to the overestimation of the τ^2 term.

The $\tilde{T}_1$ under pressure was obtained from eq 5 and 6 with $P_1^* = 513.8$ MPa, $\pi = -0.0603$, and molecular parameters by Saeki et al.[15] by assuming a constant value for $(1/2)(1 + r^{-1/2})^2$. The calculated (P,T) critical lines are given by the dotted lines in Figure 3. The agreement between the calculated and observed lines is satisfying in the region of low pressure and the dependence of $(\mathrm{d}T/\mathrm{d}P)_{c,P=0}$ on the molecular weight is in semiquantitative agreement with theoretical prediction.

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Upper and Lower Critical Flocculation Temperatures in Sterically Stabilized Nonaqueous Dispersions

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ABSTRACT: The preparation and partial characterization of poly(acrylonitrile) latex particles stabilized by poly(α-methylstyrene) in n-butyl chloride have been described. It was observed that these sterically stabilized particles flocculated both on heating and on cooling. The upper and lower critical flocculation temperatures were found to correlate qualitatively with the Θ temperatures associated with the LCST and the UCST, respectively. Consideration of a temperature-dependent excluded volume integral allows the χ parameter, and hence the free energy of interpenetration of the stabilizing chains, to be predicted as a function of temperature. These temperature-dependent functions predict that, in principle, all nonaqueous sterically stabilized dispersions should show both enthalpic and entropic stabilization provided that a large enough temperature range can be scanned. It is suggested that flocculation at the LCFT can be largely ascribed to the contact energy dissimilarity between the stabilizing polymer and the dispersion medium, while flocculation at the UCFT is dominated by the free volume dissimilarity between the stabilizing moiety and the dispersion medium.

The steric stabilization of colloidal dispersions using polymeric surfactants is a subject of considerable scientific interest[1] and technological importance.[2] This method of stabilizing particles against coagulation has been found to be effective in aqueous and nonaqueous media. It is especially useful in nonaqueous media of low dielectric constant where electrostatic stabilization appears to be comparatively ineffective.

Three types of experiment involving sterically stabilized dispersions have been reported in the literature. They are incipient flocculation,[3] stability in polymer melts,[4] and measurement of the repulsive interactions between stable particles.[5,6] Incipient flocculation has been the most extensively reported measurement, and can be induced by changing the solvent quality of the dispersion media relative to that of the stabilizing polymer. This can be carried out through addition of nonsolvent or by changing the temperature (or pressure) of the system.[7] It has been observed that incipient instability is a reversible phenomenon[7] and that spontaneous redispersion occurs if the solvency of the disperse medium is improved with respect to the stabilizing polymeric moiety.

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Table I
Types of Steric Stabilization

type	Δ-H_R	Δ-S_R	$\|\Delta H_R\|/T\|\Delta S_R\|$	Δ-G_R	ψ	κ	remarks
entropic	−	−	<1	+	+	+	flocculates on cooling
enthalpic	+	+	>1	+	−	−	flocculates on heating
enthalpic-entropic	+	−	>1 or <1	+	−	+	no flocculation

The free energy of close approach (ΔG_R) of the particles must be positive for a sterically stabilized dispersion to be stable. Napper has observed that there are three ways of obtaining a positive ΔG_R in the vicinity of the critical flocculation point[7] and these are summarized in Table I. When the enthalpy (ΔH_R) and entropy (ΔS_R) of close approach of the particles are both negative and $|\Delta H_R| < T|\Delta S_R|$ the enthalpy change favors flocculation and the entropy term opposes it. Since the entropy term dominates the free energy then this is known as *entropic stabilization* and the dispersion flocculates on cooling. When the enthalpy and entropy are both positive and $\Delta H_R > T\Delta S_R$ the enthalpic term dominates and this is known as *enthalpic stabilization* and is characterized by flocculation on heating. When ΔH_R is positive and ΔS_R is negative then both terms contribute to stability and in principle such systems cannot be flocculated at any accessible temperature.

