Thermodynamic properties of polyolefin solutions at high temperature: 1. Lower critical solubility temperatures of polyethylene, polypropylene and ethylene-propylene copolymers in hydrocarbon solvents

Gérard Charlet and Geneviève Delmas
Département de Chimie, Université du Québec à Montréal, C.P. 8888, *Succ. A, Montréal, Québec, Canada, H*3*C* 3*P*8

(*Received* 26 *August* 1980; *revised* 15 *December* 1980)

Lower critical solubility temperatures (*LCST*) of linear polyethylene (PE), isotactic polypropylene (PP) and of five random ethylene-propylene (EP) copolymers of different composition have been measured in (i) five linear alkanes (n-C_5 to n-C_9); (ii) sixteen branched alkanes and (iii) four cycloalkanes. The effect of correlations of molecular orientations (*CMO*) on the *LCST* was investigated. The main results of this work are the following: (1) the *LCST* for PE are much lower than those for PP although the expansion coefficients of the two polymers are similar. Calculations using the van der Waals model for a liquid would predict them 10° to 20° apart while the experimental difference can reach 90°. (2) In PE solutions, the linear alkanes are much better solvents than those which are branched. This constitutes a rare example in non-polar solutions in which the magnitude of the equation of state term is not sufficient to predict or even to compare the *LCST*. The importance on χ of polymer-segment and solvent shapes even above the boiling point of the solvent is to be noted. (3) The *LCST* of the five copolymer samples are almost a linear function of their composition over all the composition range. (4) These results can be understood if the existence of CMO between the (CH_2–CH_2) sequences is assumed in the pure PE melt and in the copolymers but not between the $CH(CH_3)$–CH_2 sequences. CMO in solution between the polymeric chains and the linear alkanes make the linear alkanes better solvents than the branched ones. From *LCST* data in n-C_7 and its isomers, the temperature to which CMO in PE disappear can be estimated to be above 170°C, a value which is consistent with those found for long linear alkanes. (5) Branched volatile alkanes such as 2,2-dimethylpentane appear to be a good choice for dosage of the ethylene content of an EP copolymer because of the large interval of *LCST* between PP and PE in such solvents. *LCST* measurements could become a sensitive and routine analytical tool for polymer and copolymer characterization for some polymers in well-chosen solvents.

INTRODUCTION

Properties of different polyolefins would be expected to vary from those of polyethylene in a manner similar to the variation between branched and linear alkanes. The melting points of branched alkanes are much lower than those of the linear alkanes due to the difficulty of ordering an irregularly-shaped molecule. The distinction between linear and branched is less obvious for the polymers since those made from the repetition of branched segments can order themselves by taking a helicoidal conformation if the side group is placed regularly relatively to the hydrocarbon backbone. Then the melting points are as high or higher than that of polyethylene (PE). The random copolymers are expected to behave like atactic rather than isotactic polymers because by alternating the two units, long-range order is prevented. Since the stereoregularity does not drastically affect the properties in solution[1] (end to end distance, solvent quality), one would expect the copolymers to have solution properties intermediate between those of the pure homopolymers in spite of the fact that the homopolymers are ordered and crystalline and the copolymers are not. Furthermore, in the particular case of the ethylene–propylene (EP) copolymers, solution properties should be similar since analysis of the thermodynamic properties of linear and branched alkanes[2] has indicated a rather small force field difference among the $-CH_2-CH_2-$, CH_3-CH_2- or $-CH(CH_3)-CH_2-$ groups.

Intrinsic viscosities at 25°C of EP copolymers[3,4] (excluding the crystalline homopolymers) have shown that the expansion of the polymer coil in a well-chosen solvent is sensitive enough to relate precisely to the amount of one of the monomer so that the $[\eta]$ can be used as a method of dosage[3]. These measurements also support the existence of short-range order or correlations of molecular orientations (*CMO*) in solution.

The temperature to which a polymer solution separates into two phases, the lower critical solubility temperature (*LCST*), is at a high enough temperature, so that solution measurements are possible even with crystalline polymers. *LCST* measurements have the double advantage of giving data over all the composition range of ethylene,

0032-3861/81/091181-09$02.00

between PP and PE and indicates whether *CMO* apparent at 25°C persist at higher temperatures.

Correlations of molecular orientations (CMO)

Systematic thermodynamic measurements of linear and branched alkanes[5] and on their mixtures as well as results of depolarized Rayleigh[6] scattering on the same systems seem to document the following description of liquids or solutions consisting of anisotropic non-polar molecules such as the n-alkanes: In the pure state, a molecule made of a succession of $-CH_2-$ segments will tend to correlate its direction with that of the surrounding molecules for a better energetic contact. One or several $-CH_3$ groups along the chain diminishes the possibility of correlations of orientations. Ultimately, a highly-branched alkane such as the 2,2,4,4,6,8,8 heptamethylnonane (br-C_{16}) becomes globular and loses the orientations existing in the straight chain molecule n-C_{16}. The *CMO* diminishes when the temperature increases, i.e. when the free volume of the molecule increases. An extension of this description can be made for more polar molecules made up of groups other than $-CH_2-$, the correlation of molecular orientations increasing with the anisotropy of the molecules. In solution with a second component, the *CMO* are usually destroyed. However, in some cases, they can be only reduced or even increased. The two parameters which decide on what will occur in solution are the shape of the second component, (i.e. its ability to fit with the molecules of the ordered pure liquid) and the free volume in the solution. Globular molecules such as the branched alkanes destroy the order of the linear alkanes particularly if they are volatile. Short linear alkanes also diminish the order of long linear alkanes, although their mutual fitting is good, because they increase the free volume of the long alkane in the mixture. An increase of orientational order in solution occurs when the segments of the two components fit and when the free volume is smaller in solution than in the pure alkane. This has been found[7] when a linear polymer of low free volume (the 75%E-EP copolymer) is mixed with a linear alkane. The negative value of the heats of mixing or of the Flory X_{12} parameter is indicative of the ordering in solution.

The above description has been drawn mainly from analysis of heats of mixing of small molecules and atactic polymers in linear and branched alkanes. Since an ordering or a disordering process produces on the entropy of mixing an effect of the same sign than it does on the heats, their combined effect will be smaller in the free energies, this being an example of the usual enthalpy–entropy compensation[8]. Vapour pressure measurements on mixtures of alkanes or of other chain-like molecules[8,9] indicate that, at the concentration where there is a maximum in the excess Gibbs free energy mixing (G^E), *CMO* in solution diminish the free energy but the effect is not noticeably large. In the case of polymer solutions, the effect of *CMO* on the free energy has been investigated by comparison of intrinsic viscosities in non-polar solvents likely or unlikely to correlate with the polymer segments. Results on linear polymers such as the EP copolymers[4,10] polypentenamer[10] and polybutadiene[11] indicate that, at this extreme of the concentration range, there is less enthalpy–entropy compensation so that *CMO* definitely favours the mixing. The same evidence is given by phase diagrams of PBD[12] where *CMO* between the polymer and the linear alkanes make the latter much better solvents than the branched alkanes.

