

# Amorphous Binary Polymer Systems

## Prediction of their UCST Points

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A previous empirical method to predict the UCST points of several binary systems of amorphous polymers in both polar and non-polar solvents is revised in order to enlarge the field of application and to improve accuracy. The new method still retains the main points of the previous one. However, a relevant improvement is obtained mainly by splitting in the three classes the mixtures constituted by non polar polymers in polar solvents. Further, the reliability of the method is increased by processing a wider choice of experimental data which encompasses a great variety of solvents' molecular structures.

The prediction of the unusual phase diagrams found in the field of polymer solutions and blends in both the low and high temperature range still has not found a satisfactory solution in spite of the relevant interest of these phenomena. While the description of very complex phase diagrams, which involve also two critical points [1], has reached a high degree of sophistication (see, for example, [2-4]), no method can be recommended which enables an a priori reliable calculation of the UCST and LCST points which characterize the liquid-liquid equilibria of the polymer-solvent mixtures. Theoretical methods not only involve several empirical constants which cannot be generalized even only for a family of mixtures, but they make an instrumental use of the Flory parameter,  $\chi$ , which is treated as a receptacle of all the approximation linked to the evaluation of the other empirical parameters. In order to overcome all these difficulties, very recently Vetere [5] proposed an empirical method to predict both the UCST and LCST points through six generalized correlations aimed to cover all kind of binary systems reported in literature with the exception of the polar polymers in polar solvents. These relations are simple compounds of two or three well known properties of the pure compounds [6], being

$$T_u(K) \text{ or } T_L(K) = F(M_1, \rho_1, \rho_2, r^{0.5}) \quad (1)$$

for both the UCST and LCST points. In relation (1) only the  $r^{0.5}$  term has some theoretical significance, being linked to the Shultz-Flory equation.

The author defined his method as "brutal but very efficient" [5]. Admittedly, the adjective "brutal" can be accepted by everyone, but the efficiency of the new method was questioned with some good arguments by Imre and Van Hook [7], at least for the prediction of the UCST points. While some of their criticisms related to the prediction of the UCST point of non polar polymers in linear paraffins and in cyclic hydrocar-

bons were overcome by a paper published in this Journal a month after the reception of their letter [6], it remains that the predictive method proposed by Vetere for non polar polymer in polar solvents was clearly inadequate. As a result, we can face the following scenario: the prediction of the UCST and LCST points according to rigorous method is still impractical, while less demanding empirical methods cannot avoid the suspect that their reliability is illusory.

In this work the empirical route is pursued further, with the aim of dispelling doubts on the basis of the results obtained in the prediction of the UCST points reported in literature for a very large set of experimental data. Although the capability of treating a great number of systems which encompasses a large variety of molecular structures is the only touchstone to evaluate the reliability of the proposed method, a link will be stressed of this latter with the physical model of polymer solutions reported elsewhere [8]. Our main assumption is that empirical methods also must respect the proper balance between the entropic and the enthalpic contributions to the non-ideality of polymeric mixtures which, admittedly, is the more difficult task pursued by all theories aimed to evaluate the properties of polymer solutions.

### Thermodynamic considerations

In this work the LCST predictions are disregarded, since the experimental data are understandably scarce, in view of the relevant experimental difficulties involved by this type of determinations.

Before examining the analytical form of the proposed relations to calculate the UCST points, it is useful to stress some fundamental features of the relationship between the solvent structure and the demixing phenomena at low temperature. To summarize:

- the ramification of an hydrocarbon solvent lower its solvency and lead to a corresponding increase of the critical point temperature,  $T_u(K)$ ;
- cyclic hydrocarbons are better solvents than linear paraf-

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fins, that is their  $T_u(K)$  is, coeteris paribus, lower;  
 -  $T_u(K)$  tends to increase with the polymer molecular weight.  
 The first property was stressed with much emphasis by Delmas and de Saint-Romain [9]: "the branching of a given alkane has a dramatic effect on the solvent quality: the substitution of a  $CH_2$  group in the n-heptane by a side methyl group greatly reduces its solvent quality".

These authors give two possible explanations: the difference in the Hildebrand solubility parameters between linear and branched paraffins, that is an enthalpic contribution to the system non ideality, and a different structural arrangement, that is a difference in the entropic term contribution.

