Phase Equilibria in Cellulose Acetate–Acetone Solutions. The Effect of the Degree of Substitution and Molecular Weight on Upper and Lower Critical Solution Temperatures

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ABSTRACT: Upper and lower critical solution temperatures have been determined for acetone solutions of cellulose acetate samples with varying degrees of substitution. The Patterson–Delmas theory of corresponding states, based on the Prigogine theory, has been used to describe the molecular weight dependence of these critical temperatures. This method is most successfully applied to the primary acetate, but the data for the secondary acetate are less amenable to this theoretical approach, possibly because of the copolymeric nature of such samples.

Phase separation in polymer solutions has been studied extensively, particularly in systems where immiscibility occurs as the temperature is decreased. By recording the precipitation temperatures T_p at several concentrations for each polymer fraction it is possible to estimate from the resultant cloud point curves an upper critical solution temperature (UCST) which, in the limit of infinite polymer molecular weight, is equal to the well-known Θ or Flory temperature. Such solutions exhibit endothermic heats of mixing and can be described with reasonable accuracy by the Flory–Huggins lattice theory, which predicts that the characteristic interaction parameter of the system χ_1 assumes a value of 0.5 at the Θ temperature and decreases with increasing temperature.

The opposite effect, where the polymer precipitates as the temperature is increased, was originally reported for certain polar systems and attributed to the existence of specific interactions between the polymer and solvent which were thermally labile.[2] More recently Rowlinson and his coworkers[3,4] showed that nonpolar systems also underwent phase separation on elevation of the temperature, but now precipitation occurred well above the boiling point of the liquid. In fact in these nonpolar systems T_p is often quite near the critical point of the solvent in contrast to many of the polar solutions where the polymer usually separates at temperatures below or near the solvent boiling point. From measurements at these elevated temperatures a lower critical solution temperature (LCST) can be estimated in a manner analogous to that for the UCST, except that it is now the minimum of the coexistence curve which is recorded (see Figure 2).

The simpler two-parameter theories cannot predict the LCST, but application of the three-parameter Prigogine theory,[5,6] which also considers the effect of the changes in free volume of the components, leads to a new expression for χ_1

$$\chi_1 = (-U/RT)\nu^2 + (C_p/2R)\tau^2 \qquad (1)$$

The temperature dependence of this relation now allows χ_1 to vary as shown schematically in Figure 1 (left), thereby providing for the appearance of two temperatures at which phase separation may be observed. Here $-U$ is the energy of vaporization of the solvent, C_p is its configurational heat capacity, R is the gas constant, and ν and τ are temperature-independent parameters. The factor ν is related to the cohesive energy and segment size of the solution components, while τ characterizes the free volume difference between solvent (1) and polymer (2) and is defined by

$$\tau = 1 - \frac{T_1^*}{T_2^*} \qquad (2)$$

As use is made of the law of corresponding states to provide a basis for comparison of LCST's in various solvents[5,6] one can, by choosing a suitable reference liquid, reduce all appropriate parameters to dimensionless quantities on division by a reduction parameter. Thus the reduced temperature $\tilde{T} = T/T^*$, where T^* is the characteristic reduction parameter for a given component. Equation 2 expresses τ in terms of these reduction temperatures.

Patterson and Delmas[7] have derived an expression for χ_1 at the critical miscibility point, using the Prigogine theory, in which it is related to the reduced volume $\tilde{V}_1$ of the solvent

$$\chi_1(\text{crit}) = \frac{c_1\nu^2}{1 - \tilde{V}_1^{-1/3}} + \frac{c_1\tau^2}{2(4/3\tilde{V}_1^{-1/3} - 1)} = 1/2(1 + r^{-1/2})^2 \qquad (3)$$

where $3c_1$ is the number of external degrees of freedom possessed by the solvent molecule. χ_1 can also be related to the molecular weight of the polymer through r which is the ratio of the molar volume of the polymer to that of the solvent and is taken to be independent of temperature. If the reduced volume $\tilde{V}_1$ is calculated and the constants $c_1\nu^2$ and $c_1\tau^2$ are estimated, then the

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[2] (a) F. E. Bailey and R. W. Callard, *J. Appl. Polym. Sci.*, **1**, 56 (1959); (b) W. Burchard, *Int. Symp. Macromol. Chem., Toronto, Prepr.* (1968).