Temperature dependence of correlations of orientations

At low temperature, the free volume of an ordered solvent is reduced so that its order increases. Low temperature measurements have not been performed on long alkanes due to their high melting point. However, the increase of the intrinsic viscosities of EP copolymers between 60° and 20°C in n-C_{16} and 25° and −10°C for n-C_8 indicates an improved solvent quality at low temperatures, probably a consequence of better *CMO*[11]. At higher temperatures, however, increased free volume and thermal agitation reduce the order in the liquids. For the solutions, the extent of the decrease of *CMO* depends mainly on the free volume of the order-breaker molecule. From the magnitude of the heats of mixing (h^E) and the shape of $h^E(T)$ of linear alkanes with squalane, one would estimate that orientational order is minimal around 45°C for n-C_{10} and around 100°C for n-C_{16}[13]. Similar results are found using polyisobutylene[14] instead of squalane as order-destroyer of the long alkanes. For longer alkanes, heats of mixing are hardly possible so that one has to turn to free energy parameters for evidence of *CMO*. Using gas liquid chromatography (g.l.c.) data with the n-alkanes n-C_{28}, n-C_{32} and n-C_{36} as solvents and small branched and linear alkanes as solutes and comparing the data with those obtained with the branched alkane, squalane as solvent, de Ligny *et al.*[15] have recently given conclusive evidence of *CMO* in these long chain alkanes up to 120°C. By plotting these three temperatures *versus* $1/n$ (n being the carbon atom number) the disappearance of *CMO* for PE can be predicted to occur above 165°C. Evidence of orientational order in melt PE has been reported[16] using X-ray diffraction diagrams.

The aim of this work was to confirm, by *LCST* measurements, the existence of *CMO* at high temperatures in low free volume liquids consisting of suitably shaped molecules and to investigate their effect on the χ parameter. *LCST* data was obtained for PE and compared with those for PP and five EP copolymers of different composition.

The solvents used are (a) five linear alkanes from n-C_5 to n-C_9, (b) sixteen branched alkanes with 5,6,7,8 and 9 carbon atoms chosen among sterically hindered molecules such as 2,3-dimethylpentane and non-sterically hindered molecules such as 2,4-dimethylpentane and (c) four cycloalkanes.

Lower critical solubility temperature (LCST)

In qualitative terms a *LCST* occurs generally in a polymer solution because of the difference of size or chain length between polymer and solvent molecules, thus resulting in a large difference of free volume between polymer and solvent. At high temperatures, the expanded solvent has to 'condensate' on the polymeric liquid so that the corresponding diminution in free volume or entropy is no longer favourable to the mixing. *LCST* have been found to occur above the boiling point of the solvent[17] but the opposite could happen if the chemical difference between the polymer and the solvent was sufficiently large. In order to predict the *LCST*, the polymer–solvent interaction parameter χ must increase with a rise of temperature contrary to the Flory–Huggins theory. Prigorine *et al.*[18] made the first quantitative formulation

Table 1 Selected physical data on solvents and amorphous polymers

		$d^{25^\circ C a}$ (g ml^{-1})	$10^3 \times \alpha^{25^\circ C b}$ (K^{-1})	T_c^h (K)	Zg^i
n-Butane	4	0.5730	1.942^d	425.2^a	
n-Pentane	5	0.62139	1.647^d	469.6	
n-Hexane	6	0.65481	1.396	507.4	0.94
n-Heptane	7	0.67951	1.252	540.2	1.27
n-Octane	8	0.69849	1.155	568.8	1.60
n-Nonane	9	0.71381	1.062^c	594.6	1.98
n-Decane	10	0.72625	1.033^c	617.4	2.34
n-Dodecane	12	0.74516	0.904	658.2	3.03
2-Methyl butane	5a	0.61462	1.643^c	460.4	
2,2-Dimethyl butane	6a	0.64446	1.465	488.7	
2,3-Dimethyl butane	6b	0.65702	1.411	499.9	2.36
2,4-Dimethyl pentane	7a	0.66832	1.312	519.7	2.00
2,2-Dimethyl pentane	7b	0.66953	1.294	520.4	2.00
2-Methyl hexane	7c	0.67439	1.241	530.3	1.64
3-Methyl hexane	7d	0.68295	1.224	535.2	2.48
2,2,3-Trimethyl butane	7e	0.68588	1.236	531.1	4.00
2,2,4-Trimethyl pentane	8a	0.68777	1.208	543.9	3.00
2,5-Dimethyl hexane	8b	0.68934	1.220^c	550.0	2.35
2,3-Dimethyl pentane	7f	0.69091	1.209	537.3	3.56
3-Ethyl pentane	7g	0.69395	1.202	540.6	3.58
2,4-Dimethyl hexane	8c	0.69620	1.196^c	553.5	3.24
3,4-Dimethyl hexane	8d	0.71516	1.138^c	568.8	4.71
2,2,4,4-Tetramethyl pentane	9a	0.71563	1.069^c	556.2^a	
2,3,4-Trimethyl hexane	9b	0.7354	1.028^c	584.0^a	
Cyclopentane	5b	0.74045	1.320	511.6	
Methyl cyclopentane	6c	0.74394	1.253	532.7	
Methyl cyclohexane	7h	0.76506	1.137	572.1	
Cyclohexane	6d	0.77389	1.206	553.4	
Poly(4-methyl pentene-1)		0.838^e	0.78^f		
Polypentene-1		0.86^e	0.79^e		
Polybutene-1		0.86^e	0.755^e		
Polypropylene		0.858^e	0.801^e		
Polyethylene		0.887^e	0.72^d		
Natural rubber		0.913^g	0.654^g		
Polyisobutylene		0.917^g	0.556^g		