The second property found an explanation in the light of physical model underlying the modification of the entropic term of the Flory-Huggins previously proposed [8]. The pivoting idea is that the solvent molecules partly insert themselves in the free volume of polymer, so reducing the entropic contribution to the non ideality of the system (an unknown Referee coined for this phenomenon a very expressive word: reptation). This result automatically damps the recognized redundancy of the  $S^E$  term calculated according to the unmodified Flory-Huggins equation. As a result, a lower  $S^E$  involves a higher solvent activity coefficient and, ultimately, an increase of  $T_c(U)$ . The emerging rule is the following: the reptation decreases with the steric hindrance of the solvent, and the same happens to  $T_c(U)$ . Understandably, the normal paraffins can be allocated in the free polymer volume easier than the cyclic hydrocarbons and are characterized by a higher  $T_c(U)$  (see, for example, Table 1).

The last property is the simplest to be justified, since an increase of the polymer chain increases also the inescapable chemico-physical differences between a

monomeric solvent and a very high molecular weight solute. In summary, while the LCST points are ruled by the enthalpic part only of the Flory-Huggins equation [5], the demixing at low temperatures is inextricably entangled with both geometric (or entropic) factors and energetic (or enthalpic) factors.

**Table 1 - Prediction of UCST points of non polar polymers in hydrocarbons**

Systems	$M_1$	$M_2 \cdot 10^{-3}$	$r^{0.5}$	UCST (K)		AAD%(K)	Source
				exp.	calcd.		
<i>n-paraffins</i>							
BR/n-hexane	86.2	132.0	0.0300	271	276.6	5.6	10
BR/n-hexane	86.2	191.0	0.0250	275	275.7	0.7	"
BR/n-hexane	86.2	376.0	0.0180	283.2	247.6	8.6	"
PS/n-octane	114.2	830.0	0.0133	287	299.0	12.0	"
PS/n-pentane	72.2	1.1	0.3318	292	318.0	26.0	12
PS/n-hexane	86.2	2.03	0.2609	318	318.1	0.1	"
PS/n-heptane	100.2	4.8	0.1790	359	315.3	43.7	"
PS/n-octane	114.2	4.8	0.1885	353	327.8	25.2	"
PS/n-decane	142.3	4.0	0.2262	361	351.7	9.3	"
PS/n-dodecane	170.3	4.0	0.2423	369	367.9	1.1	"
PS/n-pentadecane	212.4	4.0	0.2694	385	388.1	3.1	"
PS/n-octadecane	254.5	4.0	0.2923	404	404.1	0.1	"
					M	11.3	
<i>Ramified hydrocarbons</i>							
BR/2-methylexane	100.2	220	0.0250	290	327.9	38.0	10
BR/2-methylexane	100.2	355	0.0190	312	330.6	18.6	"
BR/2,2,4 trimethylpentane	114.2	44.5	0.0580	308	307.8	0.2	"
BR/2,2,4 trimethylpentane	114.2	65.0	0.0480	322	312.9	9.1	"
BR/2,2,4 trimethylpentane	114.2	104.0	0.0380	345	317.9	27.1	"
PS/methylcyclohexane	98.2	10.2	0.1150	286	279.5	6.5	10
PS/methylcyclohexane	98.2	16.1	0.0910	296	294.5	1.5	"
PS/methylcyclohexane	98.2	17.3	0.0880	296	296.3	0.3	"
PS/methylcyclohexane	98.2	20.2	0.0820	299	299.7	0.7	"
PS/methylcyclohexane	98.2	34.9	0.0620	309	310.6	1.6	"
PS/methylcyclohexane	98.2	46.4	0.0540	313	314.7	1.7	10
PS/methylcyclohexane	98.2	109.0	0.0350	323	324.0	1.0	"
PS/methylcyclohexane	98.2	181.0	0.0270	327	327.6	0.6	"
PS/methylcyclohexane	98.2	719.0	0.0140	335	333.4	1.6	"
PS/methylcyclopentane	84.2	2000	0.0077	342	340.2	1.8	12
PS/methylcyclohexane	98.2	1971	0.0083	336	335.8	0.2	"
PS/ethylcyclohexane	111.2	569	0.0160	335	328.7	6.3	"
					M	6.9	
<i>Cyclic hydrocarbons</i>							
PS/cyclopentane	70.14	67.0	0.0384	286	286.4	0.4	10
PS/cyclopentane	70.14	97.2	0.0319	276	286.4	10.4	"
PS/cyclopentane	70.14	200.0	0.0222	281	286.5	5.5	"
PS/cyclopentane	70.14	2700	0.0610	290	286.5	3.5	12
PS/cyclohexane	84.2	20.4	0.0746	280	287.1	7.1	10
PS/cyclohexane	84.2	37.0	0.0554	286	287.2	1.2	"
PS/cyclohexane	84.2	80.0	0.0377	300	287.3	12.7	"
PS/cyclohexane	84.2	100.0	0.0337	294	287.3	6.7	"
PS/cyclohexane	84.2	200.0	0.0238	297	287.3	9.7	"
PS/cyclohexane	84.2	2700.0	0.0065	304	287.4	16.6	12
PS/cycloheptane	98.2	100.000	0.0036	289	288.4	0.6	"
PS/cyclooctane	112.2	100.000	0.0038	286	289.3	3.3	"
PS/cyclodecane	140.3	100.000	0.0041	288	291.1	3.1	"
PS/t-decaline	138.3	2700	0.0077	291	290.9	0.1	"
PS/1-phenyldecane	218.4	600	0.0211	296	295.9	0.1	"
					M	5.4	

