Lower Critical Solution Temperature Behavior of Ethylene Propylene Copolymers in Multicomponent Solvents

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Synopsis

The lower critical solution temperature (LCST) locus for ethylene-propylene copolymers has been determined as a function of pressure in a variety of single and multicomponent solvents. The lower critical end-point temperature (LCEP), which is the intersection of the LCST locus with the vapor-pressure curve, was found to be predictable from the solvent density as previously established for single-component solvents by Charlet and Delmas.[1] Dissolving a low-molecular hydrocarbon gas such as propylene in an alkane has a dramatic effect on lowering the LCEP, and can reduce phase-separation temperatures to levels at which this technique becomes attractive as a practical method for polymer recovery from diluents such as those used in solution polymerizations. Temperatures considerably above the LCEP are needed to minimize the residual polymer concentration in the solvent in the two-liquid-phase region. The solvent critical temperature must be approached for essentially complete elimination of the polymer from the solvent phase. The LCST locus was found to be a linear function of pressure for all of the systems investigated, and the slope of the line, $d(LCST)/dP$, could be well correlated as a function of solvent density and critical temperature. From the relationship between the LCEP and solvent density and the correlation for d(LCST)/dP, the location of the LCST locus can be readily predicted from a knowledge of solvent properties.

INTRODUCTION

It has long been recognized that most solutions of amorphous, nonpolar polymers in nonpolar solvents show a positive or endothermic heat of mixing, and that below a certain critical temperature (upper critical solution temperature or UCST) phase separation of the polymer solution occurs. This positive heat of mixing arises from the replacement of energetically preferred solvent–solvent and polymer–polymer contacts by unlike solvent–polymer contacts when a solution is formed.

In 1960, Freeman and Rowlinson[2] demonstrated that polymer-solvent systems also have a lower critical solution temperature (LCST), so that separation of the solution into multiple phases results from raising the solution temperature. Furthermore, since the LCST usually occurs at temperatures approaching the solvent critical temperature, pressures above atmospheric accompany it, and unlike the UCST, the LCST tends to be very pressure dependent.

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Essentially, as the system temperature approaches the critical temperature of the solvent, the solvent molecules tend toward a gas-like configuration, with all distinction between liquid and gas finally disappearing at the critical point. However, the very high-molecular weight polymer is far removed from its critical point and, consequently, undergoes no such 'dilation' effect as the temperature is raised. Accordingly, the polymer has a contracting effect on the solvent molecules, confining them to a more rigid matrix, and this lesser degree of spatial disorder for the solvent between the dilated and confined states results in a decreased entropy of mixing which leads to phase separation.

The phase behavior of a polymer solution at high temperature is shown schematically in Figure 1 as a function of temperature and pressure. The dashed line is simply the vapor pressure curve for the solution, and at temperatures below the lower critical end point (LCEP), one liquid phase exists above the vapor-pressure curve and a liquid and vapor phase exist below it. Polymer separation occurs when the temperature reaches the LCEP. Thus, two liquid phases, one polymer rich the other polymer lean, are present in this pressure/temperature region as long as the pressure is below the solid curve denoted as the liquid-liquid transition locus (temperatures along this locus are LCST's). At higher pressures, the polymer redissolves to give a single liquid phase. Below the vapor-pressure curve, two liquid phases and a vapor phase coexist.

Phase separation at the LCST has potentially significant practical applications for the recovery of polymers produced by solution polymerization. At present, solution polymers are isolated by solvent evaporation techniques, such as steam stripping, which have a high energy cost. A phase-separation method could reduce energy requirements appreciably. This was recognized by Anolick and Goffinet,[3] shortly after the appearance of Freeman and Rowlinson's paper, who investigated the separation of ethylene-propylene copolymer (EPM) from hexane solution at the LCST. Since ethylene-propylene elastomers are produced as relatively dilute solutions of
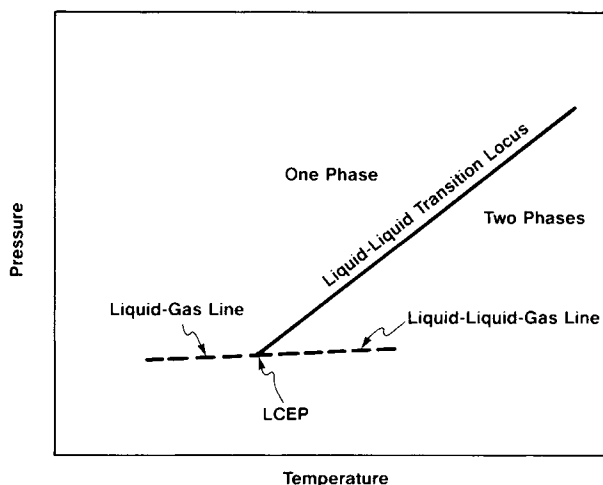

Fig. 1.   Polymer solution phase diagram.

about 10% concentration, there is considerable incentive to develop a more energy-efficient recovery process for the polymer.

Charlet and Delmas[1] studied the LCST behavior for EPM in a wide range of solvents, and found that for C_6 and C_7 alkanes, as would typically be used in an EPM polymerization process, the LCST is 20–80°C less than the solvent critical temperature. This leads to relatively high temperatures for polymer separation at the LCST, and consequently, a process based on this phenomena would require a substantial investment in heat-exchange equipment. To get around this problem Irani, Cozewith, and Kasegrande[4] showed that dissolving a low-molecular weight hydrocarbon gas, such as ethylene or propylene, in an EPM solution reduces the LCST considerably. By using a dissolved gas in combination with a relatively poor solvent, polymer can be separated from solution at temperatures not far from the polymerization temperature. For example, in the EPM/propylene/isopentane system the LCST is 63°C as compared to 170°C for EPM/n-hexane. Thus, by proper choice of the solvent for a given polymer, polymer recovery by phase separation at or above the LCST can be quite attractive.

This paper presents the result of an experimental study of the phase behavior of EPM in various solvents and solvent mixtures, with and without dissolved propylene. The LCST locus was determined as a function of pressure, and the composition of the separated solvent phase at temperatures above the LCST was measured to determine the efficiency of polymer recovery. From these results, correlating equations were developed for the lower critical end point (LCEP) and slope of the LCST locus as a function of solvent density and critical temperature. This provides a method for predicting the phase-separation characteristics of EPM solutions over a broad range of solvent compositions.

EXPERIMENTAL

Two EPM copolymers and one EPDM terpolymer obtained from the Exxon Chemical Company were used in this study. The relevant properties of these polymers denoted as EPM-1, EPM-2, and EPDM-1, appear in Table I. The pure solvents tested were obtained from commercial suppliers at 99% purity while Exxsol hexane, a mixed hexane commercial solvent which had the composition shown in Table II, was obtained from the Exxon Chemical Company.

The experimental program was executed in two parts. Visual studies in a sight glass apparatus were used to determine the pressure-temperature

TABLE I
Polymer Characteristics

Sample	$M_n{}^a$	$M_w{}^a$	M_w/M_n	Polymer composition, wt%	
				Ethylene	Diene
EPM-1	70,000	140,000	2	43	0
EPM-2	20,000	400,000	20	40	0
EPDM-1	60,000	300,000	5	46	9

[a] $\overline{M}_n$, $\overline{M}_w$ = Number and weight average molecular weight.

range over which phase separation takes place, and autoclave experiments were carried out to measure the residual polymer concentration in the solvent phase after phase separation. The two experimental procedures will be discussed separately.