[a] R. R. Dreisbach Physical properties of chemical compounds. ***Adv. Chem. Ser. Am. Chem. Soc.*** Washington, DC, 1959
[b] Thermal expansion coefficient at 25°C from "Michel Barbe, ***Ph.D. Thesis***, McGill University, Montreal, 1978
[c] From densities at several temperatures, from (a) above
[d] From equation of state for normal alkanes in D. Patterson, J. M. Bardin, ***Trans. Faraday Soc.*** 1970, **66**, 321
[e] O. G. Lewis, Physical properties of linear homopolymers, N.Y. Springer Verlag, 1968
[f] Estimated value; an unrealistic value of 0.638×10^{-3} K^{-1} is given in (e)
[g] Reference 20c
[h] Solvent liquid—vapour critical temperature (K) from A. P. Kudchaker, G. H. Alani, B. J. Zwolinsky, ***Chem. Rev.*** 1968, **68**, 659
[i] Mean number of *gauche* conformations, reference 15b

of the effect of free volume dissimilarity on the thermodynamics of solutions. Extension of the theory has been made by Patterson and coworkers to predict and interpret quantitatively the *LCST* of polyisobutylene (PIB), polydimethylsilozane (PDMS) and polyethylene (PE) solutions in linear and branched alkanes[19a,b,c]. Using the Van der Waals model for the energy, Flory *et al.*[20a,b,c] defined the equation of state term for the chemical potential in binary systems from which the *LCST* can be predicted.

LCST determinations were made mainly with PIB, PE and PDMS to test the theories in non-polar solvents. However, several examples of systems have been given showing the overlap of the regions of incomplete solubility, that at low temperature due to force-field difference between the two components and that at higher temperatures because of free volume difference so that the phase diagram has a characteristic hour-glass shape. Such systems containing polybutadiene[12] (PBD), PE[21], polystyrene[22,23] (PS), PIB[25] and cellulose[24] solutions have been investigated. However, comparison of the *LCST* of various polyolefins has attracted little attention probably because no unusual effect was anticipated.

EXPERIMENTAL

Materials

Solvents. They were purchased from both the Aldrich Co (Milwaukee) or the Chemical Sample Company (Columbus Ohio) and were used without purification. Physicochemical data such as the density, *d*, expansion coefficient, α, critical temperature, T_c, and mean number of *gauche* conformations, *Zg*, are given in *Table 1*.

Polymers. Polyethylene is a Phillips (Marlex 50) product. Polypropylene (isotactic and atactic) was synthesized at the Hercules Company (Varennes P.Q. Canada). The copolymers were the same as in previous work[3,4]. The intrinsic viscosities in the solvent used for molecular weight determination are given with those of the other polymers in *Table 1* of part 2.

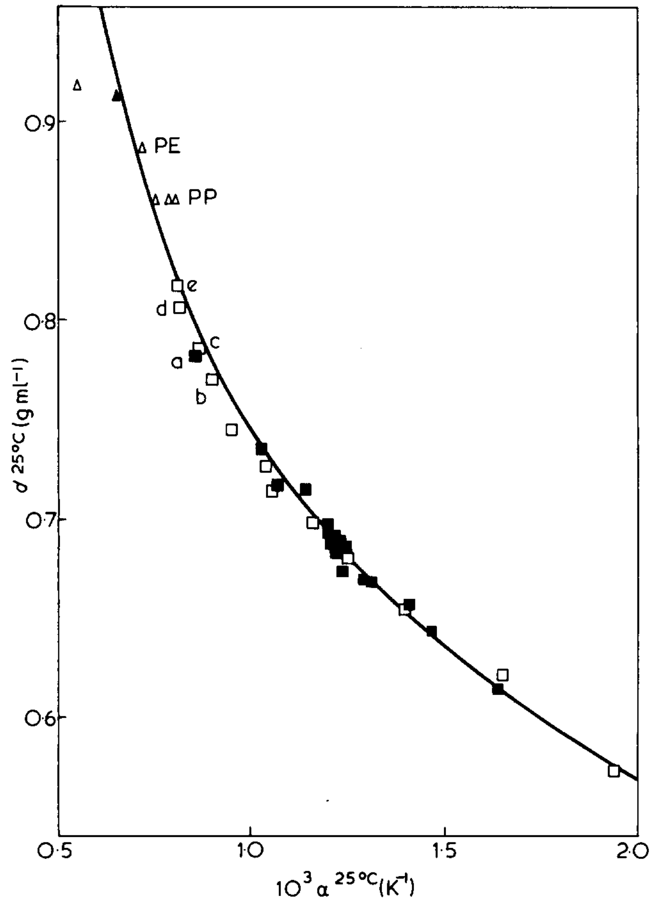

Figure 1 Density (g ml^{-1}) *versus* thermal expansion coefficient (K^{-1}) at 25°C for linear (□) and branched (■) alkanes listed in *Table 1*, for 2,2,4,4,6,8,8, heptamethyl nonane (a), n-hexadecane (b), n-eicosane (c), n-triacontane (d), nn-tetracontane (e), for 5 amorphous polyolefins (△) and for natural rubber (▲)

LCST *measurements*

A sealed tube containing the polymer solution (the weight fraction being between 0.5 and 5%) was placed in a small oven whose temperature was monitored. An X–Y recorder registers simultaneously the reading of a thermocouple placed in the oven and that of a photo-cell on the trajectory of a light beam passing through the tube. The temperature at which the transmitted light diminishes sharply is taken as the critical temperature of the solution. Two phases can be seen when the tube is removed from the oven above this temperature. The reproducibility of the *LCST* is ±0.5°C. There was no evidence of polymer degradation since successive runs of the same tube after cooling and homogenization of the two phases gave the *LCST* within the reproduction range. Consequently, no antioxidant was added to the solution. The accuracy as indicated by the melting point of pure compounds, is ±1°C.

Dependence of the LCST *on molecular weight*

For polymer systems, the *LCST* is usually measured for different fractions and the reported value is the extrapolated value, $LCST_\infty$, for an infinite molecular weight. The dependence displayed between the temperature and the molecular weight M is the same as for the upper critical solubility temperature (or θ temperature) and is a linear function of $M^{-1/2}$ for the usual range of moderate-high molecular weight. Here, it was decided to measure the *LCST* for only one molecular weight (M_v being between 1 and 3×10^5 depending on the sample) and to compare those rather than the $LCST_\infty$ from one polymer to another or in the different solvents. This seems to be justified by the following. The difference between the *LCST* for these molecular weights and the $LCST_\infty$ may be estimated either from the theoretical molecular weight dependence of the *LCST* on M or from literature data[17]. Over the temperature range measured here, the expected difference would be between 3° to 10°C, the highest value occurring with volatile solvents. An example of the variation of the *LCST* with M is given in part 2 for the system polybutene-1 n-hexane. As can be seen in *Table 2*, the spread of the *LCST* for the different polymers is about 100°C. This is 10 times greater than the maximum estimated difference between the *LCST* and the $LCST_\infty$. Furthermore, other errors such as the change in composition could have been introduced by the fractionation of partially crystalline polymers. The consistency of the results over the whole range of ethylene composition was convincing enough of the validity of the comparison of the *LCST* instead of the $LCST_\infty$.