It is now well established[7] that the critical flocculation temperature (CFT) for dilute dispersions correlates strongly with the theta (Θ) point of the stabilizing polymeric moiety in free solution, provided that desorption of the stabilizer is not a complicating factor. Therefore, Θ conditions (where polymer–polymer interactions are zero) represent the practical limit for the stability of such dispersions, provided of course that multipoint anchoring is not a significant factor.

Historically, the Θ point has always been associated with an upper critical solution temperature (UCST), which lies at the top of a two-phase region.[8] In 1959 Freeman and Rowlinson demonstrated[9] that polymer solutions also separate into two liquid phases on raising the temperature to what is known as the lower critical solution temperature (LCST) since it lies at the bottom of a two-phase region. This is shown schematically in Figure 1. The LCST usually lies above the boiling point of the solvent, but it appears to be a completely general phenomenon for high polymer solutions. Numerous polymer–solvent pairs have now been identified which show both a UCST and an LCST within an experimentally accessible range.[10,11] The limiting LCST for an infinite molecular weight polymer has also been shown to be a Θ point.[12]

Napper et al.[3] have shown that poly(acrylonitrile) (PAN) particles stabilized by poly(isobutylene) in 2-methylbutane flocculate at the Θ point associated with the LCST (enthalpic stabilization) while poly(vinyl acetate) particles stabilized by poly(12-hydroxystearic acid) in n-heptane flocculate[13] at the Θ temperature associated with the UCST (entropic stabilization).

The purpose of this paper is to demonstrate that PAN latices stabilized by poly(α-methylstyrene) in n-butyl chloride flocculate on both heating and cooling. The upper and lower flocculation temperatures correlate qualitatively with the independently determined Θ points associated with the LCST and UCST of the poly(α-methylstyrene) + n-butyl chloride system, respectively. Inclusion of a temperature-dependent excluded volume integral in the theories of steric stabilization allows the flocculation behavior to be unambiguously predicted. Finally, a brief discussion of the physical basis of the observed flocculation behavior is included, although this will be detailed in a separate publication.

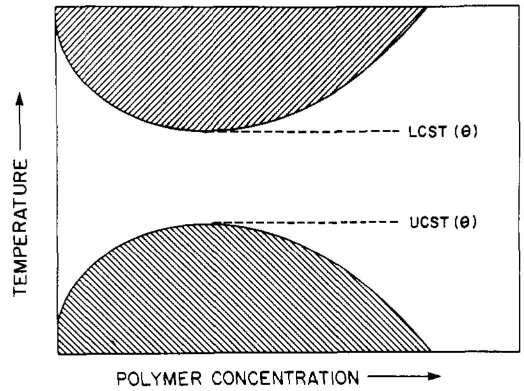

Figure 1. Schematic diagram of an infinite molecular weight polymer in a solvent which shows phase separation occurring at the UCST and at the LCST.

Experimental Section

1. **Materials.** The solvent, n-butyl chloride (Fisher Scientific), and acrylonitrile monomer (Matheson, Coleman and Bell) were distilled before use and kept over 4 Å molecular sieves. The poly(α-methylstyrene) used as stabilizer was obtained from Polysciences (Warrington, Pa.) and was characterized using GPC. The elution profile indicated a broad molecular weight distribution which was bimodal in character. From a polystyrene calibration curve and the GPC profile, it was found that $\bar{M}_w = 9400$, $\bar{M}_n = 695$, and $\bar{M}_z = 54\,700$. The polydispersity factor ($\bar{M}_w/\bar{M}_n$) was 13.5, which is smaller than expected for a rather broad MWD curve and indicates the presence of oligomers.

2. **Amphipathic Stabilizer.** The poly(α-methylstyrene-g-acrylonitrile) stabilizer was prepared by dissolving poly(α-methylstyrene) (**2g**) in n-butyl chloride (70 mL) at 343 K. The smallest amount of acrylonitrile (0.15 g) that was compatible with the formation of stable latices was added to the solution along with azobis(isobutyronitrile) as initiator (0.1 g). The reaction was allowed to proceed under constant stirring for ~12 h at 343 K. A clear solution was obtained. In order to check whether the grafting reaction had succeeded, the copolymer was precipitated by addition of hexane (Fisher) as nonsolvent and vacuum dried. It was then dissolved in fresh n-butyl chloride and its IR spectra recorded. The IR spectra showed the characteristic stretching frequencies of both polymeric species.

