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Extremely High Refractive Index Increments in Polymer/Mixed Solvent Systems

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ABSTRACT: Polymer/mixed solvent systems were sought in which the highest possible refractive index increments could be obtained, measured after the establishment of the dialysis equilibrium between solution and solvent. The refractive index increments, determined in this way, of various polymers (polypyrrolidone, polycaprolactam, polylaurolactam, poly(methyl methacrylate), and poly(hydroxyethyl methacrylate)) in the *m*-cresol/*n*-heptane mixture attain values up to 0.8 mL/g. The highest determined coefficient of selective sorption of the better solvent (*m*-cresol) on a polymer is 4.7 mL/g.

The intensity of light scattered from polymer molecules in a dilute solution is proportional to the square of the refractive index increment, $dn/dc \equiv \nu$, of the polymer in a given solvent. In the evaluation of light-scattering data, ν is comprised in the calculations of molecular weight, and/or of other parameters (e.g., of the second virial coefficient). The refractive index increment of a polymer, which in a one-component solvent is in the first approximation proportional to the difference of the refractive indices of polymer and solvent, is determined from the difference of the refractive indices of polymer solution and solvent (measured in practice with, e.g., a differential refractometer).

The ν values of polymer/solvent systems vary typically[1] between 0.1 and 0.2 mL/g. Higher values were observed only exceptionally, with polymers exhibiting an extremely high refractive index (e.g., ν = 0.3 mL/g in the system aromatic polyamide/sulfuric acid[2]). To obtain a sufficient excess scattering intensity with samples of very low molecular weights (e.g., oligomers), it is crucial to use a system with the highest possible refractive index increment. Some potentialities in this respect seem to be offered by the application of mixed solvents.[3]

The excess scattering intensity due to a polymer dissolved in a mixed solvent the components of which differ in both the refractive index and in the affinity to the polymer does not correspond to the refractive index increment measured in the conventional way, i.e., at the same composition of the mixed solvent both in polymer solution and in solvent (ν_c). The intensity of scattered light is controlled by the refractive index increment modified by the preferential sorption of one of the solvent components on the polymer. This value, ν_μ, can be obtained by measuring the difference of the refractive indices of polymer solution and solvent at fixed chemical potentials of all the solvent components in solution and solvent. In practice, this requirement can be met satisfactorily by the establishment of the dialysis equilibrium between polymer solution and solvent.[4] An essential increase in ν_μ compared with ν_c can be achieved by choosing such solvent system from which the component having the higher refractive index is preferentially sorbed by the polymer (provided the refractive index of the polymer exceeds that of the solvent, which is mostly the case). Thus, for instance, in the system poly(methyl methacrylate)/toluene(vol fraction 0.42)/methanol,[3] $\nu_c = 0.094$ and $\nu_\mu = 0.152$, or in the system polylaurolactam/*m*-cresol(vol fraction 0.35)/2,2,3,3-tetrafluoropropanol[5] $\nu_c = 0.100$ and $\nu_\mu = 0.285$.

The objective of this study has been to examine the feasibility of obtaining the highest possible refractive index increments of polymers, ν_μ, in multicomponent solvents.

Experimental Section

The fractions of polycaprolactam ($M_w = 74 \times 10^3$), polypyrrolidone ($M_w = 84 \times 10^3$), polylaurolactam ($M_w = 61 \times 10^3$), poly(methyl methacrylate) ($M_w = 1 \times 10^5$), and poly(hydroxyethyl methacrylate) ($M_w = 3.4 \times 10^5$) have been characterized earlier.[5-9] *m*-Cresol and *n*-heptane were reagent grade, rectified before use; purity, checked chromatographically, was better than 99.8%.

Each ν was determined by measuring four polymer solutions having concentrations c from 1×10^{-3} to 6×10^{-3} g/mL. The techniques of dialysis and refractometric measurements have been described elsewhere.[8]

The coefficients of selective sorption of *m*-cresol by the polymer, γ, were calculated using the relation $\gamma = (\nu_\mu - \nu_c)/\nu_\varphi$; $\nu_\varphi = 0.155$ is the refractive index increment of *m*-cresol in *n*-heptane in the absence of the polymer in a mixture where φ is the volume fraction of *m*-cresol. For this system ν_φ is a constant in the whole range of φ.