[3] P. I. Freeman and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).

[4] C. H. Baker, W. B. Brown, G. Gee, J. S. Rowlinson, D. Stubley, and R. E. Yeadon, *ibid.*, **3**, 215 (1962).

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[7] G. Delmas and D. Patterson, *Int. Symp. Macromol. Chem.*, Toronto, 1968.

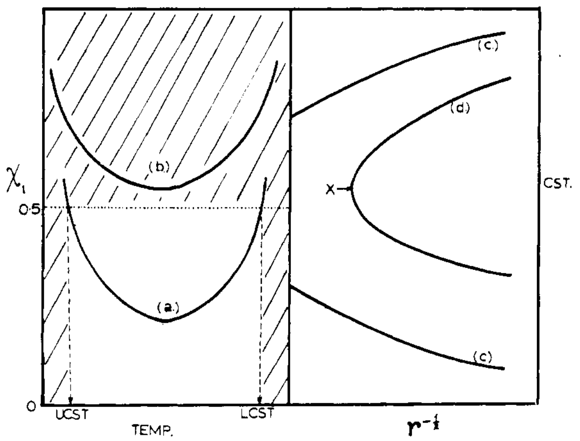

Figure 1. Left, a schematic representation of the variation of χ_1 with temperature for systems with (a) both upper and lower critical temperatures and compete miscibility in between and (b) total immiscibility and no critical temperatures. Right represents the Prigogine treatment for (c) the systems described in (a), and (d) systems in which the solubility is molecular weight dependent.

variation of CST with molecular weight can be predicted. This procedure is detailed later.

In Figure 1 (left) the two extreme types of behavior are represented for a polymer-liquid pair, (a) in which the system shows both UCST and LCST at $\chi_1 = 0.5$, with complete miscibility between these two temperatures, and (b) in which χ_1 is always >0.5, indicating the absence of total miscibility and so of both critical temperatures. The molecular weight dependence of the critical solution temperatures for system a is represented by curve c in Figure 1 (right), while curve d illustrates a system in which the solubility of the polymer is molecular weight dependent and represents a transition from a to b as the polymer molecular weight increases. Two systems which behave like those stylized in Figure 1 (right) are primary cellulose acetate and secondary cellulose acetate in acetone, and these have been examined on the basis of the Prigogine approach.

Experimental Section

Samples. (I) Cellulose Triacetate (Primary). Three fractions of fully acetylated cellulose (acetic acid content 61.78–62.56%), degree of substitution (DS) 3.0, were kindly donated by Dr. P. Howard, University of Surrey, while Dr. W. Burchard, University of Freiburg, generously provided two samples with DS of 2.88 and 2.86. A commercial sample of cellulose triacetate was fractionated as described elsewhere[8] and found to have a DS of 2.81.

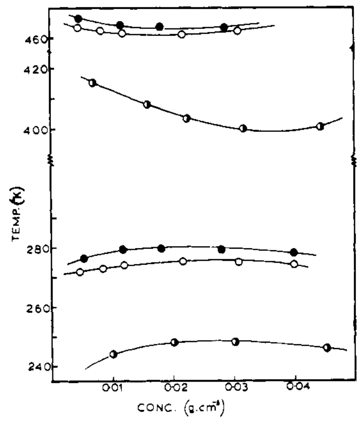

Figure 2. Coexistence curves for —●—, 3.0 acetate; —○—, 2.8 acetate; and —◑—, 2.2 acetate in acetone. The $\bar{M}_n$ for each: 55,000, 95,000, and 68,700, respectively.