3. **Dispersion Polymerization.** The amphipathic copolymer (1 g) was redissolved in n-butyl chloride (75 mL) together with acrylonitrile (5 g) and ABIN (0.1 g) initiator at 343 K. The mixture was stirred continuously and the solution became opalescent within 10 min. The reaction was allowed to proceed for approximately 6 h. After cooling, the sterically stabilized particles were centrifuged, excess solvent was decanted off, and the particles redispersed in fresh n-butyl chloride. This cleaning procedure was carried out until no more free polymer was precipitated by the addition of nonsolvent to the decanted disperse medium.

The particles were characterized using scanning electron microscopy. They were found to be surprisingly monodisperse with a diameter of ~0.2 μm. Some chaining of the particles was observed, but it was thought that this was a result of the SEM sample preparation rather than an inherent property of the dispersion.

4. **Flocculation Measurements.** Several samples of particle concentration of ~0.2 and 0.6 wt % were prepared by dilution of a concentrated sample, whose particle concentration was obtained from gravimetric measurements. Approximately 10 mL of the dispersion was placed in a Pyrex glass tube ~7 cm in length (i.d. 1.2 cm and o.d. 1.5 cm), degassed, and flame sealed under vacuum.

High-temperature flocculation measurements were carried out in a silicone oil bath which was controlled to better than ±0.1 K. The samples were allowed to stand at 343 K for 12 h before

Table II
Summary of Flocculation and Θ Temperatures

system	Θ_u/ K	Θ_L/ K	LCFT/ K	UCFT/ K	remarks
poly(α-methylstyrene) in *n*-butyl chloride	263[a]	412[a]			
PAN latices stabilized with poly(α-methylstyrene) in *n*-butyl chloride			254 ± 1	403 ± 1	exhibits entropic and enthalpic stabilization

[a] Taken from ref 11.

any measurements were made. The samples were then heated at ~1 K/min except in the vicinity of the critical flocculation point where the rate was reduced to ~0.1 K/min until the upper critical flocculation temperature was reached. This was observed visually as the point at which there was a very dramatic reduction of the number of particles in the measuring vial.

Low-temperature flocculation experiments were carried out in a dry ice + acetone mixture, the control of which was less precise (±0.5 K) than that of the silicone bath. It was found that the lower critical flocculation temperature had to be established by slowly cooling the solution to 200 K and then noting the temperature at which the flocculated dispersion redispersed on warming the system under constant shaking. This method gave reproducible LCFT data, whereas those obtained by noting the flocculation temperature on cooling were unreproducible and occurred at much lower temperatures. This behavior has also been encountered in phase equilibria measurements on polymer solutions,[11] but remains unexplained. Although the observed flocculation phenomena was reversible, it was found that the flocculated latices were difficult to redisperse, if they were allowed to stand for too long.

As poly(α-methylstyrene) is known to degrade at elevated temperatures[14] the validity of the UCFT obtained was checked by recooling solutions to the LCFT and noting the new temperature of flocculation. It was found that the flocculation temperature was, within experimental error, identical to the original value. It was therefore assumed that thermal degradation did not affect the UCFT values reported.

Results and Discussion

The PAN latex samples stabilized by poly(α-methylstyrene) in *n*-butyl chloride were found to flocculate on heating at 403 K. They were also found to flocculate on cooling at 254 K. The critical flocculation temperatures were independent of the particle concentration over the limited particle range studied. Phase equilibria measurements of poly(α-methylstyrene) in *n*-butyl chloride have been reported by Cowie and McEwan.[11] The Θ temperatures associated with the LCST and UCST were 412 and 263 K, respectively. There is therefore a qualitative correlation between the Θ point associated with the LCST and the upper critical flocculation temperature, and between the Θ point associated with the UCST and the lower critical flocculation temperature. The results are summarized in Table II.

The correlation is not exact, but this can be attributed to numerous effects. The most important are discussed below.