LCST Determination

Figure 1 shows a schematic of the sight glass apparatus which consisted of a high-pressure Jerguson sight glass (Jerguson Gauge and Valve Co., Burlington, MA) fitted with a Magnedrive stirring unit. Fresh polymer solution was introduced into the sight glass via the hand pump and the gases via a compressor. An electrical heating mantle provided the appropriate thermal environment. Temperature was measured and controlled to $\pm 0.1°C$ by a thermocouple seated in a well in the side of the sight glass. Pressure was measured to ± 5 psia by a Heiss gauge previously calibrated with the steam tables.

Prior to each LCST determination, the sight glass was cleaned, dried, and evacuated. The polymer solution to be investigated was introduced into the sight glass with the hand pump until the system was liquid full. Then the heat was turned on and the system temperature raised to a value considerably above the anticipated LCST. Throughout the heating period the system pressure was constantly adjusted by releasing some solution through the vent valve, while still maintaining the pressure at a level necessary for the solution to be one phase. The composition remained unchanged since the solution vented was always homogeneous.

With the sight glass at the desired temperature, the system pressure was slowly lowered until the first sign of turbidity was noticed in the sight glass which marked the system's transition from one phase to two phases. The pressure was now raised to bring the system back into one phase, and the temperature lowered by 5 to 10°C. After the new temperature equilibrium was established, the pressure was again lowered until a transition from one to two phases occurred. This procedure was repeated until a temperature was reached where the system went from a single liquid to a liquid-gas without any trace of turbidity. The system was now at its vapor pressure line at a temperature below the LCEP. The system was allowed to go from liquid-gas to liquid-liquid-gas above the LCEP by raising the temperature in small increments along the vapor-pressure line. Measurement of the pressure as a function of temperature along the vapor-pressure line generates the dashed curve shown in Figure 2 which intersects the one-liquid

TABLE II
Gas Chromatograph Analysis of Exxsol Hexane

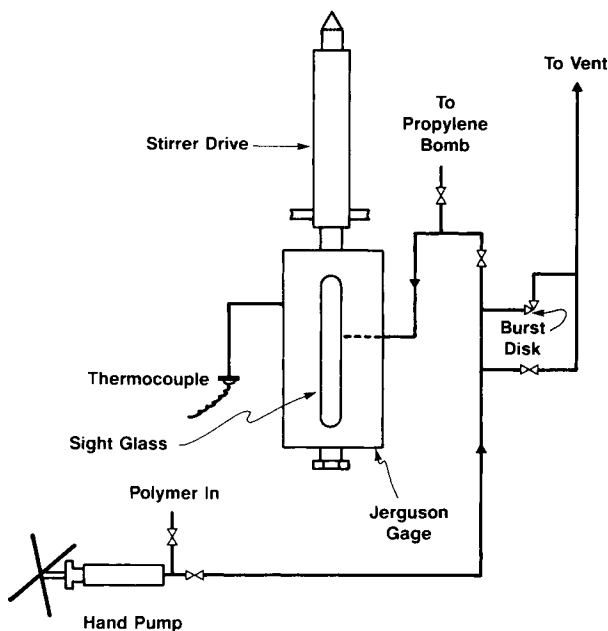| Component	Wt%
2-Methyl pentane	20.7
3-Methyl pentane	17.4
n-Hexane	38.0
Methyl cyclopentane	21.6
Others	2.3
	100.0

Fig. 2. Sight glass apparatus for LCST determinations.

phase to two-liquid phases transition line at the LCEP. The most accurate experimental procedure for determining the LCEP consists of first measuring the liquid-liquid immiscibility transition down to the vapor-pressure line, then measuring the vapor-pressure line for the liquid-gas to liquid-liquid-gas transition. The LCEP is the intersection of these two-phase loci. Since visual observation of turbidity is extremely difficult close to the LCEP, this temperature cannot be measured directly with accuracy.

A slightly different procedure was followed in order to establish the effect of propylene addition on the LCST. A small bomb was charged with a specific weight of liquid propylene in equilibrium with its own vapor, and attached to the gas entry line of the unit. Its contents were then added to the sight glass, which had known volume. After allowing enough time for the transfer, the bomb was disconnected and reweighed, the difference in weight being the amount of propylene that had been transferred to the sight glass. By measuring the density of the polymer solution and the volume of the polymer solution transferred per turn of the hand pump screw, the weight of polymer solution transferred to the sight glass to make the system liquid-liquid full could be determined. Thus, knowing the weights of the polymer solution and the propylene, the concentration of propylene could be established. By again ensuring that only a homogeneous solution was vented during heat up, the solution composition could be maintained relatively constant.

Polymer Concentration Measurements

For polymer solutions without added propylene, the cleaned and dried autoclave was filled with a 6% polymer solution and sealed. The system was then brought to the appropriate temperature (usually some value above

the LCST) with regular adjustment of the pressure to ensure that the polymer solution remained one phase. With the system at temperature, the pressure was slowly released with vigorous stirring in order to minimize any severe temperature fluctuations. The final pressure was adjusted to be between 0 and 300 kPa above the equilibrium vapor pressure. Keeping the pressure at less than 300 kPa above the vapor pressure minimizes the solubility of the polymer in the solvent phase.

With the system at conditions, stirring was stopped, and the phases allowed to settle for 15 minutes after which the top sample line was purged of unequilibrated liquid by removing 5 cc of the autoclave contents. Following the purge, approximately 40 g of the top phase was collected in a bomb, weighed, and stripped of solvent to determine the amount of polymer.

Because the top-phase sample collected was invariably very lean in polymer, the average composition inside the autoclave now exceeded 6% by weight of polymer. In order to bring the system back to its original conditions it was first necessary to introduce pure solvent, which closely resembled the extracted sample, until the system just became liquid-liquid full. The additional fluid pressure required to change from two-liquid phase to one phase was obtained by introducing 6% polymer solution into the system. This procedure had been empirically developed as being the most effective for returning the system as close as possible to the initial 6% polymer solution.

Occasionally, with the entire system in one phase either at temperatures below the LCST or at high enough pressures for temperatures above the LCST, a solvent-phase sample was removed and the solvent flashed, as described above, to establish the polymer concentration. If the composition showed deviation from the required 6%, then appropriate corrections were made. Using such a procedure it was possible to run almost indefinitely with a specific polymer–solvent system, adjusting operating parameters along the way or introducing additional components like propylene. In the event that a new polymer or solvent needed to be investigated, the entire unit was dismantled and cleaned out to remove all traces of the previous components before being recharged.