RESULTS AND DISCUSSION

When polyolefins are dissolved in hydrocarbon solvents, the contribution to χ coming from the difference in force field is small so that the only sizeable contribution left, especially at high temperatures, comes from the difference in free volume or expansion coefficient between the polymer and the solvent. In *Figure 1* densities for amorphous polyolefins and linear and branched alkanes at 25°C have been plotted against the corresponding expansion coefficients. This test of consistency between α and d is useful for the polyolefins whose crystallinity makes the determination of phisico-chemical data for the amorphous state difficult. From their position on the general curve, PP and PE have, at 25°C, rather similar state of expansion so that, in a given solvent, one would expect their *LCST* to be close to each other.

Table 2 gives the values of the *LCST* for the two homopolymers and the five copolymers in the various solvents as well as the polymer molecular weights. In *Figure 2*, the *LCST* data for the two homopolymers in 5 linear and 12 branched alkanes are plotted against the solvent density. Here the density of the solvent is selected to represent the state of expansion of the solvent and to correlate the *LCST*. In *Figure 2* the *LCST* increase when d_s becomes higher, is due to the decrease of the free volume difference between the two components. In part 2, an explicit expression to predict and correlate the *LCST* is given in terms of the $c_l\tau^2$ parameter and a comparison is made between the two correlations.

The main features of *Figure 2* are the following: (1) the *LCST*s are much lower in PE solutions than in PP. The difference is higher than 55°C for all volatile solvents ($d_s<0.65$). (2) The *LCST*s are higher in linear than in branched alkanes of the same density. However, the effect of solvent molecular shape is minimal for PP solutions. At $d_s=0.65$ for instance, the difference between the curve for the linear and that for the branched alkanes is 30°C for PE and only 8°C for PP. (3) These features appear to be a regular function of the ethylene content of the copolymer since at $d_s=0.65$ the difference as seen in *Figure 3* between the curves is 27°C for the 81% E copolymer and 10°C for

Table 2 LCST of polyethylene (PE), propylene (PP) and ethylene–propylene copolymers (in K)

			EP Copolymers					
		PE	81%E	75%E	63%E	53%E	33%E	PP^{d}
	$10^{-5} M^{a}$	1.34	1.95	1.09	2.38	1.54	1.73	2.42
n-Pentane	5^{f}	353^{c}	370	378	387	395	409	422^{c}
n-Hexane	6	411^{c}	425	427	436	443	455	470^{c}
n-Heptane	7	459^{c}	468	475	485	493	502	511^{c,e}
n-Octane	8	496^{c}	506	509	512		528	542
n-Nonane	9	531	540	542	547		558	571
2-Methyl butane	5a	ins^{b}	327		348		396	413^{e}
2,2-Dimethyl butane	6a	ins^{b}	381			407	428	441
2,3-Dimethyl butane	6b	ins^{b}	413		429	437	452	465
2,4-Dimethyl pentane	7a	395	420	425	434	445	464	481
2,2-Dimethyl pentane	7b	399	425	431	444	453	472	489
2-Methyl hexane	7c		453				486	
3-Methyl hexane	7d		459					
2,2,3-Trimethyl butane	7e	444	461		479	488	500	511
2,2,4-Trimethyl pentane	8a	495	460	469	479	484	503	510
2,5-Dimethyl hexane	8b		466					
2,3-Dimethyl pentane	7f	463	471		482	488	500	513
3-Ethyl pentane	7g	471	478		492	500	511	520
2,4-Dimethyl hexane	8c		478					
3,4-Dimethyl hexane	8d	515	522		530		541	553
2,2,4,4-Tetramethyl pentane	9a	513	519	523	528		539	548
2,3,4-Trimethyl hexane	9b	545				565		585
Cyclopentane	5b	472	474		481		490	495
Methyl cyclopentane	6c	488	493		498		512	518
Methyl cyclohexane	7h	537	541				558	564^{e}
Cyclohexane	6d	518	522		526		534	540

[a] Samples characterized in part 2 of this work

[b] Insoluble; extrapolated values (290 K in 2-methyl butane, 354 K in 2,2-dimethyl butane and 392 K in 2,3-dimethyl butane) are used in *Figures 2* and *5*

[c] *LCST* for these systems can be found in the literature, when measurements have been extrapolated to infinite molecular weight, somewhat lower values than the tabulated ones are reported (PE in references 20b and 21; PP in J. M. G. Cowie, I. J. McEwen. *J. Polym. Sci. Polym. Phys. Edn.*, 1974, **12**, 441

[d] Except when indicated, *LCST* are for isotactic polypropylene

[e] A sample of atactic polypropylene was also used for these solvents, giving similar *LCST*

[f] Identification numbers used in *Figures 2, 3* and *5*

the 33% E sample. (4) The correlation between the *LCST* and d_s is good, particularly for the branched alkanes which differ in shape. This point will be discussed in part 2 along with the *LCST* results of other polyolefins.

The results point to, in the case of PE solutions, the existence of a positive contribution to χ which becomes larger with volatile solvents and correspondingly lowers the *LCST*. This contribution is higher for the branched solvents than that for the linear solvents.

Orientational order in PE melt and not in PP melt

The χ parameter is defined as the interchange free energy when solvent–solvent and polymer–polymer contacts (both in the pure liquid phase) are replaced by polymer-solvent contacts in solution. The higher χ value for PE solutions compared to that for PP may come either from poorer contacts in solution or improved contacts in the pure state. The present results seem to be better explained by the improved contacts in the pure state. Due to the total regularity of the segments, PE in the melt has *CMO* between the chains. This hypothesis is only an extension at higher molecular weights, of what has been found with linear alkanes. The mixing with a high free volume branched alkane solvent destroys the liquid polymer *CMO* and consequently the solution is less stable than would have been expected from force field or equation of state differences. In other words, the concentrated solution of PE formed at the *LCST* is favoured compared to the dilute solution because PE regains some of the *CMO* it has in the melt phase. However, the PP chains probably do not retain in the melt, the helicoidal configuration of the solid state so that the process of mixing does not bring about any more disorder than usually comes from the mixing of two liquids. The destruction of CMO is a positive free energy process which raises χ and precipitates the phase separation. This hypothesis explains the difference between the *LCST* curves for the globular and linear solvents. The solubility is higher in linear alkanes since polymer and solvent molecules can fit their segments even if the large solvent free volume prevents extensive *CMO*. In *Figure 3* the *LCST* of the 81% E copolymer in pentane is 43°C higher than in the globular 2-methylbutane which has about the same density. More data are available for the 81% E copolymer than for PE since its reduced crystallinity makes it more soluble in volatile solvents. An interesting result of this work is the persistence at high temperatures of *CMO* in the PE melt and consequently, the effect of the solvent shape on the solvent quality at these high temperatures.