(II) Secondary Cellulose Acetate (DS 2.0–2.5). Secondary cellulose acetate (BDH) was analyzed and found to have a DS of 2.2. A sample (21 g) was dissolved in acetone (1400 cm^3) and thermostated at 25°. Fractionation was carried out using *n*-hexane as precipitant and equilibration was achieved at each stage by warming the solution to redissolve the precipitated polymer which was subsequently allowed to reprecipitate slowly at 25°. The fractions were separated by centrifugation, dissolved in acetone, reprecipitated in excess petroleum ether, and finally dried *in vacuo*. Eight fractions were isolated and further analysis of each showed that the DS varied between 2.10 and 2.38 with a tendency to increase as the molecular weight decreased.

Molecular Weights. Number average molecular weights, $\bar{M}_n$, were measured in nitromethane and in chloroform, using a Mechrolab rapid membrane osmometer at a temperature of 37°. The membranes, Pecel 600, were conditioned to the solvent in the usual stepwise manner. The dependence of the second virial coefficient A_2 on $\bar{M}_n$ for secondary cellulose acetate in acetone was determined in the same instrument at a temperature of 23°.

Light Scattering. Acetone solutions of two samples of the secondary cellulose acetate were examined in a SOFICA light-scattering instrument using vertically polarized blue light (λ 436 nm). Measurements were made in special cells with tight-fitting Teflon stoppers (after a design by Dr. W. Burchard), and the slopes of (C/I_{90}) against C were determined in the temperature range 20–90°. The cells were found to be sufficiently well sealed to ensure that the solution concentration remained constant in this temperature range in spite of the fact that acetone boils at 56°. Refractive index increments were not measured; therefore, slopes quoted are only proportional to the second virial coefficient, *i.e.*, $2A_2/K_\Theta$.

Critical Solution Temperatures. Upper and lower critical solution temperatures were estimated from cloud point curves. Several solutions of each fraction in acetone were prepared in the concentration range 0.5–5% and sealed under vacuum in capillary tubes (i.d. = 1 mm). When the LCST was being measured, the tubes were slowly warmed in a silicone oil bath and T_p were recorded as the temperatures at which the image of a copper wire situated behind each tube became blurred by the solution turbidity. Plots of T_p against solution concentration produced shallow coexistence curves typified by those shown in Figure 2. If the samples had been completely monodisperse the true critical temperatures would then be represented by the minima of the curves, but polydispersity displaces the critical point to the right. Hence the recorded minima are not true critical temperatures, but as the curves are found to be relatively flat the error involved should be quite small. This is also the case for the UCST's.

Accurate measurement of UCST's was much more difficult. Solutions were first cooled in an acetone–carbon dioxide bath and the T_p was measured by allowing each to warm up slowly. The cloud point was recorded as the temperature at which turbidity disappeared; however, as many solutions were highly viscous, stirring was impeded and the accuracy of measurement was decreased accordingly. The UCST was taken to be the maximum temperature of the cloud point curve. The most concentrated solution which could readily be prepared for samples with a DS of 3.0 was 2.5%

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[8] J. M. G. Cowie and R. J. Ranson, *Makromol. Chem.*, in press.

TABLE I
REDUCED CRITICAL TEMPERATURES FOR PRIMARY CELLULOSE ACETATES OF VARIOUS MOLECULAR WEIGHTS IN ACETONE

Sample DS	$\bar{M}_n \times 10^{-5}$	$r^{-1/2}$	LCST, °K	$\tilde{T}_{\mathrm{LCST}}$	UCST, °K	$\tilde{T}_{\mathrm{UCST}}$
2.81	0.260	0.0478	466.5	0.1034	275.0	0.0609
2.81	0.333	0.0423	465.0	0.1031	274.0	0.0607
2.88	0.530	0.0335	462.6	0.1025	278.5	0.0617
2.81	0.554	0.0328	464.4	0.1029	275.0	0.0609
3.00	0.625	0.0308	469.0	0.1038	288.0	0.0638
2.81	0.952	0.0250	461.4	0.1023	275.0	0.0609
3.00	1.005	0.0243	472.0	0.1045	290.0	0.0643
2.86	1.580	0.0194	458.5	0.1016		
2.94	2.140	0.0167	464.0	0.1029	293.0	0.0649

for reasons discussed previously,[8] but the error in estimating the maximum or minimum precipitation temperature was small because the peaks of the phase equilibria curves usually occurred between 1 and 3% where T_p rarely varied by more than ±2°.