In studies with propylene, considerable effort was made to maintain the propylene concentration constant, but as this proved extremely difficult to achieve, and a variation of $\pm 5\%$ existed over a series of experiments. The concentration of propylene present during any specific sampling step was determined by purging the sample line and then collecting roughly 40 g of sample in the accurately weighed bomb. The bomb was equilibrated to ambient conditions and the propylene was slowly vented by cracking open the top valve. Considerable care was exercised during the propylene venting step to ensure minimal entrainment of the liquid sample with the vented propylene. After venting the propylene, the bomb was reweighed, the weight of propylene and sample being obtained by difference and the percent propylene present in the sample was thus calculated. The remaining steps for sample analysis were the same as described above for the propylene-free case.

After a sample had been removed, the system was brought back to proper conditions as follows. First the weight of propylene required to return the

system to 10% propylene was calculated, and the volume of propylene required was calculated from its known room temperature density. The hand pump was now used to introduce pure solvent into the sight glass to a predetermined height after which the valve connecting the sight glass to the hand pump was closed. Using the compressor, propylene gas was pumped into the top of the sight glass and allowed to condense as a liquid layer above the solvent level in the sight glass. The narrow diameter of the sight glass together with the complete absence of mixing permitted the propylene to remain as a distinct layer on top of the solvent, while minimizing the amount of propylene that went into solution in the solvent.

Using a cathetometer, the sight glass had been previously calibrated to establish volume as a function of liquid height. Knowing the exact volume of propylene required, it was possible to vent the excess propylene from the top of the sight glass until the height of propylene coincided with the required volume. Transfer of the propylene was now completed by pushing it ahead of the pure solvent through the sight glass and into the autoclave. Introduction of pure solvent was continued until the system was liquid full, after which the pressure was raised to the desired value by again introducing a 6% polymer solution using the Ruska pump (Fig. 3).

RESULTS

LCST Studies

The temperature at which phase separation occurs in a polymer solution is a function of polymer molecular weight, molecular weight distribution, (MWD) and concentration. In order to determine the LCST, which is the minimum separation temperature in a given system, narrow MWD fractions of varying molecular weight are used and the results extrapolated to a polymer of infinite molecular weight. Furthermore, measurements must be
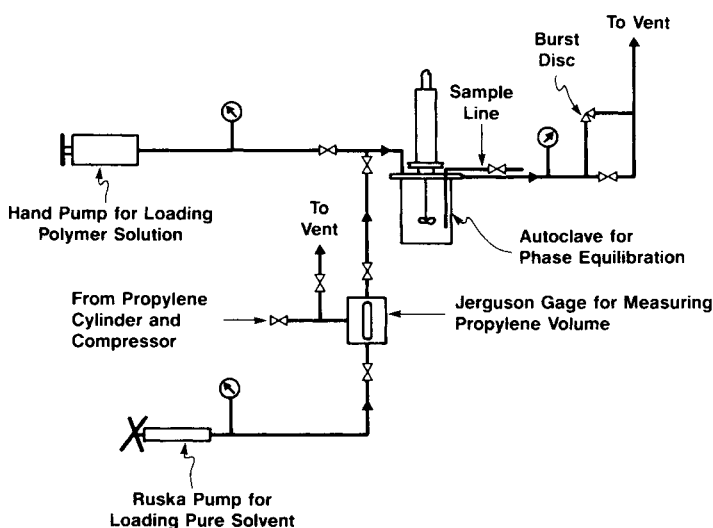

Fig. 3.   Autoclave apparatus for phase composition determination.

made over the proper range of concentrations since separation temperature usually goes through a minimum as a function of polymer concentration. In this study we were primarily interested in the phase-separation behavior of ethylene-propylene co- and terpolymers (EPM and EPDM) with molecular weight and MWD typical of commercially available materials. Thus we measured cloud-point curves rather than the true critical locus in the EP-solvent systems investigated. However, for simplicity, we refer to the temperatures along the cloud-point curve as LCST's and the temperature at which the cloud-point curve intersects the vapor-pressure curve as the lower critical end-point temperature (LCEP), as shown in Figure 1.

From the cloud-point curves for EPM-1 in n-hexane at concentrations of 0.5–10 wt% (Figs. 4 and 5), the concentration dependence of the LCEP was determined as shown in Figure 6. The results at 4 and 8 wt%, respectively, scatter from the curve, but it appears that the LCEP is relatively insensitive to concentrations between 1 to 8 wt% and the minimum value lies in this range. Consequently, most of the data in this study were obtained at 6 wt% polymer concentration.

The effect of molecular weight for these unfractionated polymers is indicated in Figure 7, which compares cloud-point curves for EPM-1 and EPM-2, two copolymers of similar ethylene content. The breadth of the MWD differs markedly for these polymers so that $\overline{M}_w$ is higher for EPM-2 than EPM-1 but $\overline{M}_n$ is lower. Since LCST behavior should be dominated by the high-molecular weight fraction of the MWD, it is no surprise that the LCST is considerably lower for EPM-2 than EPM-1. However, the 20°C difference in LCEP for these two polymers is much greater than the 3–10°C difference Charlet and Delmas[1] assumed as the maximum influence of molecular weight for the EP polymers in their study. Thus, some of the LCST vari-
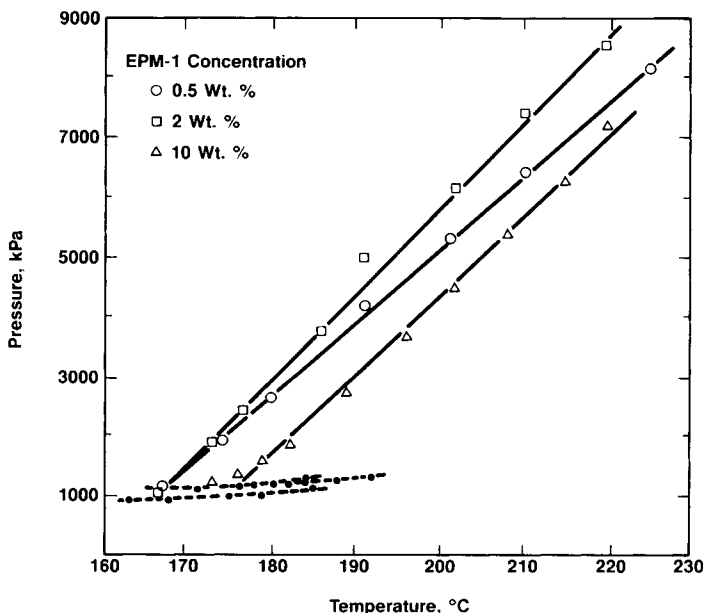

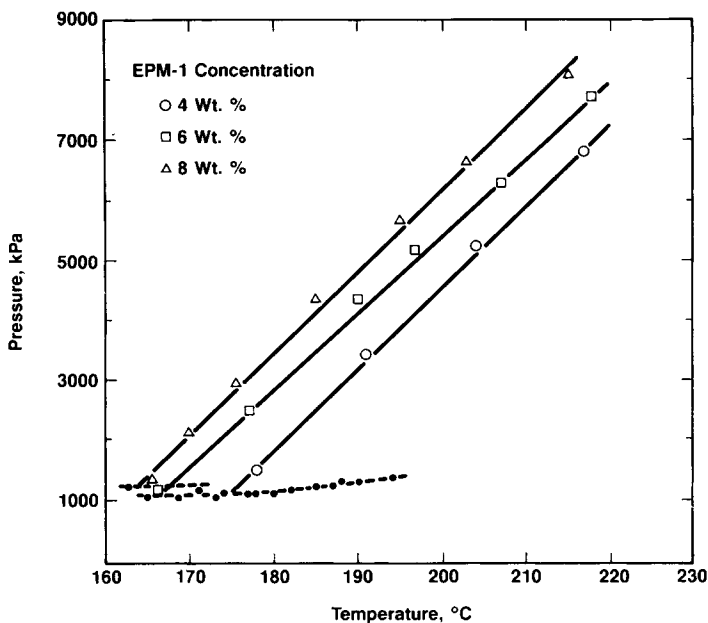Fig. 4.   Effect of polymer concentration on critical locus in n-hexane.

