Fixman relationship between $[\eta]$ and Y would worsen the agreement. The same would be true for the Flory–Huggins theory, however, so that whatever the $[\eta]-Y$ relation the Prigogine–Flory predictions must be superior. Thus heats of solution and intrinsic viscosities of polymers in mixed-solvent media provide evidence of the essential validity of the concept of interaction between molecular surfaces, as embodied in the Prigogine–Flory and Huggins theories.

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References and Notes

(1) (a) Czechoslovak Academy of Sciences; (b) McGill University.
(2) G. Delmas, D. Patterson, and S. N. Bhattaharyya, *J. Phys.Chem.*, **68**, 1468 (1964).
(3) (a) A. R. Shultz and P. J. Flory, *J. Polym. Sci.*, **15**, 231 (1955); (b) R. Noel, D. Patterson, and T. Somcynsky, *ibid.*, **42**, 561 (1960); (c) A. Dondos and D. Patterson, *J. Polym. Sci., Part A-2*, **7**, 209 (1969).
(4) (a) J. Pouchlý, A. Živny, and K. Šolc, *J. Polym. Sci., Part C*, **23**, 245 (1968); (b) J. Pouchlý and A. Živny, *J. Polym. Sci., Part A-2*, **10**, 1481 (1972); (c) J. Pouchlý, A. Živny, and K. Šolc, *Collect. Czech. Chem. Commun.*, **37**, 988 (1972).
(5) (a) G. M. Bristow, *Trans. Faraday Soc.*, **55**, 246 (1959). (b) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963].
(6) I. Prigogine (with the collaboration of V. Mathot and A. Bellemans), "The Molecular Theory of Solutions", North-Holland Publishing Co., Amsterdam, 1957.
(7) P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).
(8) M. L. Huggins, *J. Phys. Chem.*, **74**, 371 (1970).
(9) See, for example, C. H. Deal and E. L. Derr, *Ind. Eng. Chem.*, **60**, 28 (1968).
(10) E. A. Guggenheim, *Proc. R. Soc. London, Ser. A*, **183**, 213 (1945).
(11) D. Patterson and G. Delmas, *Discuss. Faraday Soc.*, **49**, 98 (1970).
(12) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, Chapter 12.
(13) W. H. Stockmayer, *J. Polym. Sci.*, **15**, 595 (1955).
(14) (a) G. Delmas and P. de St. Romain, *Eur. Polym. J.*, **10**, 1133 (1974); (b) H. Eid and G. Delmas, unpublished.
(15) F. Danusso, G. Moraglio, and G. Gianotti, *J. Polym. Sci.*, **51**, 475 (1961).
(16) J. R. Goates, R. J. Sullivan, and B. J. Ott, *J. Phys. Chem.*, **63**, 589 (1959).
(17) From the geometrical calculation in P. J. Flory and H. Höcker, *Trans. Faraday Soc.*, **67**, 2258 (1971).

The Generation of True Cosolvency by Pressure. Solubility Limits of High Molecular Weight Polystyrene in Mixtures of Acetone and Diethyl Ether

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ABSTRACT: For sufficiently high molecular weights of polystyrene, complete miscibility with mixtures of acetone and diethyl ether can never be achieved under atmospheric pressure, irrespective of the composition of the mixed solvent. This is in contrast to the situation for low molecular weight samples, which exhibit the phenomenon of true cosolvency. It is, however, possible to re-establish this effect by pressure; for $M_w = 2.5 \times 10^6$ critical conditions are achieved for the first time at 35 bars under the condition that the temperature is −10 °C and the mole fraction of acetone 0.4. On further increasing the pressure a critical surface develops out of this point. This surface resembles a closed horn and circumscribes the conditions of complete miscibility. The combination of the Prigogine–Patterson theory and Scott's single liquid approximation proves successful again for a theoretical interpretation of the experimental findings.

In the course of our investigations on mixed solvents[1,2] we have also reported on a phenomenon we called true cosolvency.[3] This term was chosen to indicate that for the system under investigation, namely acetone/diethyl ether/polystyrene (AC/DEE/PS), the polymer is, for given atmospheric pressure, at no temperature completely miscible with either acetone or diethyl ether alone, while this is the case with the mixed solvent. Ordinary cosolvency, on the other hand, is characterized by the fact that at least one of the two components of the mixed solvent becomes completely miscible with the polymer when the temperature is changed under isobaric conditions.