LCST *and copolymer composition*

In *Figure 4*, the *LCST* for the 2 homopolymers and for 5 copolymer samples in eight solvents have been plotted

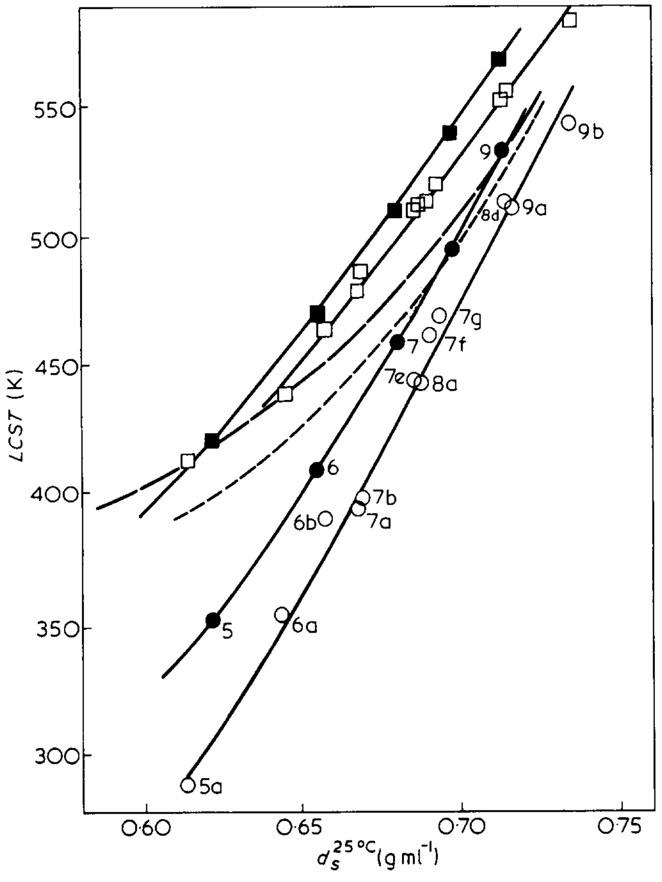

Figure 2 PE and PP *LCST* (in K) in linear (full) and branched (open) alkanes plotted against d_s (g. ml^{-1}), the solvent density. PE (○) PP (□). The lines joining the calculated values, PE (— — —) and PP (——— ———) are drawn for linear alkanes using the data from *Table 2* of part 2. Solvent identification numbers in *Table 1*

versus the molar ethylene content of the polymer as given by the company, these were 33% E, 53% E, 63% E, 75% E and 81% E respectively. In the two lower curves of the figure, one can see the striking difference in the effect of slightly changing the solvent shape (from pentane to 2 methylbutane) on the two polymers. With PP, the *LCST* is lowered by less than 10°C while with PE it is by more than 60°C. This can be understood in terms of *CMO*.

When the ethylene sequences of the copolymer chain get more frequent and longer, they can correlate better with each other. Consequently, the globular order-breaker 2-methylbutane, becomes a worse solvent. The effect is much less pronounced with the linear pentane due to *CMO* in solution. The next two branched hexanes are order-breakers like 2-methylbutane so that the difference between the *LCST* for the two homopolymers is large, i.e. higher than 32°C as measured for the 81% E sample. The next two solvents have been chosen to illustrate the limit of stability of *CMO* at high temperatures. At 170°C there is still enough *CMO* left in PE to favour by 17°C the solvent n-C_7 in which some *CMO* are possible (compared to the branched 2,2,3 trimethylbutane with the same density). At higher temperatures in cohesive solvents like cyclohexane, *CMO* must play only a minor role so that the *LCST* difference between the two polymers diminishes to about 20°C.

These features are readily seen in *Figure 5* where the difference in *LCST* of the two homopolymers has been plotted against the solvent density. The line has been drawn through the values for the linear alkanes. The broken line joins the calculated values for the same solvents. As can be seen, the experimental differences are much larger than the calculated ones and they depend on the solvent shape. This effect on the *LCST* diminishes when the solvent density increases, i.e. when the *LCST* occurs at higher temperatures. The four points on the high density part of the figure correspond to the cycloalkanes.

Disordering and free volume contributions

Figure 6 is a plot of the *LCST* of the 2 homopolymers and of the 5 copolymers of different composition in n-hexane and 2,4-dimethylpentane *versus* the polymer ethylene content. Using only the equation of state term, similar *LCST*s are predicted (broken lines) over the total range of polymer composition. The experimental crossing over of the two curves when the polymer composition changes is an illustration of the 2 contributions to χ. In PP solutions or propylene-rich copolymers, the free volume term, a little larger for the more volatile n-C_6, is dominant so that the *LCST*s are lower in n-C_6 than in 2,4 dimethylpentane. As the ethylene content of the copolymer increases, the term resulting from the destruction of the *CMO* in the polymer increases. This increase is faster with 2,4 dimethylpentane than with n-C_6. Consequently 2,4 dimethylpentane becomes less good a solvent than n-C_6. Going from PP to PE, the difference between the two polymers changes sign, the more volatile n-C_6 becoming a better solvent due to the setting of *CMO* in solution.