Results

Primary Cellulose Acetate. The data from the coexistence curves, typified by those shown in Figure 2, for the primary cellulose acetate in acetone are compiled in Table I. The solubility of the polymer shows no significant dependence on the molecular weight over the range available for study, and apparently corresponds to type a (c) of Figure 1.

In Figure 3 the critical temperatures are converted to reduced temperatures $\tilde{T}$ and plotted against $r^{-1/2}$. The reduced temperature $\tilde{T}$ is calculated from the ratio $T/T_1{}^*$ where T is the measured critical temperature and $T_1{}^*$ the reduction parameter calculated from the reduced volume $\tilde{V}_i$ through eq 4 and 5

$$T_i{}^* = \frac{T\tilde{V}_i{}^{4/3}}{(\tilde{V}_i{}^{1/3} - 1)} \qquad (4)$$

in which $\tilde{V}_i$ is derived from the expression

$$\tilde{V}_i = \left[\frac{\alpha_i T}{3(1 + \alpha_i T)} + 1\right]^3 \qquad (5)$$

where α_i is the coefficient of thermal expansion. For acetone a value of $T_1{}^* = 4509$ was calculated, while $T_2{}^* = 7904$ was estimated for primary cellulose acetate using a literature value[9] of $\alpha_{2L} = 6.53 \times 10^{-4}$ at 443°K. The curves in Figure 3 are derived from eq 3 with the aid of an Elliott 4130 computer; c_1 for acetone was taken as unity by comparison with hydrocarbons of similar structure, and τ was obtained from eq 2. The parameter $c_1\nu^2$ must be estimated and a limiting value can be calculated from[7]

$$c_1\nu^2 = {}^3/_8[{}^1/_3 - ({}^4/_3c_1\tau^2)^{1/2} + c_1\tau^2] \qquad (6)$$

using the calculated $c_1\tau^2$. This provides a starting point and $c_1\nu^2$ is then varied slightly until the most satisfactory fit between the experimental and calculated points is found. The computed curves were derived using $c_1\tau^2 = 0.184$ and $c_1\nu^2 = 0.0071$; this latter value was slightly lower than the limiting value of $c_1\nu^2 = 0.0082$.

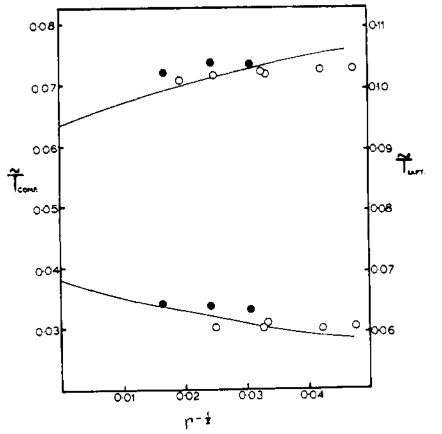

Figure 3. Comparison of experimental reduced temperatures $\tilde{T}$ in acetone for (—●—) 3.0 acetate and (—○—) 2.8 acetate, with the theoretical curves.

Secondary Cellulose Acetate. The introduction of an appreciable number of hydroxyl groups in the chain alters the solubility characteristics of the polymer markedly.[8] The primary acetate is more difficult to dissolve initially but the secondary acetate, while dissolving readily in acetone when $\bar{M}_n$ is less than $\sim 10^5$, then becomes insoluble when $\bar{M}_n$ exceeds this value. This limit is only an approximation and will vary with sample and DS. The data in Table II are plotted[10] in Figure 4, and exhibit the region of immiscibility predicted also by the theoretical curve, which is computed in a slightly different manner from that used for the primary acetate.[12]