The effect of true cosolvency was independently also observed by Cowie and McEwen,[4] who stated that this phenomenon cannot be observed for the above mentioned system under atmospheric conditions if the molecular weight of the polystyrene exceeds approximately one million. Since we knew from our pressure investigations on a polystyrene sample of $M_w = 1.1 \times 10^5$ that the mixing volumes are negative at the lower critical solution temperature as well as at the upper critical solution temperature, we asked ourselves whether the effect of true cosolvency could be re-established for molecular weights higher than one million by the increased mixing tendency at higher pressures.

In addition it seemed interesting to check whether our hitherto quite successful theoretical approach[2,3,5] also proves useful for the prediction of molecular weight influence.

Experimental Section

Apparatus. For the investigation of the demixing conditions for systems which can only be made homogenous at elevated pressures, an apparatus had to be constructed that allows stirring of its contents in order to promote dissolution at elevated pressures. For this purpose we used a cell, holding a deepening below the light beam passing it. The magnetic stirrer contained in this cavity is moved by a strong permanent magnet outside the cell.

A schematic picture of the entire measuring device is given in Figure 1. Since most of this representation is self-explanatory, a very brief statement of the experimental procedure should suffice. Readers interested in more details are referred to ref 5.

Experimental Procedure. Measurements were performed for one approximately critical polymer concentration only, since previous results[5] have shown that the demixing conditions are nearly independent of the precise polymer concentration, as long as one is not too far from the extrema in the isothermal or isobaric sections

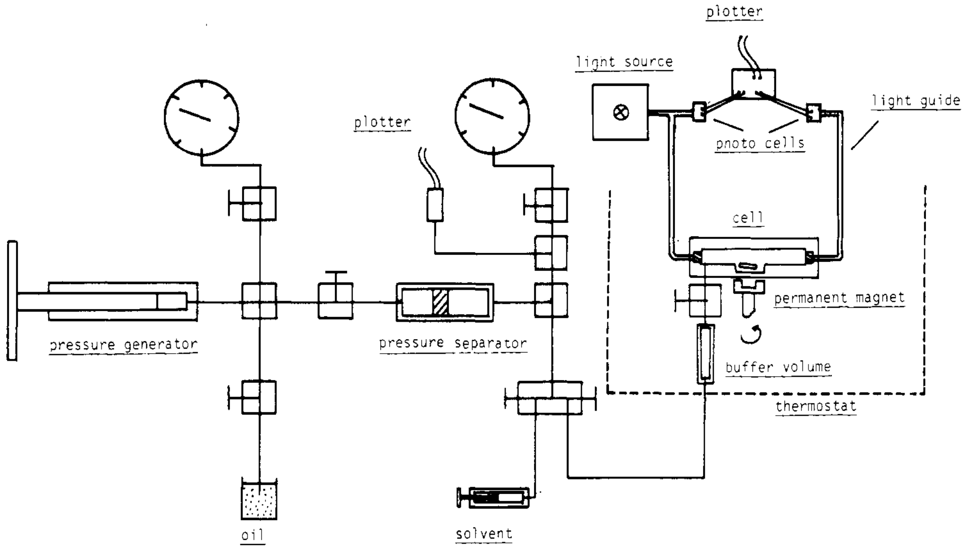

Figure 1. Schematic representation of the pressure apparatus constructed for the investigation of systems which cannot be homogenized under atmospheric pressure.

