These results show that it is quite general to find values depending on the solvent and that this behavior is not limited to the examples we have shown in Tables I and II. They show also that, in order to have measurable effects, one has to deal with polymers having either polar side groups or side groups able to form hydrogen bonds easily.

All these results can be explained at least qualitatively if one introduces the three following possibilities.

(a) If the polymer can form a strong association with the solvent, making hydrogen bonds, or if there are strong dipole associations, one can treat the complex (side group–solvent) as a large side chain; this will introduce a larger apparent molar volume of the monomer and therefore will increase K_Θ and σ.

(b) If the solvent is making autoassociations, as are well known for methanol and nitromethane, it has already been shown that K_Θ values are lower than in nonassociating solvents. A qualitative explanation of this phenomenon is not very easy. We could venture to say that internal rings involving two monomeric units and a few solvent molecules are formed, preventing the expansion of the chain and therefore diminishing its K_Θ value.

(c) In the case of polar polymers, one can also imagine that, due to the dipole–dipole interactions, conformations with strong coupling between dipoles could be preferred, introducing a contraction of the chain.

We shall try now with the help of these three hypotheses to explain at least qualitatively the observed facts. We have suggested[21] that association with solvent, either by hydrogen bond or dipole–dipole interactions, can increase the apparent molar volume of the side group, thus K_Θ and σ.

This type of explanation can be applied for instance to P2VP in chloroform and ethanol. In both solvents, it has been found that the monomer can form hydrogen bonds.[25,26] Dimethylformamide can also be bound to acrylonitrile and ϵ-caprolactone, thus increasing the size of the molecule. Therefore, as soon as it is possible to find strong interactions between polymer and solvent, one can predict that one will get a σ value above average.

As can be seen in Figure 1, there are also σ values below the average given by the straight line obtained for nonpolar polymers. We have said that this could happen if we have strongly associating solvents like methanol, nitromethane, and acetonitrile interacting with the polymer.[27] For instance,

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[18] T. G. Fox, *Polymer*, 3, 111 (1962).

[19] D. Froelich, Thesis, Strasbourg, 1966.

[20] G. Noël and L. Monnerie, *J. Chim. Phys. Physicochim. Biol.*, **65**, 2089 (1968).

[21] A. Dondos, *Makromol. Chem.*, **135**, 181 (1970).

[22] M. Ueda and K. Kajitani, *ibid.*, **108**, 138 (1967).

[23] M. Matsumoto and Y. Ohyamagi, *J. Polym. Sci.*, **50**, S1 (1961).

[24] J. V. Koleske and R. D. Lundberg, *ibid.*, *Part A-2*, **7**, 897 (1969).

[25] M. Tamres, S. Searles, E. M. Leighly, and D. W. Mohrman, *J. Amer. Chem. Soc.*, **76**, 3983 (1954).

[26] S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951).

[27] A. Dondos and H. Benoit, *Makromol. Chem.*, **129**, 35 (1969).

TABLE III
UNPERTURBED DIMENSIONS OF P2VP AND PS IN MIXED SOLVENTS AT 25°

Polymer	Mixed solvents	$K_{\Theta_1} \times 10^2$	$K_{\Theta_2} \times 10^2$	$K_\Theta \times 10^2$	$100(X-1)$	ΔG^E, cal mol^{-1}	Ref
P2VP	$CHCl_3$–dioxane	8.75	7.1	6.4	−20	−160	*a*
P2VP	$CHCl_3$–benzene	8.75	7.1	7.05	−11	−45	*b*
P2VP	$CHCl_3$–ethanol	8.75	8.3	10.3	+21	+137	*c*
P2VP	Benzene–ethanol	7.1	8.3	10.7	+39	+220	*d*
P2VP	Benzene–methanol	7.1	7.1	10.1	+42	+258	*e*
P2VP	Benzene–propanol-2	7.1	6.7	9.2	+32	+200	*g*
PS	$CHCl_3$–dioxane	8.0	7.9	6.3	−21	−160	*a*
PS	Benzene–cyclohexane	7.9	8.1	9.4	+18	+75	*f*

[a] M. L. McGlashan and R. P. Rastogi, *Trans. Faraday Soc.*, **54,** 496 (1958). [b] J. A. Barker and F. Smith, *J. Chem. Phys.*, **22,** 375 (1954). [c] G. Scatchard and C. L. Raymond, *J. Amer. Chem. Soc.*, **60,** 1278 (1938). [d] J. Brown, W. Fock, and F. Smith, *Aust. J. Chem.*, **9,** 364 (1956). [e] G. M. Wilson, *J. Amer. Chem. Soc.*, **86,** 127 (1964). [f] G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.*, **43,** 119 (1939). [g] H. H. Lewis, R. L. Schmidt, and H. L. Clever, *ibid.*, **74,** 4377 (1970).

point 12 has been obtained for PMMA in nitromethane and point 13 for P2VP in methanol.