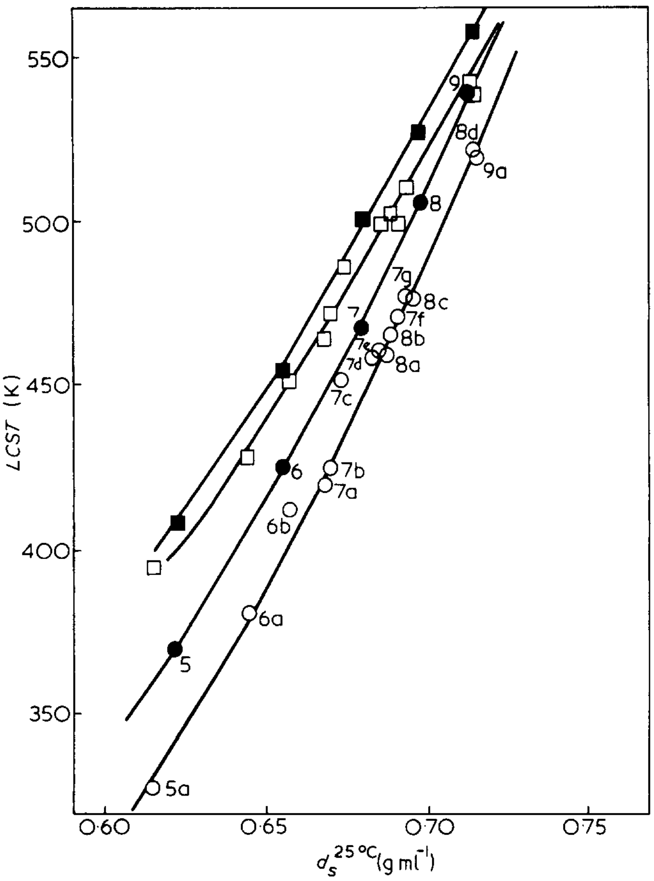

Figure 3 *LCST* (in K) for the 33%E (□) and 81%E (○) ethylene–propylene copolymers plotted against d_s (g. ml^{-1}) the solvent density in linear (full) and branched (open) alkanes. Solvent identification numbers in *Table 1*

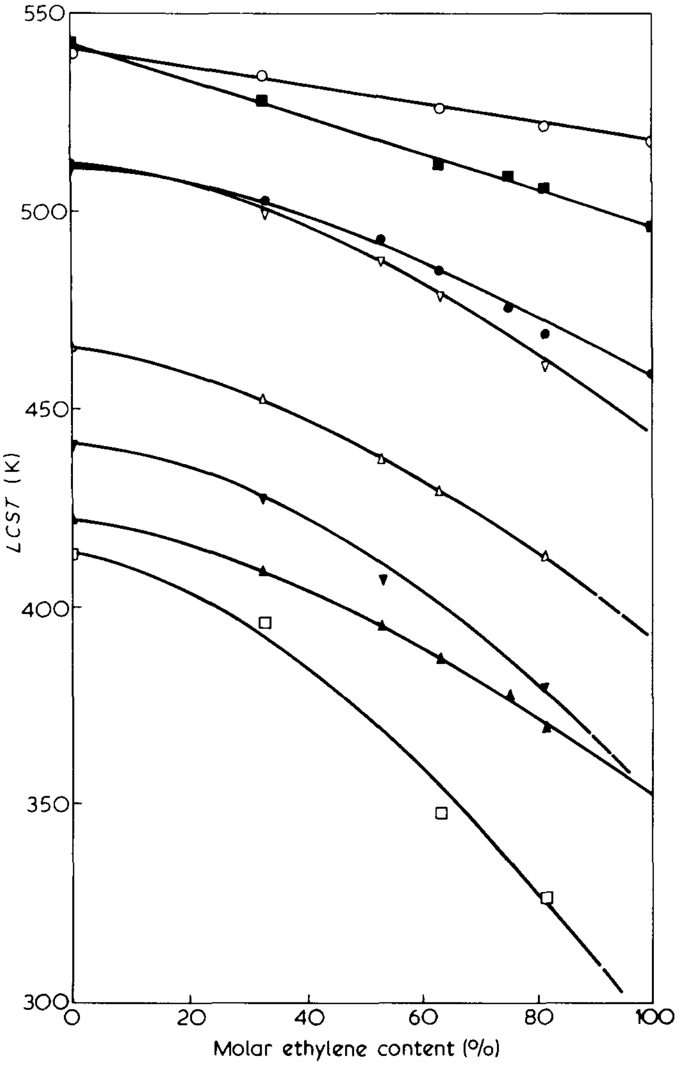

Figure 4 *LCST* (in K) for PP, PE and 5 ethylene–propylene copolymers as a function of the polymer molar ethylene content in 8 solvents: (□), 2 methylbutane; (▲), n-pentane; (▼), 2,2 dimethylbutane; (△), 2,3 dimethylbutane; (▽), 2,2,3 trimethylbutane; (●), n-heptane; (■), n-octane and (○), cyclohexane, in decreasing order of *CMO* breaking ability. Both shape and free volume contribute to the effect

Range of orientational order in the copolymers

Detailed analysis of the i.r. and n.m.r. spectra of the copolymers[25] leads to the reasonable conclusion that the samples with a high ethylene content have, on the average, longer ethylene sequences than the ethylene-poor samples. By analogy with the linear alkanes, one could have expected that a minimum length (about 7 carbon atoms) of these ethylene sequences was necessary to make the *CMO* possible in the copolymer melt. The consequences on the *LCST* would have been a nearly constant *LCST* near that of PP followed by a rapid drop towards the *LCST* of PE for a given ethylene concentration corresponding to a minimum length for *CMO*. It can be seen in *Figures 4, 6* and *7* that this does not occur since the *LCST* decrease has an almost linear dependence on the ethylene content. This implies that *CMO* exists even with short $-CH_2-CH_2-$ sequences at the condition, that the free volume around these sequences is low as is the case for polymers.

When a homopolymer is mixed in a binary solvent, its thermodynamic properties are not a linear dependence of the solvent composition. The deviation from the line joining the polymer properties in the pure solvents depends on the thermodynamic properties of mixing of the two solvents (heat or free energy of mixing). In the present case of a copolymer mixed with one solvent, the deviation from the straight line is related to the mixing properties of the two sequences in the polymer. The

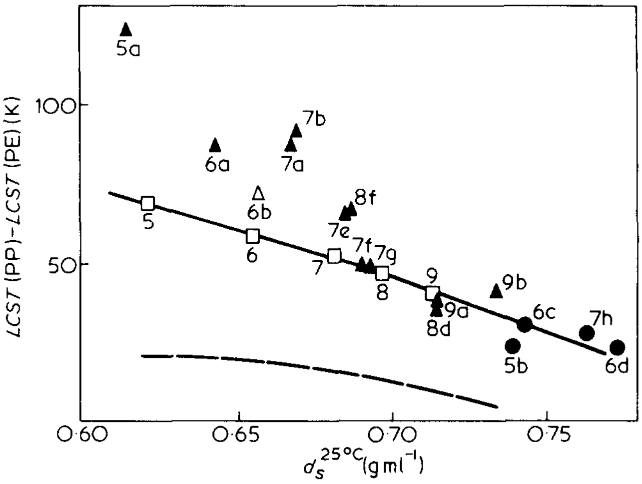

Figure 5 Difference between the *LCST* for PP and PE in linear (□), branched (▲) and cyclic (●) alkanes plotted against d_s (g. ml^{-1}) the solvent density. The solid line is drawn through the linear alkanes. The broken line joins the calculated difference for linear alkanes. The branched alkanes (▲) are better probes of the difference between the two polymers than the linear alkanes (□). Independent of the solvent shape, the difference decreases when the density (or the *LCST*) increases. Solvent identification numbers in *Table 1*