Results and Discussion

In the search for solvent systems in which the polymer would exhibit the highest ν_μ, we tried to meet the following criteria:

(1) Components of the mixed solvent should differ from each other as much as possible in their refractive indices in order to obtain high ν_φ.

(2) The solvent component with the higher refractive index should be a very good solvent of the given polymer, while that

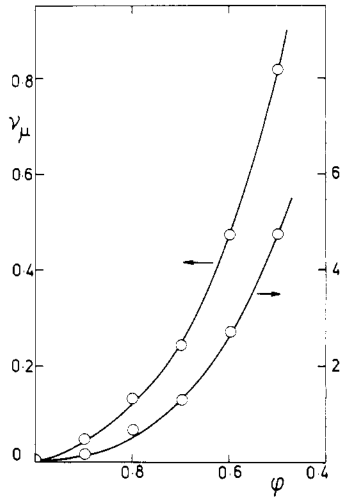

Figure 1. Dependence of the refractive index increment ν_μ (mL/g) and of the coefficient of selective sorption γ (mL/g) of *m*-cresol for polycaprolactam on the volume fraction, φ, of *m*-cresol in the mixture *m*-cresol/*n*-heptane at 25 °C.

having the lower refractive index (which must be lower than that of the polymer) should be an effective precipitant of the polymer in order to yield a large coefficient of selective sorption.

(3) Affinity of the better solvent to the particular polymer should be higher than its affinity to the second solvent component. It has been assumed that this condition is best met with such solvent mixtures which at a given temperature and composition are not far from phase separation.

A solvent system satisfying the above criteria was found in the mixture *m*-cresol/*n*-heptane, which could be used for a number of polymers, and especially for polyamides. The difference of the refractive indices of both components is large ($\nu_\varphi = 0.155$), and a mixture with $\varphi = 0.5$, in which the majority of polymers under study are still readily soluble at room temperature and common concentrations (up to 1%), undergoes itself phase separation at ca −4 °C.

The refractive index increment ν_μ and the coefficient of selective sorption of *m*-cresol γ increase for the polymers investigated with increasing content of *n*-heptane in the mixture (Table I), far beyond the values reported up to now. With solutions of polypyrrolidone and polycaprolactam in mixtures with a higher content of *n*-heptane ($\varphi = 0.4$ and 0.5), a bluish opalescence stable in time was observed, similar to that exhibited by, e.g., a solvent mixture with $\varphi = 0.5$ without polymer at ~0 °C, i.e., several degrees above the phase-separation temperature (−4 °C). A tentative explanation of the bluish opalescence of solutions may consist in that the polymer coil swollen with the preferentially sorbed *m*-cresol (at $\varphi = 0.5$ by ca. fourfold its original weight) forms in dilute solution microdomains strongly differing in the refractive index from the ambient solvent. Continuous dependences of ν_μ and γ on the composition of the solvent (Figure 1) indicate that the change from clear to bluish opalescent solutions (in Figure 1 between $\varphi = 0.3$ and 0.4) is not a true sudden phase transition. Similarly, no dependence of ν_μ on the polymer concentration could be observed even if solutions at lower polymer concentrations were clear, and more concentrated solutions appeared opalescent to the naked eye (e.g., polycaprolactam in a mixture with $\varphi = 0.4$).

The temperature dependences of ν_μ of polycaprolactam in *m*-cresol/*n*-heptane mixture of two different compositions (Table II) confirm the suggested relation between the magnitudes of ν_μ or γ and the tendency of the solvent mixture to phase separation. With decreasing temperature the mixture closer to phase separation ($\varphi = 0.5$) shows a pronounced increase in ν_μ and thus also in γ; γ raises because ν_c and ν_φ, which along with ν_μ determine its value, vary but little with temperature.