Fig. 5.   Effect of polymer concentration on critical locus in n-hexane.

ations these workers attributed to composition changes may have been due to molecular weight effects. We also note that the slope of the LCST locus is similar for EPM-1 and EPM-2 at low pressure, but as the pressure increases, the EPM-2 curve deviates from linearity. This may be a consequence of the very broad MWD of this material, but not enough data is available to make a firm conclusion.

The cloud-point curve for EPDM-1, which is a terpolymer containing about 46 wt% ethylene and 9 wt% ethylidene norbornene is also shown in Figure 7. This polymer has a lower LCEP than EPM-2 despite a lower value of $\overline{M}_w$. We attribute this to compositional differences between the polymers. EPM-1 represents the lower end of the ethylene content and molecular weight range for commercially available EPDM polymers. Thus, the LCST
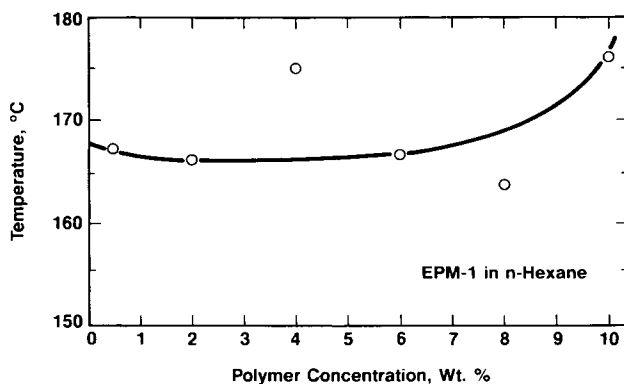

Fig. 6.   Effect of polymer concentration on the LCEP.

for this polymer represents a worst case in terms of ease of separation when considering the practical application of phase separation to polymer recovery. Consequently, most of our work was done with EPM-1.

Phase diagrams for EPM-1 in a variety of C_5-C_6 aliphatic solvents are shown in Figures 8 and 9. The LCEP values, as given in Table III, generally increase with the solvent molecular weight and with the solvent structure in the order linear < branched < cyclic. Charlet and Delmas[1] have reported similar results, and our LCEP values in *n*-pentane and *n*-hexane agree well with theirs. For EPM-1 in *n*-butane at 1.5 wt% concentration, an LCEP of 37°C has been measured in our laboratory.[5] Normal butane is a borderline solvent for EPMs and at moderate pressure can only completely dissolve polymers of low ethylene content.

The critical locus in Figures 8 and 9 appears to be remarkably linear over a broad pressure range for all of the EPM-1/solvent systems investigated. Similar linearity was found for polyisobutylene[6] and polystyrene[7] in various solvents. There is no reason to expect a linear relationship in general, and indeed Zeman et al.[6] found results for polydimethylsiloxane to show a strongly curved critical locus. However, the linearity for EPM solutions is fortunate since a knowledge of only the LCEP and the slope of the cloud-point curve, $d(LCST)dP$, will allow prediction of the P,T phase diagram.

The presence of dissolved propylene in EPM/solvent systems has a dramatic effect on lowering the LCEP as shown by the data in Figures 10 and 11 and Table III for propylene mixtures with *i*-pentane and Exxsol hexane. In the case of hexane, 10 wt% propylene lowers the LCEP by about 40°C, while for *i*-pentane, 10% propylene would give an LCEP of about 65°C, which is close to EPDM polymerization temperatures. Thus, in this latter system, it would be possible to recover the polymer by phase separation with little or no additional heating.
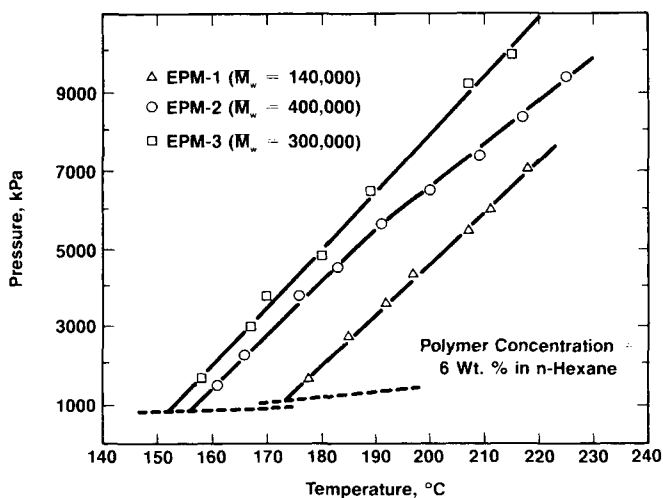

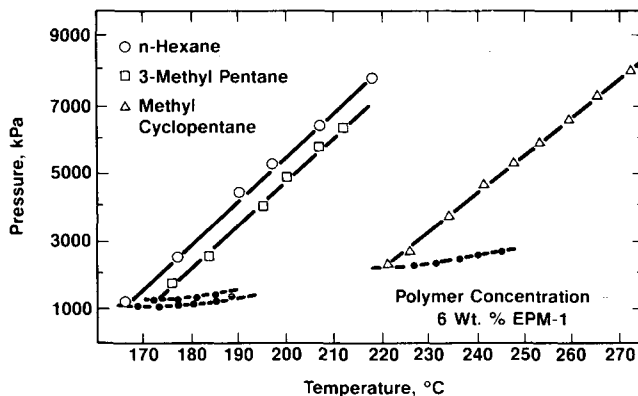Fig. 7. Effect of EP properties on the LCST.

Fig. 8. LCST locus in various solvents.

Similar results have recently been published by MacHugh and Guckes[8] for a polymer similar to EPM-1 in *n*-hexane solvent with ethylene and methane added to the solution. As would be expected, these lower molecular weight hydrocarbons have a greater effect on lowering the LCEP than propylene. LCEP and d(LCST)/dP results from reference[8] have been included in Table III for comparison. MacHugh and Guckes also show that at sufficiently high concentrations of dissolved gas (i.e., about 14% for methane), the UCST and LCST loci merge resulting in polymer insolubility at all temperatures.