(a) The Θ points shown in Table II were obtained using the well-known Shultz–Flory expression[15] which relates the critical miscibility temperature (T_c) of the polymer in the solvent to the Θ temperature, viz.,

$$\frac{1}{T_c} = \frac{1}{\Theta}\left[1 + \frac{1}{\psi}\left(\frac{1}{r^{1/2}} + \frac{1}{2r}\right)\right] \qquad (1)$$

ψ is the entropy parameter for the system and is considered to have a constant value and r is the number of segments of the polymer. Equation 1 predicts that a plot of T_c^{-1} against $r^{-1/2} + (2r)^{-1}$ should be a straight line of slope $(\psi\Theta)^{-1}$. The data for poly(α-methylstyrene) in *n*-butyl chloride show nonlinear behavior (see Figure 1c of ref 11). This curvature in the plots is attributed to a temperature-dependent ψ parameter. By drawing tangents to the data Cowie and McEwen were able to determine ψ and Θ from the slope and intercept. However, Θ temperatures obtained using eq 1 are not strictly correct since ψ is not temperature independent. By utilizing modified Shultz–Flory plots alternative Θ temperatures, which can differ by a significant amount, are obtained.[16] Therefore, in the absence of Θ data from light scattering, i.e., second virial coefficients, we do not attach a great deal of significance to the observed differences between the Θ temperature and the critical flocculation temperature.

(b) The effect of the anchor polymer, which we have ignored, would be to reduce the solubility of the stabilizing polymer in the dispersion medium through loss of configurational entropy. A quantitative correlation with the Θ point can therefore be considered as a limiting case in which the anchor polymer acts as a featureless and structureless moiety. In the experiments reported here, we have only grafted as much acrylonitrile on to the stabilizing polymer as is necessary for the preparation of a stable latex. If multipoint anchoring of the soluble polymer to the surface of the particle was significant then we would not expect any correlation between the Θ and critical flocculation temperatures. This is a subject which deserves closer experimental scrutiny on well characterized latices, since it is of fundamental importance.

Everett and Stageman have recently reported[17] that polystyrene particles stabilized with a low molecular weight poly(dimethylsiloxane) (PDMS) dispersed in a series of short chain *n*-alkanes flocculate on both heating and cooling. The LCFT values were found to be almost solvent independent, which suggests that these authors were observing flocculation caused by surface-induced crystallization of the PDMS, which allowed the attractive van der Waals forces to become operative. The bulk crystallization temperature of PDMS is reported to be 233 K[18] which is approximately the same temperature as the observed LCFT. Furthermore, no Θ temperature associated with the UCST has been found for PDMS + short chain *n*-alkane systems. It is significant that these latices[17] were heated to temperatures in excess of 473 K and remained as discrete particles, since the glass transition temperature (T_g) of polystyrene is 373 K and the particles might have been expected to disintegrate at $T >> T_g$. That this did not occur further attests to the utility of these interesting materials. Napper has also indicated[7] that he has observed upper and lower flocculation temperatures for PAN particles stabilized by polystyrene in methyl acetate. No details of these experiments have yet been reported.

1. Theories of Steric Stabilization. Theories of steric stabilization fall into three main classes which may be classified as entropy, solvency, or entropy plus solvency theories.[7] The entropy plus solvency theories[19–21] assume that the total free energy of interaction (ΔG) can be written as the sum of a mixing (ΔG^M) or osmotic term and an elastic (ΔG^E) or volume restriction term, thus

$$\Delta G = \Delta G^M + \Delta G^E \qquad (2)$$

The mixing term results from excluded volume effects and the elastic term results from a loss of configurational entropy of the stabilizing chains as the two particles approach one another. The available experimental evidence from incipient flocculation experiments on dilute dispersions indicates that the elastic contribution is of minor importance.[22] We can therefore ignore the ΔG^E term. Napper has also argued[7] that van der Waals forces are very weak and play little part in the incipient flocculation of such latices; therefore, the interaction is dominated by the mixing term. Two regimes of close approach of the particles have been defined by Smitham et al.[22] They are the interpenetration domain which is defined by $L \leq d < 2L$, and the interpenetration plus compression domain in which $d < L$, where L is the thickness of the stabilizing barrier and d is the distance of separation of the stabilizing chains. Since the experiments reported here are for a dilute dispersion, where the particles are spaced well apart, we consider the interpenetration domain to be the correct domain to consider.