Table I
Refractive Index Increments, ν_c(mL/g) and ν_μ (mL/g), and the Coefficient of Selective Sorption, γ(mL/g), of *m*-Cresol for Some Polymers Depending on the Composition of the Mixture *m*-Cresol/*n*-Heptane [a]

φ	ν_c	ν_μ	γ	φ	ν_c	ν_μ	γ
	Polycaprolactam				Polypyrrolidone		
1	0.005			1	0.015		
0.9	0.020	0.047	0.17	0.9	0.028	0.042	0.09
0.8	0.031	0.132	0.64	0.8	0.035	0.121	0.55
0.7	0.045	0.243	1.28	0.7	0.055	0.234	1.15
0.6	0.053	0.471	2.70	0.6	0.079	0.415	2.17
0.5	0.083	0.816	4.72	0.5	0.089	0.710	4.0
	Polylaurolactam				Poly(methyl methacrylate)		
1	−0.020			0.5	0.040	0.349	1.99
0.9	−0.004	0.036	0.26				
0.8	0.006	0.075	0.45		Poly(hydroxyethyl methacrylate)		
0.7	0.022	0.182	1.03				
0.6	0.043	0.340	1.92	0.5	0.033	0.361	2.12

[a] φ is the volume fraction of *m*-cresol, $t = 25$ °C.

Table II
Temperature Dependence of the Refractive Index Increment ν_μ (mL/g) of Polycaprolactam in the Mixture *m*-Cresol/*n*-Heptane for the Volume Fraction of *m*-cresol $\varphi = 0.3$ and 0.5

φ	20 °C	25 °C	37 °C	45 °C
0.3	0.246	0.243	0.241	0.240
0.5	0.853	0.816	0.711	0.640

The extremely high ν_μ values in Tables I and II may at first sight seem at variance with the common refractive indices of the components of the system polycaprolactam ($n = 1.548$)-/*m*-cresol (1.540)/*n*-heptane (1.385). Unlike ν_c, ν_μ is not proportional to the difference of the refractive indices of the scattering particle and of the surrounding solvent. The exorbitant ν_μ can be understood better if the conception of a complex is introduced consisting of the polymer molecule with the solvent component sorbed selectively (the quantity of which is given by the coefficient γ), i.e., in an amount exceeding that corresponding to the content of this solvent component in the solvent mixture.[10–12] These complex particles are the actual scattering entities which determine the intensity of scattered light. The complex concentration, c, can be expressed as

$$c^* = c(1 + \gamma\bar{v}^{-1})$$

where $\bar{v}$ is the partial specific volume of the selectively sorbed solvent component. For low polymer concentrations c it can be written in good approximation

$$\nu \doteq \Delta n/c$$

where Δn is the measured difference of the refractive indices of a polymer solution with the concentration c and the solvent. From the experimentally determined Δn, either the refractive index increment of the polymer alone (without the selectively sorbed solvent), ν_μ, or the refractive index increment of the complex, $\nu_\mu{}^*$, can be calculated. These two refractive index increments are connected by the relation

$$\nu_\mu{}^* = \Delta n/c^* = \nu_\mu/(1 + \gamma\bar{v}^{-1})$$

In the system polycaprolactam/*m*-cresol/*n*-heptane at $\varphi = 0.5$ and $t = 25$ °C (Table I), $\nu_\mu = 0.816$. If in an approximate calculation the specific volume of *m*-cresol, $v = 0.97$ mL/g, is substituted instead of its partial specific volume, the refractive index increment of the complex becomes $\nu_\mu^* \doteq 0.816/(1 + 4.72 \times 1.03) = 0.14$, which is a reasonable value, in the first approximation proportional to the difference of the refractive indices of the complex and of the surroundings. The tabulated ν_μ are extremely high, because the measured difference of the refractive indices, Δn, is related to a considerably lower concentration of the polymer alone and not to that of the complex.

