Notes on Differential Refractometry and Light Scattering of Polymer or Copolymer Solutions in Mixed Solvents*

P. KRATOCHVÍL and Z. TUZAR

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6

This paper is a review of some conclusions drawn from a systematic study of the refractive index increments and light scattering of dilute polymer and copolymer solutions in mixed solvents. The following problems are discussed: 1. Differential refractometric determination of the coefficient of selective sorption. 2. Selective sorption in cosolvent mixtures. 3. Differential refractometric method of determination of the composition of copolymers having isorefractive components. 4. Advantages of mixed solvents in the determination of the heterogeneity of the chemical composition of copolymers. 5. Determination of the heterogeneity of the chemical composition of copolymers with isorefractive components.

At the Institute of Macromolecular Chemistry in Prague, systematic investigations have been carried out for several years, devoted to the refractive index increments and light scattering in diluted polymer and copolymer solutions in mixed solvents. This paper is a survey of some of the results of a rather general validity.

Coefficients of selective sorption

As a rule, an increased affinity of the polymer to some components of multicomponent solvents is characterized quantitatively by means of the so-called coefficient of selective sorption, γ [1]. In most cases, the values of γ are measured by the light-scattering method, by comparing the true molecular weight, M_w (obtained by measuring the light scattering in a one-component solvent), with the apparent molecular weight, M_w^*, obtained by measuring the light scattering from a solution in a mixed solvent. For a binary solvent, the relationship is valid

$$\gamma = \frac{(dn/dc)_u[(M_w^*/M_w)^{1/2} - 1]}{dn/du_1}, \tag{1}$$

where $(dn/dc)_u$ is the refractive index increment of a polymer in a mixed solvent at fixed concentrations of both low-molecular-weight components in both the solution and solvent, and dn/du_1 is the refractive index increment of the solvent component 1 with respect to the binary solvent of a given composition. The concentration of the solvent components is represented in the volume fractions, u.

We have shown [2] that the coefficient of selective sorption can also be determined without using the light-scattering method, only on the basis of differential refractometric measurements. In addition to the conventional value of the refractive index increment of the polymer, $(dn/dc)_u$, it is also necessary to determine the refractive index increment under conditions when all the low-molecular-weight components have the same chemical potentials in both the solution and solvent, $i.e.$ $(dn/dc)_\mu$; the condition of equality of the chemical potentials can be fulfilled with relative ease by establishing dialysis equilibrium between the polymer solution and the solvent. The value of γ for a binary solvent is then determined by the relationship

$$\gamma = \frac{(dn/dc)_\mu - (dn/dc)_u}{dn/du_1} \ . \eqno(2)$$

We compared the values of γ determined by both methods for a number of systems (e.g., poly(methyl methacrylate)—2,2,3,3-tetrafluoropropanol—water, poly(ethylene glycol monomethacrylate)—propanol—water [2], etc.), and found a good agreement in all cases. We believe the differential refractometric method to be generally a better one, since it is unaffected by the presence of supermolecular formations in the solution. It is known (cf. e.g. [3]) that a series of important polymers does not form perfectly molecular solutions, and the presence of aggregates complicates considerably (and in some cases even makes impossible) the determination of M_w by the light-scattering method. In these cases, the light-scattering method for the determination of γ fails, whereas the differential refractometric method yields correct results.

Some time later the differential refractometric method for the determination of γ was also suggested by Japanese authors [4], who verified it on the solutions of poly-α-methylstyrene in two binary solvents.