The problem of the interpenetration of two polymer chains in solution has been treated by Flory and Krigbaum.[8] Napper et al.[7] have adapted this approach to the problem of steric stabilization. The interpenetrational free energy of interaction of sterically stabilized particles (ΔG_I^M) is given by[7]

$$\Delta G_I^M = 2\pi N\omega^2(v_2^2/V_1)(\tfrac{1}{2} - \chi)aSkT \tag{3}$$

where ω is the weight of stabilizing moiety per unit surface area and v_2 the partial specific volume. V_1 is the molar volume of the disperse medium, a is the radius of the particles, N is Avagadro's number, and χ is a parameter which is a measure of the antipathy between the stabilizing polymer and the solvent (dispersion medium). The S function describes the distance dependence of the interaction and is a function of the size of the stabilizing chain. The simple constant segment density model applicable to low molecular weight stabilizers gives[23]

$$S = 2\left(1 - \frac{d_0}{2L}\right)^2 \tag{4}$$

where d_0 is the minimum distance of separation of the chains which must lie between $L \leq d_0 \leq 2L$.

Equation 3 predicts that ΔG_I^M will be a positive quantity when $\chi < {}^1/_2$ and the dispersion remains stable. When $\chi > {}^1/_2$ then the dispersion will flocculate since the interaction between the chains becomes attractive. The critical condition (χ_c) for phase separation is given, from Flory–Huggins solution theory, by[8]

$$\chi_c = \tfrac{1}{2}(1 + r^{-1/2})^2 \tag{5}$$

Since the steric stabilizer acts as a polymer of infinite molecular weight $r^{1/2} \rightarrow 0$ and $\chi_c = {}^1/_2$ which gives $\Delta G_I^M = 0$. Equation 3 therefore predicts a sharp transition from stability to instability on passing through the Θ point (i.e., $\chi_c = {}^1/_2$) which is what has been observed experimentally. However, the theory is unable to predict whether the flocculation temperature is an upper or lower critical flocculation temperature.

2. Excluded Volume Integral. The "ideal" or Θ temperature defined by Flory is given by[8]

$$\Theta = \kappa T/\psi \tag{6}$$

where κ is identified from solution theory as the enthalpy of dilution parameter and ψ the entropy of dilution parameter. They are related to the χ parameter through

$$\tfrac{1}{2} - \chi = \psi - \kappa \tag{7}$$

It is of interest to note that χ is therefore a free energy function and that when $\chi_c = {}^1/_2$, $\psi_c = \kappa_c$. From eq 6 and 7 it follows that

$$\tfrac{1}{2} - \chi = \psi - \kappa = \psi\left(1 - \frac{\Theta}{T}\right) \tag{8}$$

Equation 8 is the functional form for the temperature dependence of the excluded volume in the vicinity of the Θ point. It does not hold over an extended temperature range since it predicts that the solvent power increases with increasing temperature. That this is not the case is evident from the observation[10] that some polymer + solvent systems are only miscible between the temperatures bounded by the UCST and the LCST. An analysis of these critical temperatures[24] shows that ψ and κ must both change sign (see Table I) from positive to negative as the temperature of the dilute polymer solution is increased from the UCST to the LCST. This has been confirmed experimentally[11,12] and must also be true for the nonaqueous sterically stabilized dispersions as they pass from the LCFT to the UCFT. Such a change of sign implies that the excess partial molar heat capacity of mixing ($\bar{C}^E_{p,1}$) is of a negative sign and of considerable magnitude. Eichinger has recently considered[25] the case when ψ and κ (and thus χ) are treated as temperature-dependent functions instead of constants. The analysis is confined to those systems where $\Theta_L > \Theta_u$, which will generally exclude aqueous based systems.