The application of systems possessing extremely high refractive index increments to light-scattering measurements with polymers of low molecular weight will be reported later. Preliminary measurements indicate that some complications can arise; these may be due to various causes, such as, e.g., the dependence of γ and ν_μ on molecular weight, changes in solvent composition in the space between the individual macromolecules induced by the addition of even a small amount of the polymer, or the not negligible changes in the intensity of light scattered from the solvent system with the variation of temperature common in measurements with a standard temperature control.

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Effect of Diluent on the Stress–Strain Isotherms and Ultimate Properties of a Crystallizable Polymer Network[1]

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Received April 15, 1977

ABSTRACT: The crystallizable networks investigated consisted of *cis*-1,4-polybutadiene chains cross-linked by means of a peroxide cure, a conventional sulfur cure, and γ radiation. The networks were studied in elongation to their rupture points, at 25 and 10 °C, both in the undiluted state and swollen with a nonvolatile diluent. (Values of the volume fraction v_2 of polymer in the networks were 1.00, 0.80, 0.60, 0.40, and 0.20.) The linear portions of the resulting isotherms were represented in terms of the equation $[f^*] = 2C_1 + 2C_2\alpha^{-1}$, where $[f^*]$ is the modulus or reduced stress, α is the relative length of the sample, and $2C_1$ and $2C_2$ are constants independent of α. The constant $2C_2$, which is a measure of the extent to which an actual isotherm departs from the form predicted by the simplest molecular theories, is found to decrease markedly with decrease in v_2, but approximates zero only in the limit of infinite swelling ($v_2 \to 0$). The constant $2C_1$ is independent of dilution to within experimental error, a result which supports the use of this component of $[f^*]$ in the calculation of network cross-link densities. Strain-induced crystallization, as evidenced by departures from this simple linearity at high elongations, was observed to decrease markedly with decrease in v_2. The changes observed do not support the existence of significant contributions to $[f^*]$ from "limited chain extensibility". When crystallites do form at high elongation, they would be expected to act simultaneously as physical cross-links and reinforcing filler particles. This was confirmed by the observation that suppression of strain-induced crystallization by increase in the amount of diluent present significantly decreased both the ultimate strength and elongation to break the networks. The fractional decrease in these quantities is much larger than it is in the case of noncrystallizable networks of poly(dimethylsiloxane).

One of the most important properties of a deformable polymer network is its resistance to rupture, as characterized by its ultimate strength and maximum extensibility. These two "ultimate properties" are much enhanced in the case of networks which can undergo strain-induced crystallization,[3,4] since the crystallites thus formed have a strong reinforcing effect within the network structure.[3,5] This crystallization would be expected to be diminished by swelling the network with diluent ("plasticizer"), which decreases the melting point T_m of the system.[3] An extremely important experiment is, therefore, the quantitative determination of the extent to which dilution diminishes the stress and elongation exhibited by a network at its rupture point. The most useful interpretation of such data would involve comparison of the fractional decrease in these quantities in the case of a crystallizable polymer network, with the corresponding decreases observed for a network known to be immune to strain-induced crystallization.[6–13] The crystallizable polymer chosen for the present investigation was *cis*-1,4-polybutadiene (*cis*-PBD). A previous study[7] of the ultimate properties of networks of this polymer in the unswollen state clearly demonstrated that it very readily undergoes strain-induced crystallization, as was shown earlier for networks of natural rubber[6,13] and synthetic *cis*-1,4-polyisoprene.[6] The required stress–strain isotherms for these same networks[7] were therefore determined, in elongation, at various degrees of dilution or network swelling. Corresponding results for a noncrystallizable network are already available, from a study[8] of the ultimate properties of unswollen and swollen networks of poly(dimethylsiloxane) (PDMS) at 30 °C, at a temperature sufficiently high in the case of this polymer to suppress entirely any strain-induced crystallization.[8,9]

The detailed shape of the isotherms just prior to rupture is also of considerable importance, particularly with regard to attempts[10,11] to interpret anomalous properties of networks at high elongation in terms of the "limited extensibility" of network chains. Specifically, if the marked increase or upturn in the network modulus $[f^*]$ which is frequently observed at