Another case where it is possible to obtain small values of K_Θ is the case where the polymer is polar and dissolved in a nonpolar solvent, *i.e.*, a solvent with low dielectric constant. Examples of this type are furnished by P2VP or PMMA in benzene, points 1 on Tables I and II (Figure 1).

II. Case of Ternary Mixtures (Polymer + Two Solvents). It would be important to be able to give a theroetical basis to the experimental evidence we have collected in this paper. At first sight, this seems to be very difficult since all our qualitative explanations are based on specific interactions like hydrogen bonds or dipole–dipole coupling and there is very little hope that these facts could be put into strict thermodynamic language.

Before entering into this discussion it is important to review some results obtained for K_Θ values in the case of solvent mixtures. We have shown previously[28,29] that in this case, one can observe large changes in K_Θ. More precisely, we have introduced the quantity $X = K_\Theta/(K_{\Theta_1}\varphi_1 + K_{\Theta_2}\varphi_2)$, where K_{Θ_1} and K_{Θ_2} are the observed K_Θ values in solvents 1 and 2, φ_1 and φ_2 are the volume fractions of solvents 1 and 2, and K_Θ is the observed value in the mixture. We have shown[29] studying P2VP and PS in different solvent mixtures that the sign of X was the same as the sign of ΔG^E, the free enthalpy of mixing of both solvents. If ΔG^E is positive, we observe a K_Θ value which is larger than could be obtained from the addition rule, while if ΔG^E is negative, ΔK_Θ also is negative.

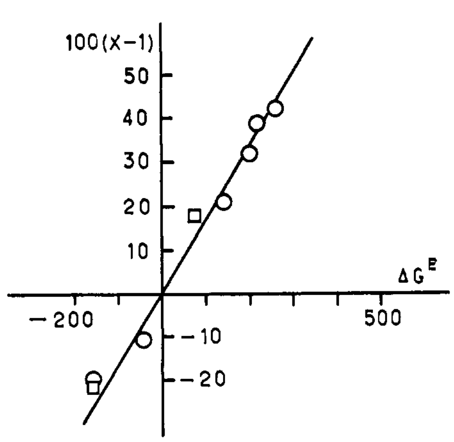

Figure 2. Relation between the increment of K_Θ in mixtures and the excess free enthalpy of mixing of the solvents.

It can be shown that this qualitative agreement can be put in a more quantitative form. Using the $100(X - 1)$ values for $\varphi_1 = \varphi_2 = 0.5$ and the ΔG^E values found in the literature for the same composition, one finds results which are collected in Table III. There seems to be a strong correlation between ΔG^E and $X - 1$. This is better explained when one looks at Figure 2 where we have plotted $100(X - 1)$ as function of ΔG^E. All points, even those corresponding to two different polymers, lie on a curve which is almost a straight line. This indicates that, contrary to what might be expected, it is possible to explain, in the case of mixed solvents, the variation of unperturbed dimensions using only thermodynamic arguments.

As we said in the introduction, the basic assumption in interpreting experimental results for polymer solutions has been usually that the Θ conformation of chains is due only to intramolecular forces and that these forces are not affected by the nature of the solvent. We shall try to show that this behavior could not be as general as has usually been assumed; for this purpose, and in order to avoid difficulties due to long-distance interactions, let us look at the thermodynamic properties of a small volume including solvent and a small part of the chain. It is practically always assumed that the chain has an average internal energy due to interactions between neighboring elements and a mean-square end-to-end distance which are independent of solvent. Let us now assume that the chain can have different rigidities or different unperturbed dimensions. For these different conformations the number of contacts between the polymer segments and the solvents will be different. Thus, in order to find the real unperturbed dimensions in this given solvent one has to write that the free enthalpy of this volume element is a minimum. This calculation is not easy, since in order to have a realistic model one should know how the average interactions between polymer and solvent change with unperturbed dimensions. Even if one is not able to write practical equations describing this phenomenon its existence seems to be very plausible. In fact, the formal statistical-mechanical theory of such effects has been given by Lifson and Oppenheim,[30] but it is not easy to apply. If one follows Flory's argument, one can write for the free enthalpy of mixing of a small part of the chain made with x segments (haivng the same volume as the solvent molecules) and n_1 molecules of solvent

$$\Delta G = Z\Delta W_{12}\frac{n_1x}{n_1 + x}$$

In this expression Z is the lattice coordination number and

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(28) A. Dondos and H. Benoit, *Eur. Polym. J.*, **4,** 561 (1968).
(29) A. Dondos and H. Benoit, *ibid.*, **6,** 1439 (1970).