A coalescence point, corresponding to × in Figure 1 (right), is chosen as the molecular weight which approximates the boundary between miscibility and immiscibility in the system, *i.e.*, the point at which UCST = LCST, and the roots of eq 3 are

$$ {}^1/_2[{}^7/_4 + ({}^3/_4c_1\tau^2 - 2c_1\nu^2)Q \pm \{{}^1/_{16} - ({}^3/_8c_1\tau^2 + c_1\nu^2)Q + ({}^3/_4c_1\tau^2 - 2c_1\nu^2)^2Q^2\}^{1/2}] \qquad (7)$$

where $Q^{-1} = (1 + r^{-1/2})^2$. $c_1\tau^2$ is calculated as before using $T_2{}^* = 8041$ which was derived from a literature

TABLE II
CRITICAL SOLUTION TEMPERATURES FOR SECONDARY CELLULOSE ACETATE

Sample DS	$\bar{M}_n \times 10^{-5}$	$r^{-1/2}$	LCST, °K	$\tilde{T}_{\mathrm{LCST}}$	UCST, °K	$\tilde{T}_{\mathrm{UCST}}$
2.38	0.269	0.0467	452.3	0.1003		
2.38	0.407	0.0380	447.9	0.0991		
2.32	0.487	0.0347	444.6	0.0986		
2.20	0.593	0.0315	438.2	0.0971	216.2	0.0479
2.30	0.631	0.0305	432.6	0.0959		
2.10	0.687	0.0292	414.7	0.0919	248.2	0.0550
2.20	0.860	0.0261	394.6	0.0875	268.2	0.0594
2.00	0.866	0.0260	389.9	0.0864		

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(9) J. Russell and R. G. van Kerpel, *J. Polym. Sci.*, **25**, 77, (1957).

(10) During the course of this work a lower critical solution temperature for a sample of secondary cellulose acetate was reported.[11] This has been included in Figure 4 and is in good agreement with the present data.

(11) L. S. Bolotnikova, T. L. Samsonova, and S. Ya Frenkel, *Vysokomol. Soedin., Ser. B*, **10**, 235 (1968).

(12) G. Delmas and D. Patterson, private communication.

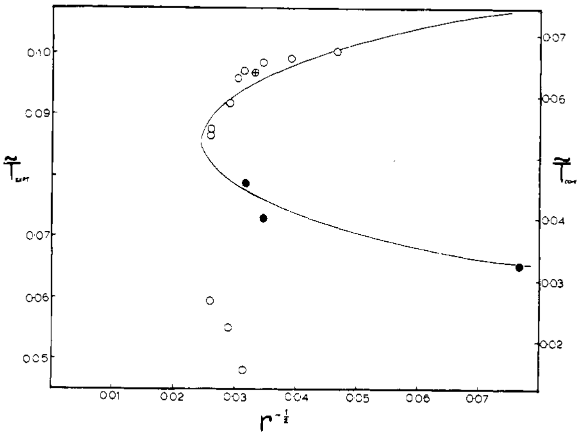

Figure 4. Comparison of experimental and theoretical reduced temperatures for the 2.2 acetate: —○—, data from precipitation measurements: —●—, points from light scattering and osmotic pressure measurements; —⊕—, obtained from ref 11.

value[9] of α_{2L} = 6.56 × 10^{-4} at 463°K. This allows $c_1\nu^2$ to be estimated for the coalescence $\bar{M}_n$ of 1.03 × 10^5, from

$$c_1\nu^2 = {}^1/_2\left\{{}^3/_4 c_1\tau^2 + \frac{1}{4Q} \pm \left({}^3/_4 \frac{c_1\tau^2}{Q}\right)^{1/2}\right\} \qquad (8)$$

The coordinates of the point × are then calculated from

$$\tilde{V}_1^{-1/3} = {}^7/_8 + {}^3/_8(c_1\tau^2 - c_1\nu^2)Q \qquad (9)$$

and the theoretical curve was finally computed using $c_1\tau^2 = 0.193$ and $c_1\nu^2 = 0.0086$.