If the value of $\bar{C}^E_{p1}/R\phi_2^2$ (where ϕ_2 is the volume fraction of polymer) is denoted by ξ, it follows that

$$\xi = T\,(\mathrm{d}\psi/\mathrm{d}T) \tag{9}$$

$$\xi = \mathrm{d}(T\kappa)/\mathrm{d}T \tag{10}$$

Evaluation of the temperature dependence of ψ and κ becomes possible by writing ξ as a Taylor series around Θ_u, such that

$$\xi = \xi_u + \xi_u'(T - \Theta_u) + \xi_u''(T - \Theta_u)^2 \tag{11}$$

where the subscript u denotes evaluation of the quantity at Θ_u and the superscript prime denotes the temperature derivative. Integration of eq 9 and 10 with the use of eq 11 leads to truncated expressions for $\psi(T)$ and $\kappa(T)$ of the form[25]

$$\psi(T) = \psi_u - \bar{\xi}\ln(\Theta_u/T) \tag{12}$$

and

$$\kappa(T) = \kappa_u(\Theta_u/T) + \bar{\xi}\left(1 - \frac{\Theta_u}{T}\right) \tag{13}$$

where for simplicity ξ has been assigned an averaged value $\bar{\xi}$ in the temperature interval between Θ_u and Θ_L. The temperature-dependent excluded volume integral can now be written as

$$\tfrac{1}{2} - \chi(T) = \psi(T) - \kappa(T) = \psi_u\left(1 - \frac{\Theta_u}{T}\right) - \bar{\xi}\left[\left(1 - \frac{\Theta_u}{T}\right) + \ln\left(\frac{\Theta_u}{T}\right)\right] \tag{14}$$

Combining eq 3 and 14 allows the free energy of interpenetration to be evaluated as a function of temperature provided for Θ_u and $\bar{\xi}$ are known or can be reliably estimated. It must also be assumed that the critical flocculation temperature can be identified with the Θ temperature. This is not strictly correct but is a reasonable approximation for practical purposes.

The correlation of the Θ point with the critical flocculation temperature indicates that the observed incipient flocculation behavior is governed largely by the ψ and κ

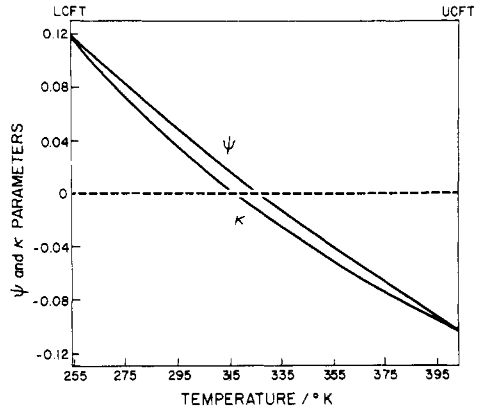

Figure 2. The temperature dependence of the ψ and κ parameters for the PAN latices stabilized by poly(α-methylstyrene) in n-butyl chloride calculated using eq 12 and 13, respectively.

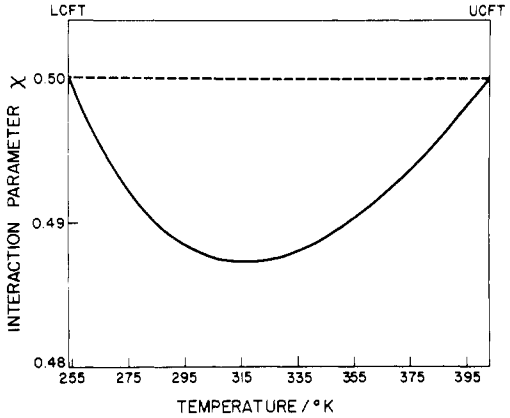

Figure 3. The χ parameter for the PAN latices stabilized by poly(α-methylstyrene) in n-butyl chloride is shown plotted as a function of temperature. Flocculation of the latices takes place when $\chi > {}^1/_2$.