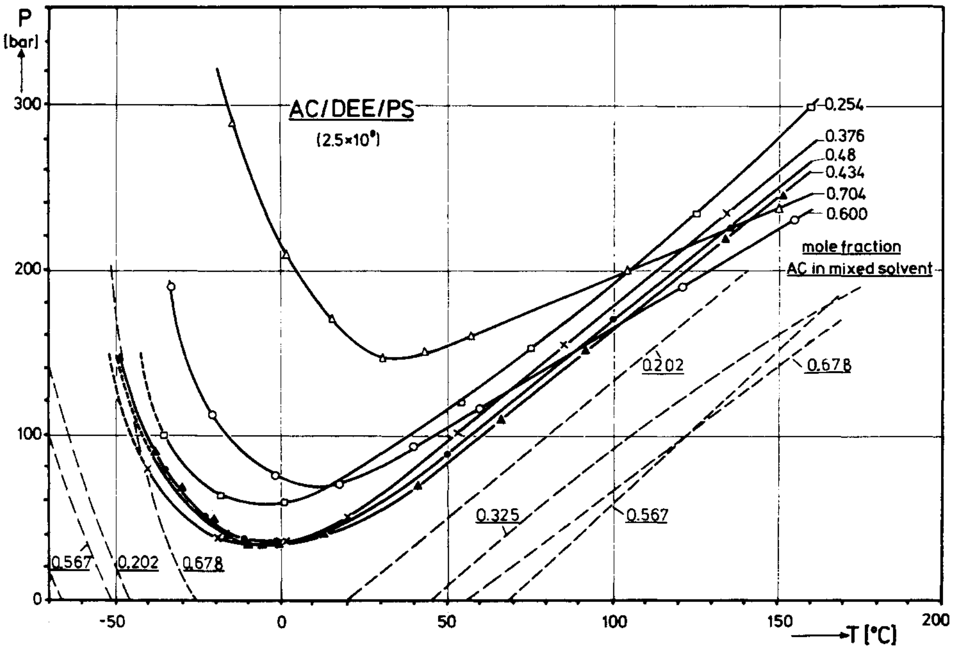

Figure 2. Sections through the spinodal surface of the system acetone/diethyl ether/polystyrene for two polymer samples at the critical polymer concentration c_{3c} (cf. text) and the indicated compositions of the mixed solvents, i.e., critical lines for the particular compositions of the mixed solvent. Full lines: $M_w = 2.5 \times 10^6$, $c_{3c} \approx 3.3$ wt %. Broken lines:[5] $M_w = 1.1 \times 10^5$, $c_{3c} = 10.0$ wt %. The regions of complete miscibility of the polymer with the different mixed solvents lie above the individual lines.

through the binodal surface. At present the precise determination of the critical conditions would have been impossible anyhow, since neither of the common methods[6,7] is practicable with the present apparatus. We have therefore extrapolated the polymer concentration of the precipitation threshold from data concerning experimental results obtained for lower molecular weight polystyrenes, which are still soluble under normal pressure[4,5] using the Flory–Huggins dependence and arrived at 3.3 wt %. The desired solutions were prepared by placing the proper amount of solid polymer into the cell, filling it with mixed solvent at room temperature, and increasing the pressure to 2000 bar. After this, a valve was closed and the solution was made homogenous by stirring. (The weight of mixed solvent contained in the cell under these conditions had previously been determined by weighing.) Thereafter the connection between the cell and the rest of the apparatus was opened again and the pressure was released, so that solution replaces the solvent in the buffer volume. This filling procedure assures that the buffer volume serves its purpose to hinder the entrance of diluting solvent into the cell under all experimental conditions. As in our previous work, we then determined the intensity of light passing through the solution as a function of pressure for several prefixed temperatures and compositions of the mixed solvent. From the thus obtained pairs of temperature and pressure at which the turbidity of a given solution becomes infinite, the spinodal surface could be constructed.

Materials. Polystyrene was a commercially available sample from the Pressure Chemical Co. with a nominal molecular weight of 2.0×10^6 and a nonuniformity $U = M_w/M_n - 1 \leq 0.3$, given by the producer. Unpublished light-scattering measurements by three different experimentalists in our institute, however, yielded $M_w = 2.5 \times 10^6$, and GPC data indicate a much higher molecular nonuniformity of $U \sim 1$. The solvents were p.a. products from Merck and were used without further treatment.