For high-temperature phase separation to be an economical method for polymer recovery, essentially all of the polymer must be removed from the solvent phase to avoid the need for additional processing steps. Since the LCEP defines the temperature of incipient phase separation, temperatures higher than this would be required to minimize the polymer content of the solvent phase. We have measured the polymer concentration in the solvent in the two liquid phase region at temperatures above the LCEP and pressures near the vapor pressure, and the results with *i*-pentane and *i*-pentane containing 10 wt% propylene are compared in Figure 12. The initial con-
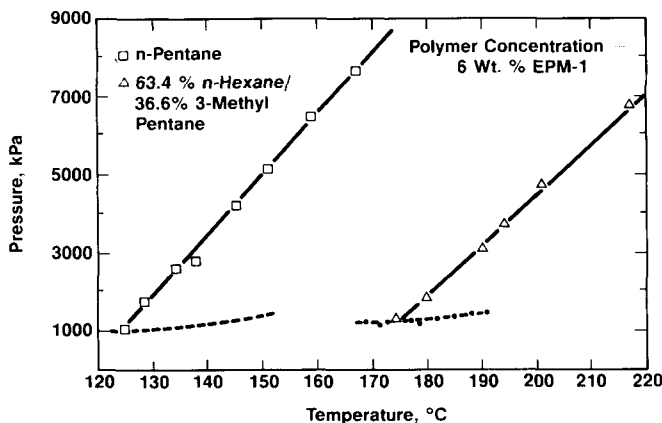

Fig. 9. LCST locus in various solvents.

TABLE III
Experimental Results Solvent Composition, wt%

System =	a[a]	b[a]	c[a]	c2[a]	d	e
Component						
Methane	11.4					
Ethylene		10.4	14.5	21.0		
Propylene					6.8	9.0
Butane						
Isopentane					93.2	91.2
n-Pentane						
n-Hexane	78.0	78.8	75.2	69.5		
2-Methylpentane						
3-Methylpentane	2.2	2.2	2.1	2.0		
Methylcyclopentane	8.4	8.5	8.1	7.5		
LCEP, °K	344	386	373	338	343	338
LCST at P = 0, °K	289	366	352	319	339	334
$d(LCST)/dP$, °K/atm	.60	.62	.54	.50	.55	.59
Solvent						
Density, g/cc at 25°C	.582	.632	.621	.605	.609	.607
T*, °K	3874	4210	4114	3962	4036	4017
P*, atm	3814	4039	3988	3906	4107	4094
T*/P*	1.02	1.04	1.03	1.01	.98	.98
Tc, °K	462	484	474	457	454	451

[a] Data of Ref. 8.

centration of EPM-1 in the solvent was 6 wt%. Temperatures considerably higher than the LCEP are needed to obtain low residual polymer concentrations. In the case of i-pentane, the polymer concentration is reduced to 0.3%, corresponding to 95% removal, 50°C above the LCEP, while 99% removal requires a temperature 75°C above the LCEP.

At any given temperature, the presence of dissolved propylene in the i-pentane lowers the polymer concentration in the solvent relative to pure i-pentane, as would be expected in view of the reduction in LCEP caused by the propylene. Similar data are shown in Figure 13 for Exxsol hexane and Exxsol hexane with 10 wt% propylene, and the presence of propylene gives about a 25°C reduction in the temperature needed for 99% removal of the polymer.
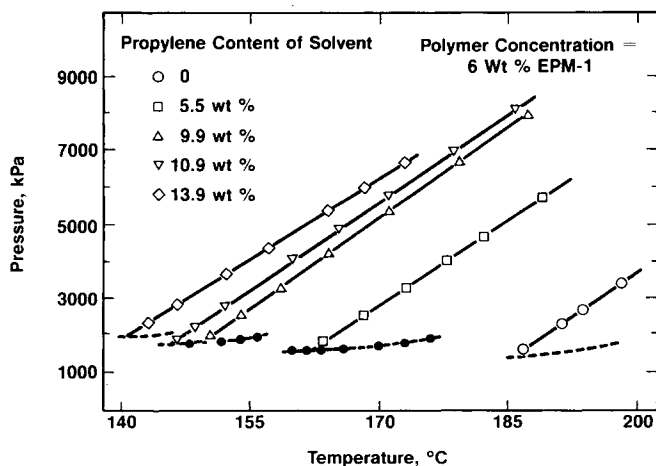

Fig. 10.   Effect of propylene on LCST in Exxsol hexane.

TABLE III (*Continued from previous page*)

f	g	h	i	j	k	l	m	n	p	q	r
					5.5	9.4	10.9	13.9			
100											
	100										
	100										
			100	38.9	36.8	35.2	34.7	33.5	63.4		
				21.2	28.0	19.2	18.9	18.3			
			17.8	16.8	16.1	15.9	15.3		36.6	100	
			21.1	20.9	20.0	19.7	19.0				100
310	358	397	439	459	436	424	420	414	447	446	494
—	355	391	441	450	425	411	407	398	439	436	474
—	.57	.65	.74	.65	.68	.65	.68	72	.79	.78	.91
.573	.615	.621	.655	.673	.655	.659	.657	.652	.657	.660	.744
—	4098	4166	4450	4446	4395	4315	4282	4244	4430	4396	4600
—	4150	4037	4167	4168	4155	4106	4084	4067	4200	4261	4185
—	.99	1.03	1.07	1.07	1.06	1.05	1.05	1.04	1.06	1.03	1.10
—	460	470	507	510	502	496	495	489	505	504	533

The data in Figures 12 and 13 are replotted in Figure 14 as percent of polymer retained in the solvent phase versus (T-LCEP)/(Tc-LCEP), where Tc is the solvent critical temperature, and this normalized temperature parameter appears to bring the results for all four solvent systems onto the single curve drawn in the figure. The correlation indicates that temperatures near critical are needed to obtain low levels of residual polymer in the solvent phase. For example, the polymer concentration is reduced to 1% of its initial value at (T-LCEP)/(Tc-LCEP) equal to about 0.9. More
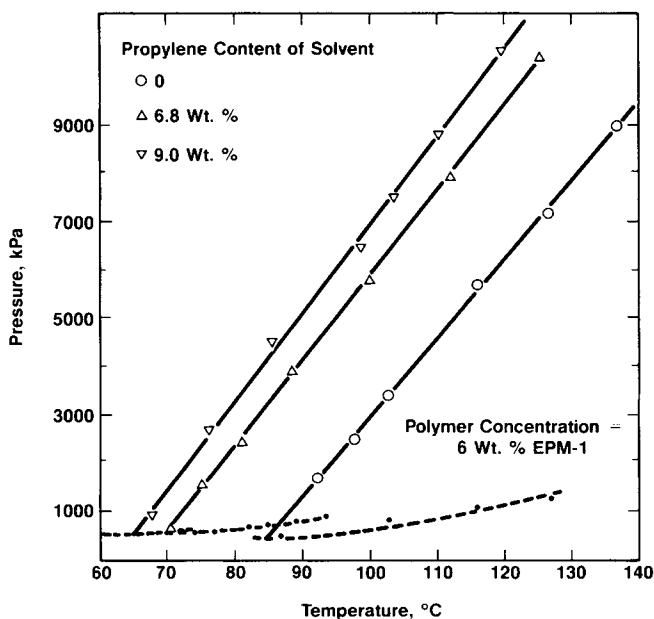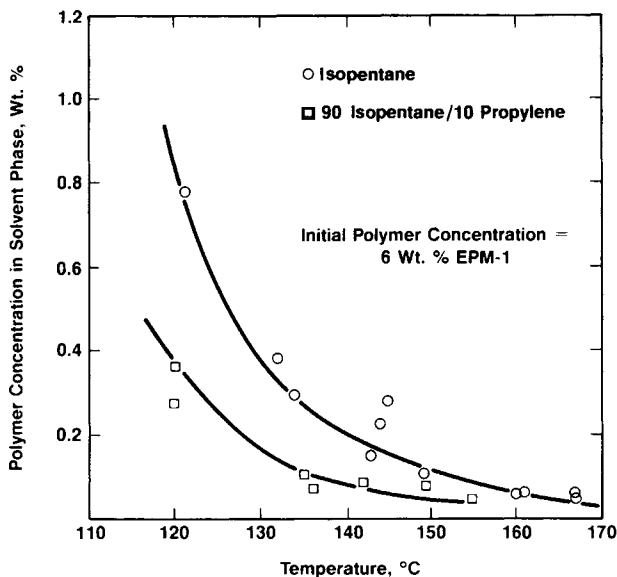