To this dicotomy are linked the difficulties found in the prediction of the UCST points, regardless to the nature of the approach, theoretical or empirical.

If this picture of the polymer solutions is correct, the standard method to evaluate the Hildebrand solubility parameter of a polymer,  $\delta_i$ , must be revised, since the best solvents for a polymer are no longer those having the same  $\delta_i$  of the polymer, the solvency being dictated by the value of the  $S^E$  term also.

## The empirical relations

Obviously, the new generalized correlations aimed to improve the previous method must respect all the three rules quoted above. Further, the difficult case of non polar polymers in polar solvents suggests a subdivision of this class in sub-classes according to the solvent polarity degree.

The corpus of the experimental data previously processed [8] is considerably enlarged to assure a better reliability of the method.

Therefore, the data reported in the Danner and High monograph [10] are integrated with those quoted by Imre and Van Hook [7], disregarding only the liquid-liquid equilibrium data of polar polymers in polar solvents for which no generalized correlation appears feasible.

According to equation (1), the less accessible quantity required by the proposed method is the solvent density,  $\rho_1$ , required to calculate  $r$ .

These values were taken from the monograph by Reid *et al.* [11] at the temperature of 20 °C or 25 °C. It must be stressed that the calculation of  $\rho_1$  at a prefixed temperature saves the truly predictive character of the method.

For sake of clarity, the treatment of non polar mixtures will be described separately from the more difficult case of mixtures containing a polar component.

## Non polar mixtures

The examined set of experimental data was sub-divided in

three classes, according to the considerations reported in the previous paragraph.

As result, we propose the following generalized relations to calculate the  $T_u(K)$  values of non polar solvents in all types of hydrocarbons:

$$T_u(K) = 734 - 1127.2M_1^{-0.2}(1-r^{-0.5})^{0.35} \quad (2)$$

for normal paraffins

$$T_u(K) = 480 - 356.3M_1^{-0.2}(1-r^{-0.5})^{-2.8} \quad (3)$$

for ramified hydrocarbons or cyclic hydrocarbons with a side chain, and

$$T_u(K) = 282 + 0.065M_1(1-r^{-0.5}) \quad (4)$$

for cyclic hydrocarbons. It should be noted that the negative exponent of  $M_1$  in equations (2) and (3) is embodied in a subtractive term, so that the third rule of the previous paragraph is not denied.

If some loss of accuracy can be tolerated, a same relation can be applied to all the hydrocarbons, namely

$$T_u(K) = 286 + 0.0098M_1^{1.5}(1-r^{-0.5})^{-4}/\rho_2^{5.5} \quad (5)$$

The results obtained are reported in Table 1.

They are generally acceptable, with the exception of 5-6 compounds whose calculated  $T_u(K)$  exceed of 30-40 °C the experimental datum. The overall AAD% value for equation (5) is 17.7% with respect to an analogous datum of 7.6% for equations (2)-(4). While the choice between the two methods is left to the reader, the wider generality of equation (5) testify that this latter can be used with a major confidence when the solvent has a very different chemical structure with respect to the solvents processed in this work.