Results and Discussion

Figure 2 shows isopleths (i.e., lines of constant composition of the mixture) for spinodal conditions, i.e., the temperature dependence of the spinodal pressure for mixed solvents of the

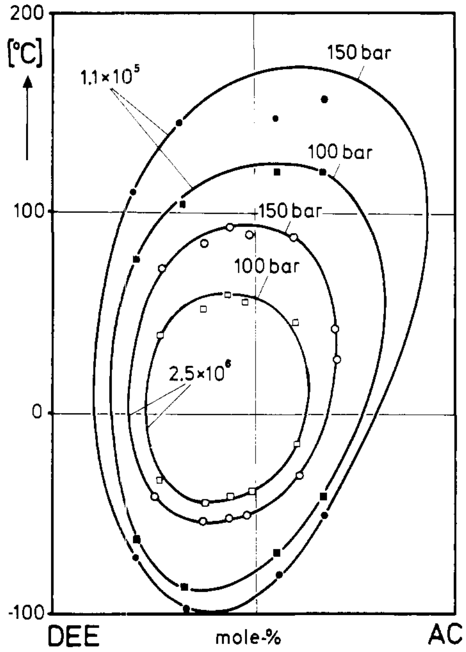

Figure 3. Comparison of the isobaric critical lines for the system acetone/diethyl ether/polystyrene and the indicated molecular weights and pressures.

indicated composition and constant approximately critical polymer concentration of 3.3 wt %.

In contrast to the low molecular weight polystyrene previously investigated (broken lines) the isopleths do not intersect the abscissa, indicating the coalescence of low and high temperature solubility gaps under normal pressure. It is also noteworthy that the isopleths for $M_w = 2.5 \times 10^6$ and the mixed solvent are quite similar in character to the critical line obtained by Zeman and Patterson[8] for $M_w = 20\,400$ and pure acetone, while the isopleths for $M_w = 1.1 \times 10^5$ and the mixed solvent resemble the critical line we have measured for $M_w = 20\,400$ in diethyl ether.[5]

With the reservations concerning the critical polymer concentration, indicated in the experimental part, isobaric critical lines can be constructed from the isopleths of Figure 2. The thus obtained critical lines for 100 and 150 bar, respectively, encircle the region of complete miscibility (Figure 3). As can be seen from a comparison with the results on the lower molecular weight polymer sample,[5] a reduction in chain length acts like an increase in pressure; this again is in qualitative agreement with the corresponding states theory.

A more synoptical representation of the demixing behavior is given in Figure 4; the always homogeneous region, now situated inside the particular surface, expands all around when the pressure is increased. Outside of it demixing is possible; how far from the critical surface it actually takes place depends on polymer concentration.

For $M_w = 1.1 \times 10^5$ the critical surface looks like a trumpet. From the extrapolation of the measurements into the negative pressure region,[5,9] it can be anticipated, however, that the isobaric critical lines should disappear (i.e., some isopleths run through a common minimum) at some 50 bar and −10 °C. In the case of $M_w = 2.5 \times 10^6$ this closing of the surface can actually be observed since the entire critical surface is displaced toward higher pressure according to its lower solubility. Thus the generation of true cosolvency can be determined. At approximately 35 bar, 40 mol % acetone in the mixed solvent, and −10 °C the upper and lower critical solution temperatures coincide. Below the corresponding upper critical solution pressure it is impossible to achieve complete miscibility for any temperature and any composition of the mixed solvent.