Fig. 11.   Effect of propylene on LCST in *i*-pentane.

Fig. 12.   Polymer content of i-pentane in two-phase region.

data in additional solvents and at different initial polymer concentrations would be needed to establish the generality of the correlation in Figure 14. However, assuming as a first approximation that it can be applied to other solvent systems, then the temperature/polymer concentration relationship in the two-phase region above the LCST can be estimated knowing only the solvent density, which allows the LCEP to be predicted,[1] and the critical temperature.

Correlation of Results

A large number of papers have been devoted to applying the polymer solution thermodynamics theories of Patterson and co-workers[9] and Flory[10] to the correlation of phase behavior at the LCST. The conclusion from this work (see, for example, Refs. 1, 6, 10a, and 11) is that the theory gives a good qualitative picture of the important variables that influence the critical locus and a good prediction of the shape of the phase boundaries in a phase diagram. However, quantitative agreement between data and theory is usually poor. This is especially true for polyethylene and EPM[1] because of the existence of interactions in solution between the long sequences of ethylene monomer that exist in the polymer chains.

Despite the complex physical interactions that lead to the LCST, and which make it difficult to develop a quantitative theory, Charlet and Delmas[1] have found a remarkably simple correlation between the LCEP and solvent density at 25°C which is shown in Figure 15 for EPM containing 43% ethylene. (In some cases the points in the figure are interpolated from results in Ref. 1 at other compositions.) Separate curves exist for linear, branched, and cyclic alkanes. The lowering of the LCEP with density is expected due to the increasing free volume differences between the polymer and solvent. However, the decrease of the LCEP at constant density as the
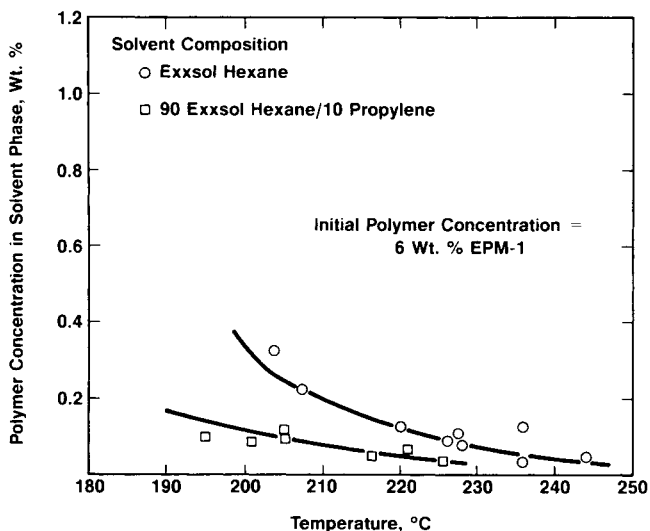
Fig. 13.   Polymer content of Exxsol hexane in two-phase region.

solvent shape is changed from linear to branched to cyclic is attributed to the greater ability of globular molecules to disrupt the polymer-polymer interactions in solution. Consequently, interaction energy can be regained by the polymer upon phase separation, and this provides the driving force for a lowered LCEP. This effect is not accounted for by present thermodynamic theories of the LCST, and as a result, quantitative theoretical predictions are especially poor for EPM systems.

Also shown in Figure 15 (letters refer to system designation in Table III) are the LCEP data from this study with both single component and mixed solvents. For the mixed solvents the density was calculated by an Exxon data library program that utilizes Riedel's[2] correlation. However, by simply
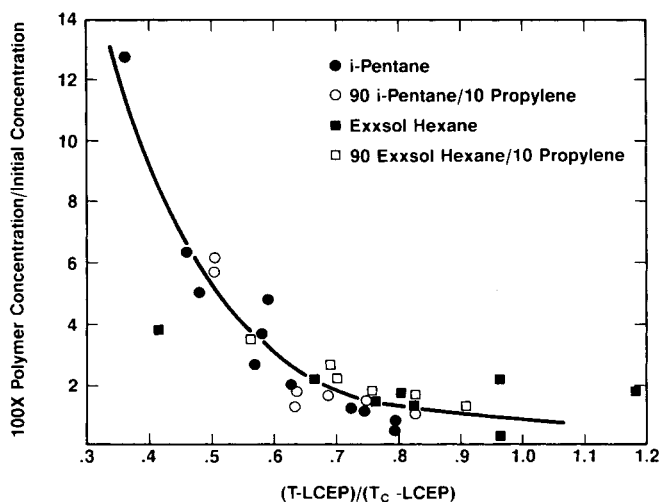

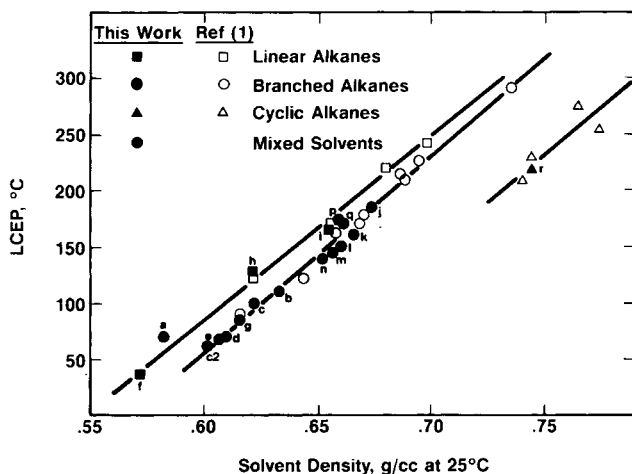Fig. 14.   Normalized residual polymer concentration.

Fig. 15. Correlation of LCEP with density.

averaging the pure component densities, similar results are obtained, differing by 0.01 g/cc at most. We agree very well with the LCEP measurements of Charlet and Delmas[1] in single-component solvents. In the mixed solvent systems, the data for isopentane/propylene fall on the density/LCEP curve established for branched alkanes, which is not unexpected. More surprising, however, is that n-hexane mixtures with nonlinear alkanes or with low-molecular weight hydrocarbon gases also give results that fall on this curve even when a high proportion of n-hexane is present in the mixture. The only exception is the result for methane/n-hexane (system a)[8] which lies above the n-alkane line. Thus, even a relatively small amount of a globular molecule appears to be sufficient to disrupt the polymer-polymer interactions in EPM solutions, if these results are interpreted in the framework for Charlet and Delmas'[1] analysis.