parameters. For the poly(α-methylstyrene) + n-butyl chloride system it has been reported that $\psi_u = \kappa_u = 0.12$.[11] Assuming that $\Theta_u \simeq$ LCFT = 254 K and $T = \Theta_L \simeq$ UCFT = 403 K, eq 19 yields a value for ξ of −0.483. The temperature dependences of $\psi(T)$ and $\kappa(T)$ between the lower and upper critical flocculation temperatures have been calculated using eq 12 and 13 and are shown plotted in Figure 2. It can be seen that both $\psi(T)$ and $\kappa(T)$ pass from positive values at the LCFT to negative values at the UCFT as expected. The ψ and κ dilution parameters are related to the better known χ parameter as is shown in eq 7. This parameter is shown plotted as a function of temperature in Figure 3. The most striking feature of $\chi(T)$ is its parabolic shape. Between the LCFT and ~320 K the χ value decreases in value, indicating that the solvent quality is increasing. At higher temperatures χ increases again until the critical value of 0.5 is reached. When $\chi > {}^1/_2$ then flocculation takes place. The shape of the $\chi(T)$ curve has been found to be generally valid for polymers in nonpolar solvent media,[26] therefore it should be expected that a nonaqueous sterically stabilized dispersion will show both enthalpic and entropic stabilization provided that a large enough temperature range can be scanned experimentally.

The shape of the $\chi(T)$ parameter can be understood by comparing eq 8 and 14. These are shown plotted in Figure 4. Curve (a), which is given by $\psi_u(1 - (\Theta_u/T))$, is a continuously increasing function of temperature and predicts that the dispersion would become more stable with increasing temperature. However, the heat capacity term (b) continually decreases with increasing temperature.

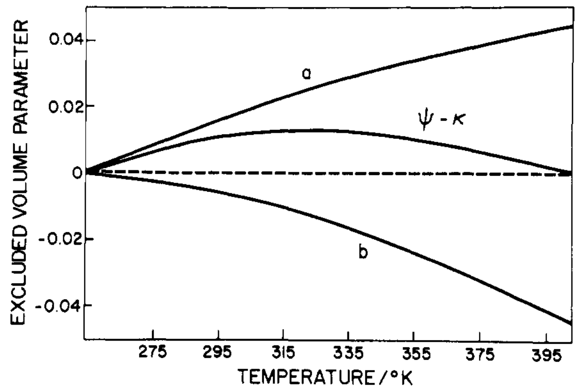

Figure 4. The excluded volume integral, eq 14, is shown plotted as a function of temperature. Curve (a) corresponds to the $\psi_u(1 - \Theta_u/T)$ term, while (b) corresponds to the $\xi[(1 - (\Theta_u/T)) + \ln(\Theta_u/T)]$ term.

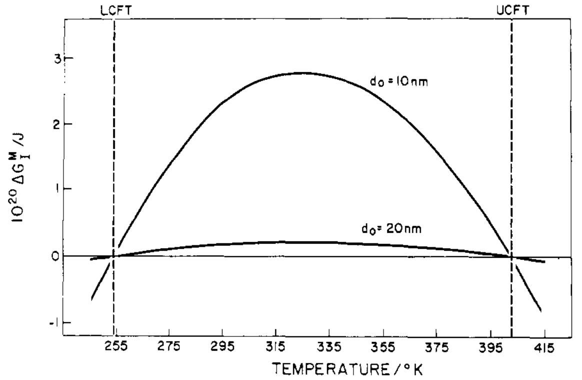

Figure 5. The free energy of interpenetration (ΔG_I^M) is shown plotted as a function of temperature for two values of separation of the stabilizing chains.

On addition, the parabolic nature of χ (or $\psi - \kappa$) becomes evident.

Modern statistical theories of polymer solutions[27,28] are able to predict the correct shape of the χ parameter as a function of temperature. The UCST is dominated by the contact energy dissimilarity between polymer and solvent, while the LCST is caused by the free volume dissimilarity between polymer and solvent. It is suggested that the LCFT and UCFT can be largely attributed to the same molecular mechanisms and this will be discussed in a separate publication.