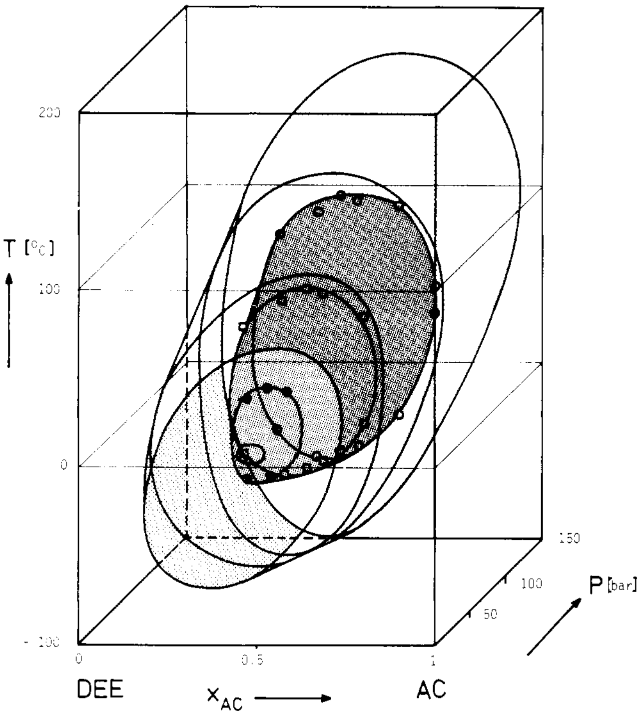

Figure 4. Three-dimensional representation of the experimentally determined critical surfaces (limits of complete miscibility in the mixed solvent acetone/diethyl ether in the strict sense) for solutions of two polystyrene samples. The larger trumpetlike surface belongs to $M_w = 1.1 \times 10^5$ the closed surface belongs to $M_w = 2.5 \times 10^6$ for which no region of complete miscibility is observable under normal pressure. The always homogenous regions lie inside the particular surface.

Theory

The present theoretical treatment confines itself to the problem of calculating the demixing behavior of the ternary system under investigation, starting from known thermodynamic data concerning the binary subsystems. This calculation is based on the so called single liquid approximation of Scott,[10] which treats the mixed solvent as one single component, whose Flory–Huggins parameter χ_{ms}, measuring the interaction with the polymer, can be calculated from the binary interaction parameters according to:

$$\chi_{ms} = x_1\chi_{13} + x_2\chi_{23} - x_1x_2\chi_{12} \tag{1}$$

The x values represent mole fractions (instead of the original segment fractions) and $x_1 + x_2 = 1$. The indices 1, 2, 3 refer to acetone, diethyl ether, and polystyrene, respectively.

Equation 1 provides the key for the understanding of the nonadditive behavior of mixed solvents. In the present case large enough positive χ_{12} values are the reason for a minimum in χ_{ms}, which means an increase of solvent power of the mixed solvent over that of either component. For the further evaluation analytical expressions for the experimentally determined variation of χ_{ij} with temperature and pressure are desirable. They were found in the theoretical equation 2 derived by Patterson and Delmas[11] in conjunction with the equations of state given by Flory and co-workers[12]

$$\chi = -\frac{\tilde{U}_1}{\tilde{T}_1} c_1\nu^2 + \frac{\tilde{c}_{p1}}{2} c_1 \left[\tau + \frac{\beta_1 P}{\alpha_1 T} \pi \right]^2 \tag{2}$$

$$\tilde{T} = (\tilde{p}\tilde{V} + \tilde{V}^{-1})(1 - \tilde{V}^{-1/3}) \tag{3}$$

$$\tilde{U} = -\tilde{V}^{-1} \tag{4}$$

tildes indicate reduced quantities, the index 1 stands for the lower molecular weight component of a binary mixture. U is the internal heat of vaporization and c_p its temperature de-

Table I
Parameters Used in the Theoretical Calculation

	T^*, K	P^*, bar		c_1	ν	τ	π
AC	3950	5880	AC/PS	1	0.201	0.300	−0.65
DEE	3750	6850	DEE/PS	1	0.151	0.360	−0.37
Mixed solvent	3600	6365	AC/DEE	1	0.148	0.187	0

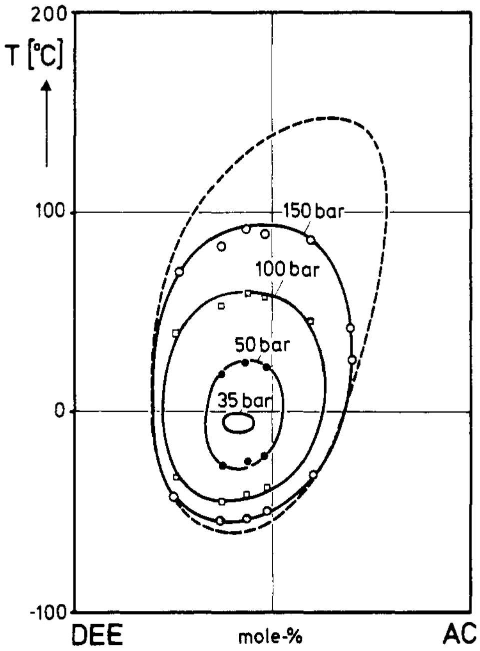

Figure 5. Comparison of the isobaric critical line calculated according to eq 1–5 for $M_w = 2.5 \times 10^6$ and 150 bar (- - -) with the experimental results. The critical lines, calculated for the other pressures, fit the experiments analogously.