It is clear from our data that the correlations these workers developed for predicting the LCEP of EPM solutions in single-component solvents as a function of density can be extended to mixed solvents if the average density of the solvent is used and if the curve for branched alkanes is used for any mixture of the linear alkane with a branched alkane or low-molecular weight hydrocarbon gas. The curves in Figure 15 apply to 43 wt% ethylene EPM; however, the additional data in Ref. 1 allow prediction of the LCEP over the entire range of copolymer compositions. LCEP data for EPM in mixtures of linear and cyclic alkane or branched and cyclic alkane are not available. The position of these curves relative to the other results in Figure 15 would be of interest.

Since the slope of the LCST-pressure locus is constant over the range of conditions we investigated, a correlation for $d(\text{LCST})/d\text{P}$ in terms of solvent properties coupled with the LCEP-density correlation would allow prediction of the cloud-point curve for EPM solutions. Patterson's theory[9] gives the slope of the critical locus at P = 0 as

$$d(\text{LCST})/d\text{P}/(\text{T}_1{}^*/\text{P}_1{}^*) = \tilde{\text{V}}_1 (1 - \tilde{\text{V}}_1{}^{-1/3})(7 - 9/2\, \tilde{\text{V}}_1{}^{1/3}) \qquad (1)$$

where $T_1{}^*$, $P_1{}^* = $ temperature and pressure reduction parameters for the solvent

$\tilde{V}_1 = $ solvent reduced volume $= V_1/V_1{}^*$

and the subscript 1 denote the solvent.

Following Zeman et al.'s[6] approach, we assume that at low pressures Van derWaal's equation of state can be used to relate pressure and temperature and that the reduced temperature is given by

$$\tilde{T}_1 = T/T_1{}^* = 0.1183 \ (T/Tc) \tag{2}$$

so that the equation of state becomes

$$0.1183 \ (LCST/Tc)_{P \, = \, 0} = (1 - \tilde{V}_1{}^{-1/3})/\tilde{V}_1 \tag{3}$$

Eliminating $\tilde{V}_1$ between Eqs. (1) and (3) gives a relationship between $d(LCST)/dP$ and $LCST/Tc$ which contains the parameter $T_1{}^*/P_1{}^*$.

$T_1{}^*$ and $P_1{}^*$ for the pure components used in this study are shown in Table IV. It was assumed that the values for ethane and propane are good approximations for ethylene and propylene. $T_1{}^*$ and $P_1{}^*$ for solvent mixtures were calculated as volume fraction averages as suggested by Cowie and McEwen.[16] Pure component densities were used to estimate the volume fractions. The critical temperatures of the solvent mixtures were obtained by Li's[17] method. Finally, the critical loci in Figures 8–11 were linearly extrapolated to $P = 0$ to find the values of $(LCST)_{P \, = \, 0}$ given in Table III.

As shown by the results in Figure 16, the theoretical equation underestimates $d(LCST/T_1{}^*)/d(P/P_1{}^*)$ at a given value of $(LCST/Tc)_{P \, = \, 0}$ by about 0.2, but the shape of the curve parallels that indicated by the data and the two variables are certainly strongly correlated. The data point for the methane/n-hexane system is the only one that widely deviates from the remaining body of data; however, the vapor pressure of the methane/n-hexane system at the LCEP is much higher than for any other solvent, and thus the linear extrapolation to obtain $(LCST)_{P \, = \, 0}$ has a much higher probability of being in error.

TABLE IV
Properties of Pure Components

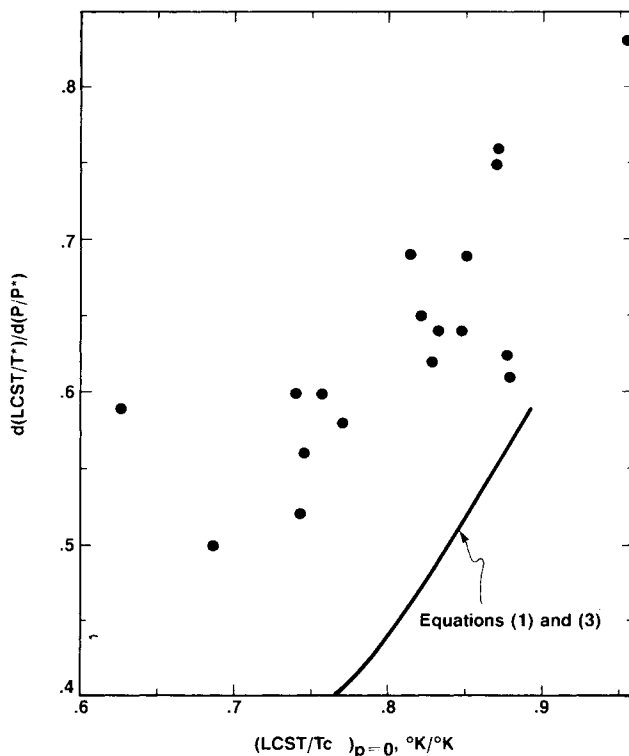|	T* °K	P* atm	Reference
Methane	1734	2500	9
Ethane	2674	3218	9
Propane	3343	3631	9
i-Pentane	4098	150	15
n-Pentane	4166	4037	9
n-Hexane	4450	4167	9
2-Methylpentane	4347	4079	13
3-Methylpentane	4396	4261	13
Methylcyclopentane	4600	4185	14

Fig. 16. Correlation of LCST slope with $(LCST)_{p=0}$.

For predictive purposes it is much more convenient to relate $d(LCST/T_1{}^*)/d(P/P_1{}^*)$ to LCEP/Tc since the LCEP can be obtained as a function of solvent density from Figure 15. The data are plotted in this fashion in Figure 17, and the data point for methane/n-hexane solvent is now in much better agreement with the rest of the results. Thus it appears that LCEP/Tc is a satisfactory correlating parameter. A simple quadratic equation fit to the data by least squares gives the result:

$$d(LCEP/T_1{}^*)/d(P/P_1{}^*) = 1.30 - 2.51 \,(LCEP/Tc) + 2.06 \,(LCEP/Tc)^2 \quad (4)$$

which is drawn in Figure 17 and has an adjusted correlation coefficient,[*] $r_a{}^2$, of 0.644.