Discussion

The molecular weight dependence of the UCST, or more correctly the maximum temperature of the coexistence curve T_c, is usually described by a linear relationship, proposed by Flory, which allows the data to be extrapolated to infinite molecular weight. This can be written as

$$\frac{1}{T_c} = \frac{1}{\Theta}\left\{1 + \frac{1}{\psi_1}\left(\frac{1}{r^{1/2}} + \frac{1}{2r}\right)\right\} \qquad (10)$$

where ψ_1 is the entropy parameter. The data for samples with DS of 3.0 are adequately represented by this equation with Θ_u = 300°K and ψ_1 = 0.78. Here we denote the Θ temperature with the subscript u to distinguish it from the analogous temperature determined in the lower critical solution region, which shall be designated Θ_L. For lower values of DS the results are less satisfactory but appear to extrapolate to Θ_u ~ 280°K.

Examination of the Patterson–Delmas theory shows that the variation of T_c with $r^{-1/2}$ is nonlinear, but although a curve is predicted, linearity in the molecular weight range 3 × 10^4 to 10^6 may be expected within the experimental error.[7]

In the lower critical solution region eq 10 provides a good representation of the data for samples with DS 2.8–2.88 and yields values of Θ_L = 454°K and ψ_1 = −1.64. The results for DS 3.0 are less accurate in this range. These figures can be compared with the extrapolations from the computed curve of Θ_L = 426°K and Θ_u = 310°K.

Several points arise from a comparison of the theoretical curves with the experimental data which are worth noting. At no time is the absolute value of the critical temperature (or $\tilde{T}$) predicted correctly by the theory. In order to match the theoretical curves with the experimental points it is necessary to displace the temperature axis. For the primary acetate this temperature shift amounts to ~169° while a shift of ~148° was required for the secondary acetate. In the polystyrene–methyl acetate system[7] the temperature shif- was of the order of 80°.

The trend in $(d\tilde{T}/dr^{-1/2})$ is also overemphasized by the theoretical curves, which accounts for the reported variation in the extrapolated values of Θ. There is, however, a remarkably good prediction of the spread between the upper and lower precipitation temperatures for the primary acetate, which provides a reasonably well-defined picture of the region of total miscibility for the system. For the 2.2 acetate the correlation is somewhat less obvious, and although the molecular weight dependence of the polymer solubility can be predicted, the region of miscibility is now much greater than the theoretical curve suggests. Some indication of the reasons for this discrepancy can be found in the temperature dependence of the slopes derived from the (C/I_{90}) *vs.* C plots. Solutions of two samples, $\bar{M}_n$ = 48,700 and 58,000 in acetone, were examined and the slopes were found to vary in a rather unusual manner with change in temperature (see Figure 5). In both cases a decreasing slope was obtained with increasing temperature and the value approached zero, at a temperature which depended on the sample molecular weight. With a further increase in temperature the slopes increased instead of becoming negative as expected. If the temperatures at which pseudoideal conditions are apparently attained are plotted in Figure 4,

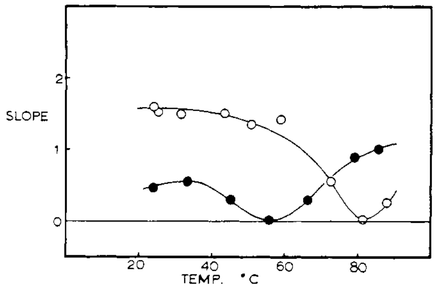

Figure 5. Slope of (C/I_{90}) *vs.* C plot as a function of temperature for 2.2 acetate: —○—, M_n = 58,000; —●—, M_n = 48,730.

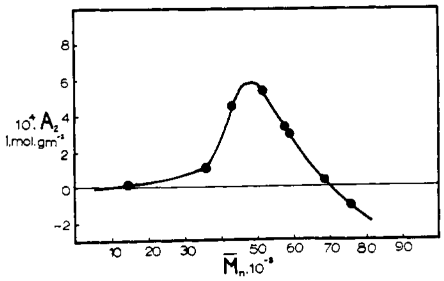

Figure 6. Variation of A_2 with $\bar{M}_n$ at 296 °K for 2.2 acetate in acetone.

they are found to lie in the upper critical region predicted by the theoretical curve. Second virial coefficients A_2, for the 2.2 acetate–acetone system, were also measured at a fixed temperature of 296°K for a range of molecular weights. These varied in the manner shown in Figure 6, which indicates that the solubility limit is above 80,000 and that $A_2 = 0$ for $\bar{M}_n \sim 10{,}000$. This latter value is also plotted in Figure 4 and again lies on the theoretical curve.