rivative; c_1 constitutes one-third of the number of external degrees of freedom of the solvent. For the present calculation c_1 is taken to be unity. The parameters ν, τ, and π measure the dissimilarities of the components in "chemical nature", reduction temperature, and reduction pressure, where the reduction parameters themselves are obtained from measured thermal expansivities α and isothermal compressibilities β by means of eq 3.[12] In the case of the polymer containing binary subsystems the parameters ν, τ, and π were obtained from the critical lines measured for the low molecular weight sample of 20 400. The critical interaction parameter χ_c was calculated from the degree of polymerization N (neglecting the difference in the segment size of solvent and polymer) by means of the Flory–Huggins expression:

$$\chi_c = 0.5(1 + N^{-0.5})^2 \tag{5}$$

ν, τ, and π were adjusted such that eq 1–4 yield χ_c for each point of the particular critical line.

In the case of the mixed solvent ν and τ were adjusted to the temperature dependence of χ_{12} as determined from published vapor pressure data and heats of mixing.[3] π was assumed to be negligible. The data[5] necessary for the calculation of χ_{ms} as a function of temperature, pressure, and mixed solvent composition are summarized in Table I.

Provided eq 5 gives the correct molecular weight dependence of the critical χ value, the molecular weight influence on the critical surface could be calculated by determining the conditions under which the corresponding χ_c value is realized. Our earlier measurements[3,5] ($M_w = 1.1 \times 10^5$) have, however, disclosed that the extension of the homogenous region as calculated on the basis of eq 5 is largely overestimated. Practically quantitative agreement can be achieved though, if χ_c is set 0.45 instead of 0.53.

Similar discrepancies have also been reported by Zeman and Patterson[8] who suggested the use of an empirical constant instead of the factor 0.5 in eq 5. According to our abovementioned measurements this constant should amount to 0.4 for the present ternary system. In fact the relatively best agreement between the observed and the calculated critical surface can be achieved for $M_w = 2.5 \times 10^6$ when χ_c is calculated from eq 5 with 0.4 instead of 0.5. Figure 5 gives some measured isobars together with the critical line calculated for 150 bar. This theoretical result is only meant as a typical example, since the deviation of the other calculated isobars from the theoretical curve is quite similar. All calculated lines fit the experiments well at low temperatures but they overestimate the homogenous region considerably at the high ones.

There are at least two possible explanations for the remaining discrepancies: One is the relatively high molecular nonuniformity as compared with the lower molecular weight products, which could become more effective at higher temperatures where the differences in the expansivities between polymer and solvent play a decisive role. The other one lies in the uncertainty of the modified eq 5, i.e., in a possible dependence of χ_c on the variables of state. The observed deviations are, however, of minor importance as compared with the opportunities to predict the demixing behavior of the ternary system at the worst in a qualitative way from thermodynamic data concerning the binary subsystems, as long as the components of the mixed solvent do not become too dissimilar.

References and Notes

(1) B. A. Wolf, J. W. Breitenbach, and H. Senftl, *J. Polym. Sci., Part C*, **31**, 345 (1970).
(2) B. A. Wolf and G. Blaum, *J. Polym. Sci, Part A-2*, **13**, 1115 (1975).
(3) B. A. Wolf and R. J. Molinari, *Makromol. Chem.*, **173**, 241 (1973).
(4) J. M. G. Cowie and I. J. McEwen, *J. Chem. Soc., Faraday Trans. 1*, **70**, 171 (1973).
(5) B. A. Wolf and G. Blaum, *Makromol. Chem.*, **177**, 1073 (1976).
(6) R. Koningsveld and A. J. Staverman, *J. Polym. Sci., Part A-2*, **6**, 325 (1968).
(7) B. A. Wolf, *Makromol. Chem.*, **128**, 284 (1969).
(8) L. Zeman and D. Patterson, *J. Chem. Phys.*, **76**, 1214 (1972).
(9) B. A. Wolf, *Ber. Bunsenges. Phys. Chem.*, **75**, 924 (1971).
(10) R. L. Scott, *J. Chem. Phys.*, **17**, 268 (1949).
(11) D. Patterson and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1969).
(12) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507, 3515 (1964).