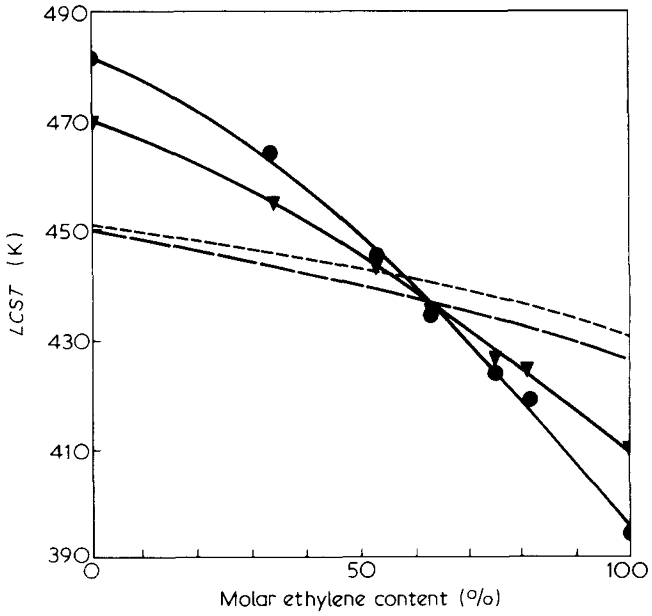

Figure 6 *LCST* (in K) for PP, PE and 5 ethylene–propylene copolymers plotted against the polymer molar ethylene content in n-hexane (▲) and 2,4 dimethylpentane (●). The broken lines are the calculated curves for n-hexane (– – –) and 2,4 dimethylpentane (—— ——). Calculations were carried out assuming that the thermal expansion coefficients of the copolymers vary linearly with the composition between the PE and PP values. The decreasing solvent quality of the branched alkane for ethylene-rich copolymers and PE, due to the destruction of *CMO*, is responsible for the crossing over of the two curves

present results confirm that the free energy of the mixing of the $-CH(CH_3)-CH_2-$ and $-CH_2-CH_2-$ groups is not high. Other parameters, such as the surface to volume ratio of the different groups, can contribute to change the magnitude of the deviation from linearity as represented by *Figures 4*, *6* and *7*.

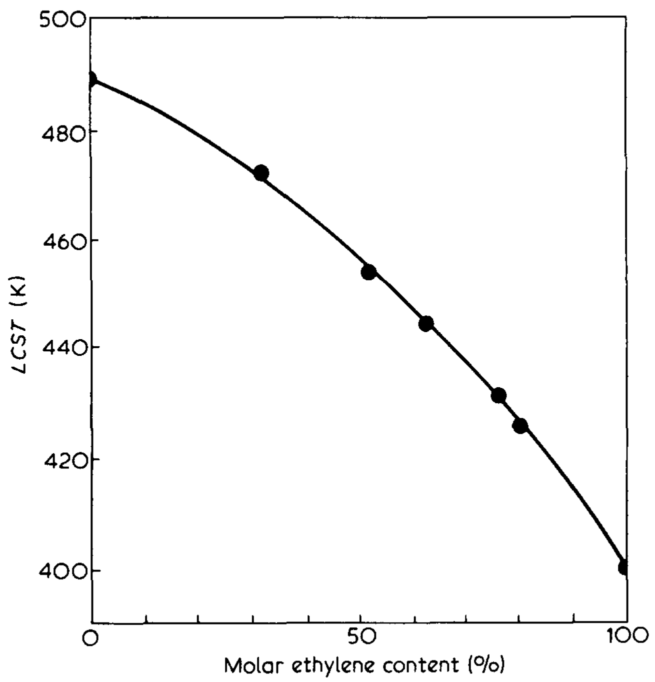

Figure 7 Dosage of the ethylene content. The *LCST* of PP, PE and 5 ethylene–propylene copolymers in 2,2 dimethylpentane plotted against the polymer molar ethylene content. Due to the large spread in the *LCST* between the 2 homopolymers, the ethylene content is obtained with an accuracy equal to that of the i.r. dosage (~2%)

Comparison with calculated LCST

With reasonable approximation of the negligible difference in force field between the polymers and the hydrocarbons, the *LCST* can be calculated, as explained in Part 2, without adjustable parameters by using only physico-chemical data on the pure components (*Table 1*). Lines joining the calculated *LCST* can be drawn and compared to the experimental ones in *Figure 2*. To make the figure clearer only the curves for the linear alkanes have been drawn. The curves for the branched alkanes are parallel to those of the linear alkanes but are situated about 5–7° lower. Other models give curves at higher or lower temperatures but the trend for the two polymers with that of solvent density would be the same. As can be predicted from the state of expansion of the two homopolymers, the temperature interval between the *LCST* is nowhere as large as the experimental one. For solvents with $d_s = 0.65$, the calculated difference is about 15°C compared with the experimental value of 62°C. For PP and propylene-rich copolymers (*Figure 3*), the trend of the *LCST versus* the solvent density is described by the theory reasonably well. It should be noted too that for PE or ethylene-rich copolymers (*Figure 3*), the difference between the *LCST* for branched and linear polymers increases considerably for the volatile solvents, a feature not predicted by the free volume contribution to χ.

Thermodynamic dosage of the ethylene content of the EP copolymers

The large spread of the *LCST* over the whole composition range suggests that measurement of *LCST* could be used as an analytical tool for the dosage of a copolymer. As an example, the data obtained in 2,2-dimethylpentane for the 2 homopolymers and the 5 copolymers have been plotted against the polymer composition. The 90°C difference between the *LCST* of the 2

Table 3 Comparison of the thermodynamic dosages of the ethylene content of ethylene–propylene copolymers

Molar[a] ethylene content	*LCST*[b] (K)	Viscosity at 25°C $10^7([\eta]_{lin} - [\eta]_{br}) \times M^{-1}$ [c,e]		Calorimetry $(h^E_{cis} - h^E_{trans})$[d] (J g^{-1})
		dodecanes	hexadecanes	
0	489			
33	472	−2.3	−13.0	2.4
53	453		−2.1	
63	444	8.0	4.6	3.7
75	431	14.7	12.8	4.2
81	425	17.4		
100	399			
Accuracy	1–2%	1–2%		1–2%
Range of composition	All range	Limited to atactic or partially crystalline samples		Limited to atactic or partially crystalline samples
Range of molecular weight	All range, with calibration	Preferably $M > 0.5 \times 10^5$		Independant of *M*
Time required	1–2 h	24–48 h Including dissolution		3–4 h

[a] As given by the company and measured by i.r.

