Thermodynamic properties of polyolefin solutions at high temperature: 2. Lower critical solubility temperatures for polybutene-1, polypentene-1 and poly(4-methylpentene-1) in hydrocarbon solvents and determination of the polymer–solvent interaction parameter for PB1 and one ethylene–propylene copolymer

Gérard Charlet, Romain Ducasse and Geneviève Delmas
Département de Chimie, Université du Québec à Montreal, CP 8888 *Montréal P.Q. Canada, H3C 3P8*

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

Lower critical solubility temperature (*LCST*) for 3 polyolefins, polybutene-1 (PB1), polypentene-1 (PP1) and poly(4-methylpentene-1) (P4MP1), and the χ interaction parameter in concentrated solutions for PB1 and the 33% ethylene ethylene–propylene copolymer have been measured in linear, branched, cyclic alkanes and some other solvents. Effects on χ of the equation of state term, of correlations of molecular orientations (*CMO*) and of the solvent steric hindrance were investigated. The solvent density d_s is found to be a good empirical parameter to characterize the equation of state term and to correlate the *LCST*. The parameter d_s/d_p (where d_p is the polymer density) affords an excellent correlation for the *LCST* of all polyolefins in normal and branched alkanes (polyethylene (PE) excepted). In dilute solution (at the *LCST*) the effect of *CMO* and solvent steric hindrance could not be distinguished from equation of state effects. However, values of χ, found to be higher in branched than in linear alkanes in solutions of the linear polymer (PE) but not with the branched PB1 and the copolymer, are indicative of the importance in concentrated solutions of *CMO* even at high temperatures (100°–135°C). Furthermore, the lowering of χ from linear PE to the branched PE and to the ethylene–propylene copolymers, following the expected diminution of *CMO* in the corresponding melts, is another indication of the persistance of *CMO* at high temperature. Solvent steric hindrance is seen to lower χ (measured here by gas-liquid chromatography).

INTRODUCTION

In part 1 of this work the *LCST* for polyethylene (PE), polypropylene (PP) and ethylene–propylene (EP) copolymers were measured in branched and linear alkanes[1]. The much lower values of the *LCST* in PE than in PP that would be expected from the difference in the expansion coefficients of PE and PP lead to the conclusion that PE was a special polyolefin. Due to the regular shape of the repetitive segment, it presents order in the liquid state. The destruction of this order by high free volume solvents lowers the *LCST*, since it is equivalent to the addition of a chemical term in the χ parameter. Other polyolefins, made with branched segments, manage order in the solid state in spite of the side group by having a helicoidal conformation.

Three polyolefins $(-CHR-CH_2-)_n$ were studied in the present work, namely PB1 ($R = C_2H_5$), PP1 ($R = C_3H_7$) and P4MP1 ($R = CH_2-CH-(CH_3)_2$). The original aim of this work was to measure the *LCST* of P4MP1 which has unusual bulk[2] and solution[3] properties. Its solubility near room temperature in small size solvents such as CS_2, cycloC_5 or cycloC_6, points to a helicoidal conformation of the polymer in these solvents. Such a hypothesis has been advanced on isotactic polyolefins having a side group like PB1 and PP1[4,5].

However, it appeared on first measurements that the expanded character of P4MP-1 shifted the *LCST* so high that, at these temperatures, there was no possibility of having a conformation other than the statistical coil. Although it was likely that the difference in free volume between polymer and solvent was the main factor in the *LCST* of the three branched olefins, data were taken in a large variety of linear and branched solvents in order to analyse the results for an indication of the persistence of the two effects seen at room temperature in non-polar solvents, namely the correlations of orientations and solvent steric hindrance. Measurements of the free energy parameter χ at high polymer concentration were taken on one branched polyolefin and one sample of EP copolymer. In a like manner, they were compared with the literature results on PE and one EP copolymer.