(30) S. Lifson and I. Oppenheim, *J. Chem. Phys.*, **33,** 109 (1960).

ΔW_{12} the interaction free energy change associated with the formation of a contact between polymer segment and solvent. In classical theory it is assumed that Z and ΔW_{12} are constants. Now if we assume that they could depend on the average chain conformation, *i.e.*, on the unperturbed dimensions, one has to write, in order to find the equilibrium value, that ΔG is minimum, and it is not absolutely necessary that this minimum is always obtained for the same value of $\overline{r_0^2}$.

This type of argument could be extended to solvent mixtures very easily. Changes in average conformation can change the interactions polymer–solvent 1, –solvent 2 and the number of contacts between solvent 1 and solvent 2. There are many more possibilities in this case than in the case of pure solvents; it is therefore not surprising that for these solvent mixtures one usually obtains larger effects.

At first sight, one does not see any reason to try to put the explanation of the observed phenomena in thermodynamic terms rather than to use a molecular description of the intermolecular forces of the type we have given at the beginning of this paper. But this point of view is strongly supported by our results on solvent mixtures. In this case we have shown that it is not only the interactions between solvent and polymer (χ_{13} and χ_{23}) which are responsible for the changes in K_Θ but also the interaction between solvent 1 and solvent 2. This way of presenting the results eliminates the effect of each solvent and shows the importance of the thermodynamic properties of the solvent mixture, associating ΔK_Θ to ΔG^E. The fact that we obtain the same function for PS and P2VP is somewhat surprising. It means that ZW_{12} is the same function of the unperturbed dimensions for these two polymers and that this quantity does not depend on the nature of the side groups. Since the geometry of two chains is very similar, this can perhaps be understood. It would be interesting to check if this relation can be generalized to other polymers.

Conclusion

In this paper we have tried to give a systematic review of K_Θ values for different polymers. It seems that this quantity is not always independent of the solvent but, especially when one is dealing with polar polymers or polar solvent, there is an influence of the polymer–solvent interaction on its value.

We have tried to give a qualitative explanation of these facts. At first sight, it seems to be difficult to correlate these results with classical thermodynamic properties of solutions, since one has to take into account specific interactions between polymer and solvent. But in the case of mixed solvents there seems to be a correlation between these effects and the free enthalpy of mixing of the solvents, indicating that this effect is not only due to interactions between polymer and solvent but also to the interactions between solvent molecules.

Recently, Vrij[31] has proposed to take into consideration interfacial energies between the coil and the surrounding solvent. This kind of argument would perhaps also explain our results, but more experimental data are needed in order to confirm the validity of this theory.

(31) A. Vrij, *J. Polym. Sci., Part A*-2, 7, 1627 (1969).

Conformational Transitions of Poly(L-tyrosine) in Mixed Water–Ethanol Solvents[1]

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ABSTRACT: The conformation of poly(L-tyrosine) (PT) was investigated in mixed water–ethanol solvents as a function of the degree of ionization, the solvent composition, and the polymer concentration by means of ORD, ir, and potentiometric titration techniques. While a slow transition from coil to antiparallel β conformation is observed in water and in the prevailing aqueous region, the α helix is the only stable form for ethanol concentrations greater than 45%. It was found that in the region between 20 and 40% PT may assume either the α-helical or the β conformation, depending on kinetic factors. The effect of concentration, as well as the role of solvent on the conformational states of PT, is discussed and some related thermodynamic data are reported.

ORD and CD techniques alone cannot solve the problem of determining the conformation of poly(α-amino acids) bearing optically active chromophores in the side chain: typically, the CD and ORD spectra of the ordered conformation of poly(L-tyrosine) (PT) have been described by Fasman[2a] and Beychok,[2b] but their interpretation of the experimental curves in terms of the α-helical conformation was largely hypothetical, mainly because there is an extensive overlapping between peptide and side chain bands near 224 mμ.

On the other hand, a recent theoretical approach by Pao[3] was not successful in fitting the gross features of the dispersion curves. Recently,[4] we investigated the charge-induced conformational transition of PT in aqueous solution by means of potentiometric titrations, sedimentation velocity experiments, and infrared spectroscopy. An aggregation process was detected around the pH value at which the transition occurs and the ordered conformation was recognized as possessing an antiparallel β conformation. Further work was directly concerned with the factors responsible for the

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(2) (a) G. Fasman, E. Bodenheimer, and C. Lindblow, *Biochemistry*, 3, 1665 (1964); (b) S. Beychok and G. Fasman, *ibid.*, 3, 1675 (1964).

(3) Y. H. Pao, L. Longworth, and L. Kornegay, *Biopolymers*, 3, 519 (1965).

(4) E. Patrone, G. Conio, and S. Brighetti, *ibid.*, 9, 897 (1970).