$T_1{}^*/P_1{}^*$ does not vary significantly (see Table III) for the solvents we studied because $T_1{}^*/P_1{}^*$ is close to one for the C_5 and C_6 alkanes that were the major component of these solvents. Thus, our data can be equally well correlated as $d(LCST)/dP$, and in fact data scatter is reduced somewhat by the quadratic least squares fit.

$$d(LCST)/d\,P = 1.24 - 2.62 \,(LCEP/Tc) + 2.31 \,(LCEP/Tc)^2 \quad (5)$$

[*] $r_a{}^2 = 1 - (1 - r^2)(n - 1)/(n - p)$
where r^2 = correlation coefficient
      n = number of data points
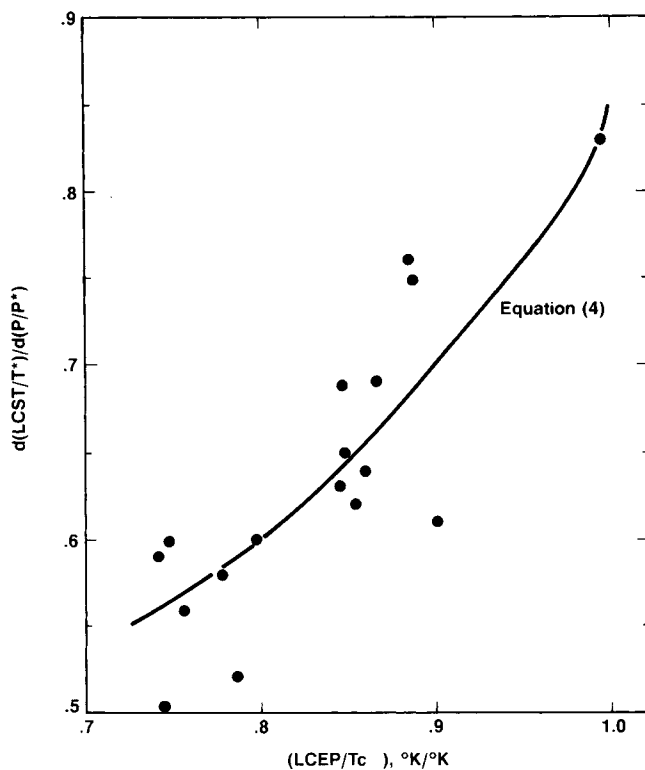 p = number of independent variable plus one.

Fig. 17.   Correlation of LCST locus slope with LCEP.

which increases $r_a{}^2$ to .768.

Since the LCEP is a function of solvent density, we also tested correlations of $d(\text{LCST})/dP$ with density and critical temperature using various functional forms for the equations. Only a limited number of the many possible combinations of terms were examined; however, it appears that good fits to the data can readily be obtained with density, ρ, and Tc as the independent variables. For example, the five-term equation below is reasonably simple and gives a $r_a{}^2$ value of 0.815:

$$d(\text{LCST})/dP = -49.8 + 12.8/\rho^2 - 7.57 \times 10^{-5}\rho^2\text{Tc}^2$$

$$+ 2.17 \times 10^4/\text{Tc}\ \rho - 1.15 \times 10^4/\text{Tc}\ \rho^2 \quad (6)$$

As shown by the comparisons of measured and predicted $d(\text{LCST})/dP$ values in Figure 18, the largest deviation from Eq. (6) is .07°K/atm. We recommend the use of this relationship for predicting $d(\text{LCST})/dP$, however, it is limited to solvents based on C_5 and C_6 alkanes and EPM's with about 40-50 wt% ethylene. It is not known at present if polymer composition affects $d(\text{LCST})/dP$ to the same extent as the LCEP.

CONCLUSIONS

Our study of the phase behavior of EPM in various solvent systems extends the finding of Charlet and Delmas[1] that the LCEP is a linear function of solvent density in single-component solvent to multicomponent solvents
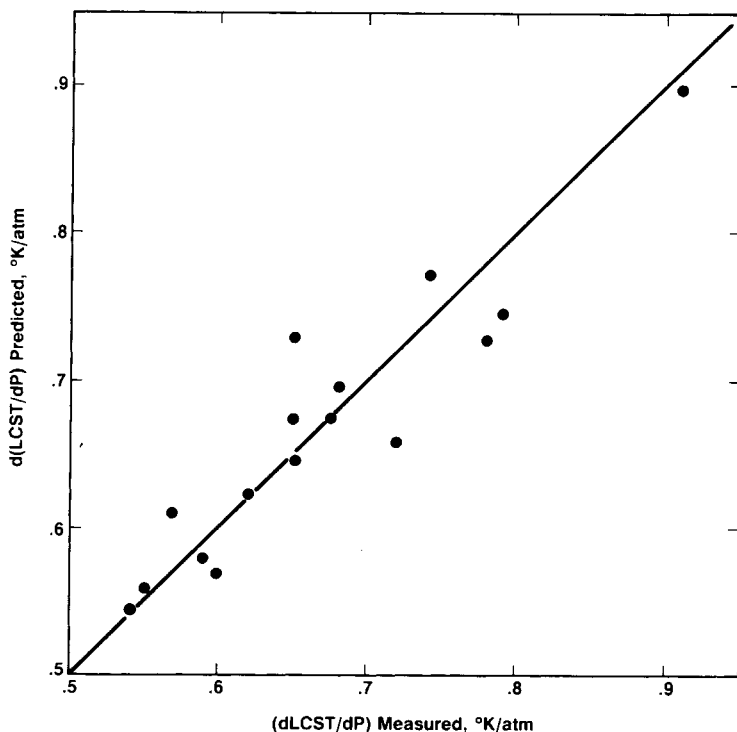
Fig. 18   Correlation of $d(\text{LCST})/d\,P$ with eq. (6).

as well. Addition of a low-molecular weight hydrocarbon gas to a solvent lowers the LCEP substantially. For a gas dissolved in a branched alkane solvent, this effect is due to the increased free volume difference between polymer and solvent (lower solvent density). However, in a linear alkane, an additional decrease in the LCEP is observed due to the effectiveness of small globular molecules in disrupting the interactions that occur in solution between EPM chains of sufficient ethylene content.

Measurement of the residual polymer content in the solvent phase in the two-liquid phase region indicates that temperatures well above the LCEP are needed to separate essentially all of the polymer from the solvent. Indeed, the critical temperature of the solvent must be approached to obtain 99% polymer removal from the solvent for a polymer with a $\overline{M}_w/\overline{M}_n$ ratio of about two. For the one polymer we investigated in several solvents, residual polymer content appears to be a monotonic function of temperature as defined by the parameter (T-LCEP)/(Tc-LCEP). Consequently, by raising the ethylene content or the molecular weight of the EPM, which reduces the LCEP, or by lowering the solvent critical temperature, which in addition lowers the LCEP, phase separations giving high levels of polymer recovery at reasonably low temperatures can result.

The slope of the LCST locus was not in agreement with the quantitative predictions of thermodynamic theory, as expected from previous studies of the LCST, but the theory does correctly indicate that $d(\text{LCST}/T_1{}^*)/d(P/P_1{}^*)$ is a function of $(\text{LCST}/Tc)_{P=0}$. In view of the dependency of the LCST on solvent density, we could empirically correlate $d(\text{LCST})/d\,P$ as a function

of density and Tc which provides a means of estimating the slope of the critical locus from easily established solvent properties. Since the LCST locus was found to be essentially a linear function of pressure for all of the systems studied, prediction of the LCEP from a solvent density correlation and $d(\text{LCST})/dP$ from density and Tc allows the location of the LCST locus to be determined with a fair degree of accuracy. However, the results in this paper are limited to EPM's of about 43% ethylene in linear and branched alkane solvents. Additional work is needed to establish the generality of our correlation methods with EPM's and solvents of other compositions.

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