Cosolvent mixtures

In some cases, a mixture of two precipitants is a thermodynamically very good solvent for the polymer. These so-called cosolvent mixtures are characterized by an interesting selective sorption behaviour [2]. In a cosolvent mixture, one component or the other is sorbed selectively on the polymer (Fig. 1), according to the composition of the mixture. (A negative value of γ related to a certain component of the solvent means that, at a given solvent composition, its second component is sorbed selectively on the polymer.) The fact that a mixture of two precipitating agents is a good solvent is illustrated also by the observation that both intrinsic viscosity, $[\eta]$, and the second virial coefficient, A_2, pass through a clear maximum in dependence on the composition of the mixture. It seems worth noticing that the coefficient of selective sorption, γ, is of zero value (i.e. the polymer has the same affinity to both components of the mixture, and the composition of the solvate shell of the macromolecules is the same as the composition of the solvent in the space between macromolecules) at the same composition of the mixture at which both $[\eta]$ and A_2 attain maximum, i.e. in a mixture vhich is the thermodynamically best solvent for the polymer. A conclusion can be derived, therefore, that at a given composition of the cosolvent mixture, the particular component sorbed on the polymer is the one which changes the composition of the mixture in the domain
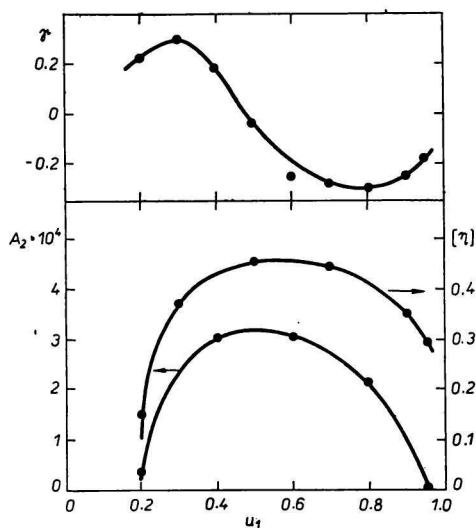
Fig. 1. Coefficient of selective sorption of propanol, γ, intrinsic viscosity, $[\eta]$ in dl/g, and the second virial coefficient, A_2 in ml g^{-2} mole, in dependence on the volume fraction of propanol, u_1, in a cosolvent mixture for the system poly(ethylene glycol monomethacrylate)—propanol—water.

of the polymer molecules in the direction of a thermodynamically most effective mixture. In other words, the polymer molecules exhibit a tendency of being surrounded by a thermodynamically most efficient solvent.

Determination of the copolymer composition

The copolymer composition is frequently determined by means of differential refractometry, because the refractive index increment of a copolymer is usually a linear function of its composition [5, 6]. For this method to be applied, the refractive indices (and thus also the refractive index increments) of both components of a binary copolymer must differ sufficiently from each other. The method fails, of course, in the case of copolymers having components with close or identical refractive indices.

The use of mixed solvents, however, allows in principle the differential refractometric determination of the composition even of such copolymers whose components have identical refractive indices. It is necessary to find such a mixed solvent whose individual components are sorbed selectively to various extents on the individual components of the copolymer, and have refractive indices differing from each other as much as possible. In this case, the refractive index increment of the copolymer measured at fixed chemical potentials of the low-molecular-weight components both in solution and solvent, $(dn/dc)_\mu$, is again, as a rule, a linear function of the copolymer composition [7]. (The value $(dn/dc)_\mu$ can be looked upon as a refractive index increment of a complex formed by a polymer or copolymer and the selectively sorbed solvent; the composition of this complex, and thus its refractive index increment obviously depend on the composition of the copolymer.)

The method was checked [7] on copolymers of methyl methacrylate with ethylene glycol monomethacrylate. The refractive indices of the copolymer components are so close that the values of the conventional refractive index increment $(dn/dc)_u$ differ by approximately 0.01 ml/g. The determination of the copolymer composition from the value of $(dn/dc)_u$ is therefore not possible, since the experimental error is
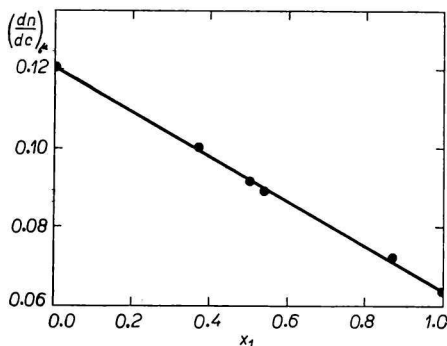

Fig. 2. Dependence of the refractive index increment, $(dn/dc)_u$, of the copolymers of ethylene glycol monomethacrylate and methyl methacrylate on their composition in a mixed solvent toluene + 62 volume % isopropanol.
x_1 is the weight fraction of ethylene glycol monomethacrylate in the copolymer.