[b] In 2,2-dimethyl pentane for molecular weights between 10^5 and 3×10^5

[c] Difference between the intrinsic viscosities in the linear alkane and the branched 2,2,4,4,6,8,8-heptamethyl nonane and 2,2,4,6,6-pentamethyl heptane. Results in reference 3 are on the hexadecanes only. However, the dodecanes are preferable for semi-crystalline samples like the 81%E which dissolves slowly in the hexadecanes

[d] h^E at infinite dilution in *cis* and *trans* bicyclo (4,4,0) decane, decalin, reference 7

[e] Viscosity measurements at higher temperatures will improve the dosage: for instance the all range of composition could be covered and less time would be required to achieve dissolution

extremes and the smooth, almost linear variation of the *LCST* with composition are a guarantee of an accurate composition determination. An accuracy of 2 degrees in the *LCST* determination would correspond to commensurate composition determination within 2%. Much lower molecular weights than those measured here, will increase the *LCST* and give too high a propylene content. A calibration curve should then be done with samples of the correct molecular weight.

The advantage of this technique is its rapidity. Even for crystalline or semi-crystalline polymers, the sample dissolution accomplished inside the measuring tube takes less than 1 h. The recording of the *LCST* may be made completely automatic with non-expensive devices.

Comparison with other theymodynamic dosages

Some solution properties, at 25°C, of the EP propylene copolymers[3,4,10] have been found to be a linear function of the composition over the range of ethylene content investigated, i.e. 33% to 75%. The present results, which could be obtained over the whole ethylene concentration range, show that the *LCST*s are also a linear function of the composition over a somewhat larger span (33% to 81%) although the overall data follow a curve with a small curvature. *Table 3* gives, for three different methods, the experimental data obtained for the samples studied.

Following the *LCST* results, the differences between the intrinsic viscosities for the same polymer in a linear and a branched alkane are listed for the various samples using either the dodecanes or hexadecanes. The last column gives the difference in heats of mixing at infinite dilution in *cis*- and *trans*-decahydronaphthalene. The sensitivity, the suitability (relative to polymer composition and molecular weight), the time required for a measurement, and the relative cost of the equipment are compared in *Table 3*. Speedier dissolution of the polymer at high temperature in a sealed tube is of great advantage to the *LCST* compared to the viscosity for which perfect dissolution and precise concentration are essential.

ACKNOWLEDGEMENTS

We acknowledge the support of the National Research Council of Canada for this work.

REFERENCES

1a Moraglio, G., Gianotti, G., Zoppi, F. and Bonicelli, U. *Eur. Polym. J.* 1971, **7**, 1

b Kinsinger, J. B. and Weisling, R. A. *J. Am. Chem. Soc.* 1959, **81**, 2908

2 Vinh te Lam, Picker, P., Patterson, D. and Tancrede, P. *J. Chem.* Soc. Faraday Trans. 2 1974, **70**, 1465

3 Delmas, G., Daviet, V. and Filiatrault, D. *J. Polym. Sci.* 1976, **14**, 1629

4 Filiatrault, D. and Delmas, G. *Macromolecules* 1979, **12**, 65, 69

5a Delmas, G. and Purves, P. *J. Chem. Soc. Faraday Trans. 2* 1977, **73**, 1828, 1838

b Philippe, R., Delmas, G. and Couchon, M. *Can. J. Chem.* 1978, **57**, 517

6 Tancrede, P., Bothorel, P., De Saint-Romain, P. and Patterson, D. *J. Chem. Soc. Faraday Trans. 2* 1977, **73**, 15

7 Phuong-Nguyen, H. and Delmas, G. *Macromolecules* 1979, **12**, 740, 746

8 Barbe, M. and Patterson, D. *J. Phys. Chem.* 1978, **82**, 40

9 Couchon, M., Phuong-Nguyen, H. and Delmas, G. *Can. J. Chem.* 1978, **56**, 2472

10 Filiatrault, D., Phuong-Nguyen, H. and Delmas, G. *J. Polym. Sci.* Parts 1 and 2 to be published

11 Filiatrault, D., Phuong-Nguyen, H. and Delmas, G., unpublished results

12 Delmas, G. and De Saint-Romain, P. *Eur. Polym. J.* 1974, **10**, 1133

13 Croucher, M. D. and Patterson, D. *J. Chem. Soc. Faraday Trans. 2* 1974, **70**, 1479

14 Dreifus, D. W. and Patterson, D. *Trans. Faraday Soc.* 1971, **67**, 631

15a Klunder, H., Hammers, W. E. and De Ligny, C. L. *J. Solut. Chem.* 1978, **7**, 485

b ibid, 1978, **7**, 475

16 Longman, G. W., Wignall, G. D. and Sheldon, R. P. *Polymer* 1979, **20**, 1063; and *ibid.* 1976, **17**, 485

17 Delmas, G. and Patterson, D. *J. Polym. Sci. (C)* 1970, **30**, 1

18 Prigogine, I. with the collaboration of Mathot, V. and Bellemans, A. 'The molecular theory of solutions', North Holland Publishing Co., Amsterdam, 1957

19a Delmas, G., Patterson, D. and Somcynski, T. *J. Polym. Sci.* 1962, **57**, 79

b Patterson, D., Delmas, G. and Somcynski, T. *Polymer* 1966, **8**, 503

c Bardin, J. M. and Patterson, D. *Polymer* 1969, **10**, 247

20a Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1833

b Orwoll, R. A. and Flory, P. J., ibid. 1967, **89**, 6814

c Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035

21 Hamada, F., Fujisawa, K. and Hakajima, A. Polym. J. 1973, **4**, 316

22 Siow, K. S., Delmas, G. and Patterson, D. *Macromolecules* 1972, **5**, 29

23 Saeki, S., Kuwahara, N., Ohho, S. K. and Kaneko, M. *Macromolecules* 1973, **6**, 246

24 Cowie, J. M. G., Maconnachie, A. and Ranson, R. J. *Macromolecules* 1971, **4**, 57

25 Liddell, A. H. and Swinton, F. L. *Faraday Soc. Discuss.* 1970, **49**, 136

26 Stover, W. H., Research Department, Imperial Oil, private communication