## Mixtures with a polar component

**Table 2 - Prediction of UCST points of non polar polymers in polar solvents with  $W_p \geq 20$**

Systems	$M_1$	$M_2 \cdot 10^{-3}$	$r^{05}$	$W_p$	UCST (K)		AAD% (K)	Source
					exp.	calcd.		
PS/Methylacetate	74.08	160.0	0.0230	27.4	281	294.9	13.9	12
PS/Methylacetate	74.08	179.3	0.0220	27.4	288	295.1	7.1	10
PS/Methylacetate	74.08	498.0	0.0130	27.4	294	296.5	2.5	"
PS/Methylacetate	74.08	180.0	0.0068	27.4	303	297.4	5.6	"
PS/Methylacetate	74.08	270.0	0.0056	27.4	311	297.6	13.4	"
PS/ethylformate	74.08	4.0	0.1456	23.1	274	273.8	0.2	"
PS/ethylformate	74.08	20.0	0.0650	23.1	295	286.6	8.4	"
PS/ethylformate	74.08	37.0	0.0480	23.1	318	289.3	28.7	"
PS/acetone	50.1	10.3	0.0806	105.1	270	282.4	12.4	12
PS/propionitrile	55.1	22.0	0.0508	212.7	364	336.6	27.4	"
PS/nitroetane	75.1	48.0	0.0400	115.2	303	328.8	25.8	"
HDPE/cyclohexanone	98.15	20.0	0.0650	80.2	389	341.5	47.5	10
HDPE/diphenylether	170.2	49.0	0.0510	23.1	412	407.0	5.0	"
LDPE/diphenylether	170.2	23.0	0.0750	23.1	398	400.2	2.2	"
LDPE/diphenylether	170.2	32.0	0.0630	23.1	403	403.6	0.6	"
LDPE/diphenylether	170.2	77.6	0.0410	23.1	410	409.8	0.2	"
					$\bar{M}$		12.6	

A reliable generalized correlations for the calculation of  $T_u(K)$  of polymers is a wide variety of alcohols is reported elsewhere [12].

The previous choice cannot be enlarged since other data reported by Ostpal *et al.* [13] refer to alcohols in mixture with a polyethylene sample having a large molecular mass distribution ( $M_w/M_n > 10$ ).

The  $T_u(K)$  values of this class of mixture are strongly dependent on the polar degree of the solvent.

A convenient screening parameter to group together polar mixtures is represented by the polar parameter  $\omega_p$ , defined as

$$\omega_p = T_b^{1.72}/M - 263 \quad (6)$$

which is nearly nil for n-paraffins and it attains its maximum value for water [14].

A part the alcohols/polymer mixtures, the  $T_u(K)$  of other polymer in strongly polar solvents characterized by  $\omega_p > 20$  can be evaluated by applying the following relation

$$T_u(K) = 130 + 7.74M_1^{0.7}(1-r^{0.5}) + 0.4\omega_p \quad (7)$$

while for solvents characterized by  $\omega_p < 20$  no relation can be derived. This is particularly evident for the mixtures of polystyrene in the esters listed by Imre and Van Hook [7].

A part methylacetate, which pertains to the family characterized by  $\omega_p > 20$ , any attempt to derive a rule for these solvents by taking into account also other properties of pure components, as the Hildebrand solubility parameter or the acentric factor, was unsuccessful.

Particularly striking is the effect of ramification, as shown by a spectacular increase of  $T_u(K)$  by passing from n-propylacetate to i-propylacetate and from i-butylacetate to t-butylacetate. The results obtained for the examined mixtures is reported in Table 2.

## Conclusions

In this work we have stressed the conflicting features of the entropic and enthalpic contributions to the non ideality of polymer solutions, from which ultimately depend the demixing phenomena in the low temperature range.

Since to treat adequately this aspect of polymer solutions is inherently difficult, no solution is still at hand which can be considered a definitive answer to the problem.

Although the number of examined systems reported in Tables 1 and 2 is, perhaps, the wider among the literature on the prediction of the UCST points, they represents only a slice of the numberless systems interesting the industrial practice.

Therefore, the relations reported in this work are not of the "ne varietur" type, being open to a possible improvement on the basis of new sets of experimental data more representative the polymer solution universe.

Nevertheless, the contribution of this paper consists in showing that at least for non polar solutions the prediction of the UCST points appears feasible with very simple tools based on few well known properties of pure compounds.

## Nomenclature

M	molecular weight
r	parameter defined by $V_2/V_1$
$SE$	excess entropy of mixing, $J K^{-1} mol^{-1}$
T	absolute temperature, K
$T_b$	normal boiling temperature, K
$T_u(K)$	absolute temperature at the UCST point, K
$T_L(K)$	absolute temperature at the LCST point, K
V	molar volume, $cm^3 mol^{-1}$

## Greek Letters

$\delta$	Hildebrand solubility parameter $J^{0.5} cm^{-1.5} mol^{-1}$
$\chi$	Flory-Huggins interaction parameter
$\rho$	density, $g cm^{-3}$
$\omega_p$	polar factor, expressed by eq. (6), $K^{1.72}$

## Subscripts

1	solvent
2	polymer

## Acronyms

BR	polybutadiene rubber
HDPE	high density polyethylene
LDPE	low density polyethylene
PIB	polyisobutylene
PS	polystyrene

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