Fig. 3. Dependence of the refractive index increment, $(dn/dc)_u$, of polystyrene (1) and poly(methyl methacrylate) (2) on the composition of the binary solvent α-bromonaphthalene—butanone.
u_1 is the volume fraction of α-bromonaphthalene.

usually $\pm$ 0.001 ml/g. However, we found some mixed solvents in which the $(dn/dc)_\mu$ values of the copolymer components differ by as much as 0.17 ml/g, which is more than sufficient for achieving a satisfactory accuracy of the determination of the copolymer composition. Fig. 2 shows that the value $(dn/dc)_\mu$ of the copolymers of methyl methacrylate and ethylene glycol monomethacrylate in the mixture toluene + 62 volume % isopropanol is a linear function of the copolymer composition, and can therefore be used in its determination.

Heterogeneity of the chemical composition of copolymers

By measuring the light scattering from solutions of binary copolymers in at least three solvents differing as much as possible by their refractive indices we obtain, in addition to the correct molecular weight of the copolymer, also two more parameters (usually designated as P and Q), which characterize the heterogeneity of the chemical composition of the copolymer [5]. (The term "heterogeneity of the chemical composition of the copolymer" implies that the composition of all the individual copolymer molecules is not the same.)
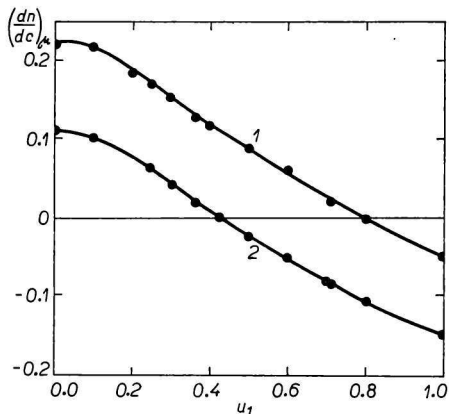
We have shown [8, 9] that the set of values, M_w, P, and Q, can be determined with most accuracy if it is true for two of the three solvents that the refractive index increment of the copolymer component A (or B) is zero, whereas the refractive index increment of the component B (or A) has the highest possible absolute value. To meet all the requirements imposed upon appropriate solvents is often not possible while using one-component solvents. On the contrary, a properly chosen mixed solvent makes possible a continuous variation of the refractive index increments of the copolymer components by changing the composition of the solvent. Simple relationships, derived for the light scattering from the copolymer solutions in one-component solvents [5], are also valid for mixed solvents [8, 9], if instead of the usual values $(dn/dc)_u$ the values $(dn/dc)_\mu$ are used.

We have found mixed solvents allowing the characterization of the following copolymers under optimum conditions: styrene—methyl methacrylate [10], styrene—butadiene [10], methyl methacrylate—ethylene glycol monomethacrylate [9]. For instance, in the solvent system α-bromonaphthalene—cyclohexane there exist two compositions at which the value $(dn/dc)_\mu$ is zero for either polystyrene or poly(methyl methacrylate), whereas the refractive index increment of the second copolymer component has a high absolute value (Fig. 3); this corresponds to the optimum conditions for the determination of the heterogeneity of the copolymer chemical composition.

Heterogeneity of the chemical composition of copolymers consisting of isorefractive components

Similarly to the determination of the copolymer composition, the determination of the heterogeneity of their chemical composition by the light-scattering method using one-component solvents is also possible in those cases only when both copolymer components are sufficiently different as to their refractive indices. In the case of copolymers with isorefractive components, the light-scattering measurements from solutions in one-component solvents do not allow us to obtain any information about the heterogeneity of chemical composition.