Figure 5 shows the temperature dependence of ΔG_I^M calculated from eq 3 for two d_0 values using the following parameters $\omega = 5 \times 10^{-8}$ g cm^{-2}, $\upsilon_2 = 0.89$ cm^3 g^{-1}, $V_1 = 104.5$ cm^3 mol^{-1}, $a = 100$ nm. The $\chi(T)$ parameter was calculated using eq 14 and the polymer layer thickness L was assumed to be temperature independent with a value of 12 nm. As expected the parabolic shape of $\chi(T)$ can also be seen in the interpenetrational free energy of close approach of the particles as a function of temperature. Between the LCFT and the UCFT the dilute dispersion is indefinitely stable, i.e., $\Delta G_I^M > 0$, but at temperatures greater than the UCFT and lower than the LCFT the dispersion is flocculated, $\Delta G_I^M < 0$. Maximum stability for the PAN latices stabilized by poly(α-methylstyrene) in n-butyl chloride would be expected to occur at ~325 K where ΔG_I^M attains its maximum value. Allowing L to be temperature dependent will enhance the parabolic shape of the $\Delta G_I^M(T)$ curve.

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Thermodynamic Properties of Polystyrene in Mixed Solvents Studied by Sedimentation Equilibrium

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ABSTRACT: The theory of the osmotic and sedimentation equilibria of polymers in mixed solvents is reviewed and the relations between the free enthalpy of mixing ΔG_{mix} and the second virial coefficient as well as the preferential adsorption of solvent components onto polymer are formulated. The method of sedimentation equilibrium is employed for measurement of the latter quantities. Three samples of polystyrene are measured in two combinations of solvents (benzene–cyclohexane and ethyl acetate–cyclohexane) over the whole range of composition of solvent mixtures. The experimental results are analyzed using a general phenomenological expression for ΔG_{mix}. For a reasonable fit, ternary interaction parameters must be introduced into the expression for ΔG_{mix}.

When a mixture of two liquids is used as a solvent for macromolecules, its solvent power is usually quite different from the averaged solvent power of the two pure solvent components. Such solutions also exhibit preferential adsorption of one solvent onto polymer.

The basic understanding of these phenomena was achieved during the 1950's and the early 1960's.[1-11] During the last decade the interest in polymers in mixed solvents has been surging. A large number of methods have been used for measurement of preferential adsorption: diffusion,[12,13] isopiestic distillation,[14] swelling of gels,[15] and membrane equilibria.[16-22] However, the method of light scattering has been used most frequently.[23-40] Sedimentation equilibrium, which may provide essentially the same information as light scattering, has been employed rather rarely.[26,41-43]

The solvent power of a mixed solvent may be studied through the second virial coefficient, which may be obtained from measurements of osmotic pressure, sedimentation equilibrium, or light scattering.[24,25,27] However, the experimentally less demanding measurement of intrinsic viscosity is routinely used for this purpose.[17,29,30,34,35,39,44-50]

Accumulating experimental evidence pointed to the inadequacy of the early oversimplified treatments. The necessity of building a more sophisticated model of three-component systems has been recognized in a series of papers.[51-56] Several publications[10,25,57,58] conveniently summarize some aspects of all these problems.

Recently, we have developed a powerful evaluation technique of sedimentation equilibriium experiments[59-61] using automatic scanning of photographic plates[62] and extensive computer analysis. The method is capable of yielding the preferential adsorption coefficient and second virial coefficient in a single experiment. In the present study, the method is applied to three polystyrene samples with narrow distribution of molecular weights dissolved in two combinations of solvents (benzene + cyclohexane; ethyl acetate + cyclohexane). The whole range of compositions of these solvent mixtures is studied.

In our hands, none of the existing theories described the phenomenon in reasonable agreement with experiment. In this study, we first describe the phenomenon and derive the basic formulas. These formulas are then applied to a phenomenological expression for ΔG_{mix}. The resulting relations are then used for the analysis of our experimental data for the second virial coefficient and the preferential adsorption parameter.

Theoretical

In this work, we will use several composition variables: number of moles n_i, concentration c_i (in g/mL), molality m_i, and volume fraction *before mixing* ϕ_i. In our notation, the indices 1, 2 will be used for the two solvent components, index 3 for macromolecules. The subscript μ means constant chemical potential of both solvent components; m_i is the constant molality of the ith component. Superscript zero will be used for designation of the quantity

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