Of course this agreement may be completely fortuitous. On the other hand as over 25% of the side groups in the chain are hydroxyls the 2.2 acetate can be regarded effectively as a copolymer. As such, one would expect a complex interaction to exist between the polymer and solvent with both hydroxyl and acetyl groups behaving in different ways. Moore[13] showed that the secondary acetate was heavily solvated by acetone and that seven solvent molecules were associated with each partially substituted glucose residue. This suggests that there is a strong interaction between solvent and polymer which may involve hydrogen bonding between the hydroxyl groups and acetone in addition to the interaction between the solvent and the acetyl groups. For random copolymers it has been suggested that the solubility behavior can be anticipated by averaging the separate homopolymer solubility parameters according to the copolymer composition, and so a copolymer consisting of polar and nonpolar residues will dissolve in solvents of intermediate polarity such as acetone.

Consequently the secondary acetate behaves partly like the primary acetate, exhibiting LCS behavior below which there is a region of miscibility which would normally finish as predicted by the theoretical curve and the decreasing A_2. Before the polymer can precipitate, as the temperature decreases further, the interaction of the hydroxyl groups with acetone enhances the solubility and prevents phase separation at the expected temperatures. This secondary solvation depresses the UCST for each sample until phase separation eventually occurs at temperatures much lower than expected. While it is unlikely that hydrogen bonding is the sole cause of the solvation, as the suggested phase separation temperatures are as high as 80° for certain samples, it probably becomes increasingly important at lower temperatures.

The degree of substitution in the cellulose molecule has a significant effect on the precipitation temperatures. In the lower critical region a decrease in DS results in a decrease in LCST; a similar trend is observed in the upper critical region.

The application of the Prigogine theory to phase separation in these systems is thus moderately successful, particularly for the primary acetate, but the complications introduced by the copolymeric character of the secondary acetate do not allow a critical assessment of this system to be made at present, especially as the polymer is semipolar and the theoretical approach is derived primarily for nonpolar systems.

(13) W. R. Moore, *J. Polym. Sci., Part C*, **No. 16**, 571 (1967).

Kinetics of Autoxidation of Atactic Polypropylene in the Presence of Cobalt Salts by Infrared Spectroscopy

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ABSTRACT: A general scheme previously reported for the uncatalyzed autoxidation of polyolefins was modified to account for the metal-catalyzed [cobalt(III) acetylacetonate] autoxidation of atactic polypropylene (APP). This modified scheme yielded various kinetic expressions relating a net maximum rate of carbonyl formation ($\rho_{\mathrm{m,net}}$) as a function of catalyst and oxygen concentrations. These expressions could satisfactorily account for the experimental data obtained. The reaction temperature ranged from 100 to 130°, the metal concentration from (0.3 to 82.0) $\times 10^{-7}$ mol/7.5 mg of APP, and the oxygen concentration [O_2] from 5 to 100 vol %. As anticipated, at relatively low catalyst concentrations [Cat.], $\rho_{\mathrm{m,net}}$ was approximately first order in respect to [Cat.] and about zero order in [Cat.] at relatively high values of [Cat.]. Further, a satisfactory relationship between $\rho_{\mathrm{m,net}}$ and [O_2] could be obtained.

Mathematical expressions derived from a general kinetic scheme have been satisfactorily applied to the uncatalyzed autoxidation of polyolefins such as polypropylene[2,3] and polybutene[2a,4,5] in the bulk phase. This scheme was recently modified by Bawn and Chaudhri[6] to account for the kinetics of manganese salts catalyzed autoxidation of atactic polypropylene

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(5) S. S. Stivala, G. Yo, and L. Reich, *ibid.*, **13**, 1289 (1969).

(6) C. E. H. Bawn and S. A. Chaudhri, *Polymer*, **9**, 81 (1968).