In this case, too, the use of mixed solvents allows in principle the characterization of the heterogeneity of chemical composition [9]. Again, we must find a solvent system in which there is a sufficient difference between the $(dn/dc)_\mu$ values of the copolymer components, owing to various affinities of the individual copolymer components to the individual solvent components. It is advisable to choose such solvent systems which at the same time provide optimum measuring conditions in accordance with what has been said above.

An example of a copolymer having components whose refractive indices differ but slightly can be seen in the above-mentioned copolymer of methyl methacrylate and ethylene glycol monomethacrylate. In the case of the solvent system methylcellosolve—α-bromonaphthalene the conventional values $(dn/dc)_u$ of both copolymer components at all the investigated solvent compositions differ very little (Fig. 4). However, owing to the selective sorption of α-bromonaphthalene on poly(methyl methacrylate) and a very strong selective sorption of methylcellosolve on poly(ethylene glycol monomethacrylate), the $(dn/dc)_\mu$ values (determined after the establishment of the dialysis equilibrium) of both components of the copolymer differ so much that it is possible to determine the heterogeneity parameters of the copolymer chemical composition with the same accuracy as in the case of copoly-
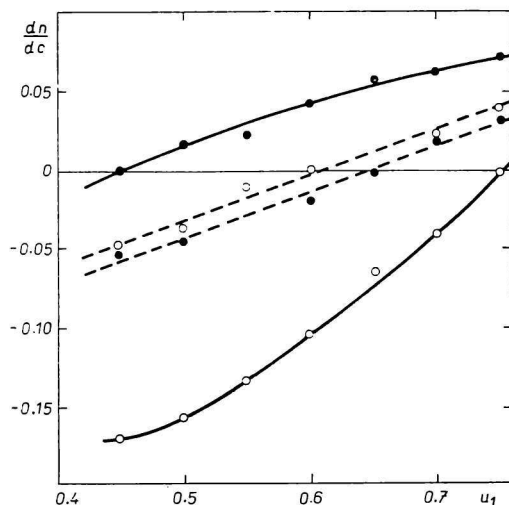
Fig. 4. Dependence of the refractive index increment of poly(ethylene glycol mono-methacrylate) ($\circ$) and poly(methyl methacrylate) ($\bullet$) on the composition of the binary solvent methylcellosolve—α-bromonaphthalene.

u_1 is the volume fraction of methylcellosolve; - - - - $(dn/dc)_u$ values, —— $(dn/dc)_\mu$ values.

mers whose components have largely different refractive indices. It can also be seen from Fig. 4 that the solvent system methylcellosolve—α-bromonaphthalene at two components' ratios meets the requirements of the optimum measuring conditions (*i.e.* $(dn/dc)_\mu = 0$ either for poly(methyl methacrylate) or for poly-(ethylene glycol monomethacrylate), whereas $|(dn/dc)_\mu|$ is large for the other component).

References

1. Ewart R. H., Roe C. D., Debye P., McCartney J. R., *J. Chem. Phys.* **14**, 1687 (1946).
2. Tuzar Z., Kratochvíl P., *Collect. Czech. Chem. Commun.* **32**, 3358 (1967).
3. Kratochvíl P., *Collect. Czech. Chem. Commun.* **30**, 1119 (1965).
4. Okita K., Teramoto A., Kawahara K., Fujita H., *J. Phys. Chem.* **72**, 278 (1968).
5. Bushuk W., Benoît H., *Can. J. Chem.* **36**, 1616 (1958).
6. Kinsinger J. B., Bartlett J. S., Rauscher W. H., *J. Appl. Polym. Sci.* **6**, 529 (1962).
7. Tuzar Z., Kratochvíl P., *Polym. Lett.* **7**, 825 (1969).
8. Kratochvíl P., Tuzar Z., *Angew. Chem.* **82**, 557 (1970).
9. Tuzar Z., Kratochvíl P., Straková D., *Eur. Polym. J.* **6**, 1113 (1970).
10. Kratochvíl P., Sedláček B., Straková D., Tuzar Z., *IUPAC International Symposium on Macromolecules*, Leiden, 1970, Book of Abstracts I, p. 399.

Translated by L. Kopecká