0032-3861/81/091190-09-02.00

Table 1 Characterization of PE, PP, EP copolymers, PB1, PP1, P4MP1

		$[\eta]$ dl. g^{-1}	$M \times 10^{-5}$	M_w/M_n [g]		Origin
PE unfractionated		1.85[a]	1.34		$[\eta] = 67.7 \times 10^{-5} M^{0.67}$	Phillips Marlex 50
81%E EP copolymer unfractionated		1.76[b]	1.95			Uniroyal
75%E unfractionated		1.45[c]	1.09			Exxon lab. Linden, N.J.
63%E unfractionated		1.75[c]	2.36		$[\eta] = 45.1 \times 10^{-5} M^{0.668}$	Exxon lab. Linden, N.J.
53%E unfractionated		1.40[c]	1.54		$[\eta] = 30.5 \times 10^{-5} M^{0.706}$	Exxon lab. Linden, N.J.
33%E unfractionated		1.34[c]	1.45			Goodrich Chem. Co.
PP isotactic unfractionated		2.23[d]	2.42		$[\eta] = 11 \times 10^{-5} M^{0.80}$	Hercules Co.
PB1 atactic						Huls (Germany)
Fractions	B3	1.00[e]	1.0		$[\eta] = 28.2 \times 10^{-5} M^{0.71}$	
	B5	0.47	0.34		ib.	
	A1	0.31	0.19			
	T	0.20	0.10[f]			Atactic part of Petrotex
Isotactic unfractionated		3.24[e,k]	5.3			Petrotex, Co. Houston, Texas (Dr. McMinn)
Fractions	1	6.42	13.7	1.19	ib.	
	2A	4.16	7.18			
	2B	3.61	6.10		ib.	
	3	2.54	3.71	1.16		
	4	1.46	1.70			
	5	0.73	0.64	1.11		
	6	0.39	0.26			
PP1 isotactic unfractionated		5.92[h]	45.0		$[\eta] = 38.1 \times 10^{-5} M^{0.63}$	ICI Hertfordshire, England
P4MP1 isotactic unfractionated		3.06	1.52[i]		$[\eta] = 19.4 \times 10^{-5} M^{0.81}$	ICI (TPX)
		3.06	4.87[j]		$[\eta] = 19.5 \times 10^{-5} M^{0.76}$	

[a] In decalin at 135°C ref. 9a
[b] In toluene at 30°C, ref. 9b
[c] In toluene at 30°C, ref. 9c
[d] In decalin at 135°C, ref. 9d
[e] In cyclohexane at 35°C, ref. 8
[f] Fraction used for g.l.c.
[g] Measured by g.p.c.
[h] In toluene at 30°C ref. 10
[i] In decalin at 135°C, ref. 11a
[j] In decalin at 130°C ref. 11b
[k] In decalin at 115°C $[\eta] = 2.40$ dl g^{-1} giving[8b] $M = 10.8\ 10^5$

The correlations of the *LCST* and χ data in the different solvents were carried out using the solvent and polymer densities as a measure of the free volume difference between the two components.

EXPERIMENTAL

Materials

The solvents were purchased from the Aldrich Company (Milwaukee) and from the Chemical Sample Company (Columbus, Ohio) and were used without purification.

Polymers

Their density and expansion coefficient as well as those of the solvents are given in *Table 1* of part 1[1].

Polybutene-1. The isotactic PB1 was given to us by Dr McMinn of the Petrotex Company, Houston, Texas. The mainly atactic polymer was either extracted from the isotactic one or obtained from the more atactic samples produced by the Huls Company (Germany).

Poly (4-methylpentene-1). This was a commercial product of the ICI Company (TPX) known to contain a small percentage (<5%) of another monomer (hexene-1 or pentene-1).

EP copolymers. Were the same as in part 1.

Polypentene-1. This was a laboratory sample sent by ICI, Welwyn Garden City, Hertfordshire (England).

Fractionation

Polybutene-1: Atactic polymer: The polymer dissolved in petroleum ether was kept for 5 h at −30°C in order to precipitate the residual isotactic component. After centrifugation, the polymer in the clear phase was reprecipitated and fractionated at 35°C using petroleum ether (50°–70°C) as solvent and acetone as the non-solvent[6,7].

Polybutene-1: Isotactic polymer: The polymer from which the atactic part has been extracted was fractionated at 85°C using dichlorobenzene as solvent and *N–N* dimethylformamide as the non solvent[7]. *N*-Phenyl β naphthylamine was added (0.05%) to avoid degradation.

The polydispersity of the isotactic fractions was measured with a standard g.p.c. apparatus (Waters Associates in *o*-dichlorobenzene at 130°C. The data for the fractions are given in *Table 1*. Published $[\eta]$-M relationships were used to obtain M_v from $[\eta]$ for PB1[8,9] unfractionated PE[9a], EP copolymers[9b,c], PP[9d], PP1[10] and P4MP1[11].

Lower critical solubility temperature

The technique has been described in part 1[1]. As previously[1] the *LCST* data tabulated in *Table 2* are, for most of the polymer–solvent systems, the values obtained for one molecular weight. For four PB1-systems however (in n-C_5, n-C_6, n-C_7 and n-C_9), the temperature of phase separation was measured for several molecular weights and $LCST_\chi$ obtained as the extrapolated value of the *LCST* at a finite molecular weight (compare with *Figure 2*).

Table 2 Calculated $c_1\tau^2$ parameter and calculated *LCST* for PIB, PE, PP, PB1, PP1 and P4MP1

Polymer		PIB[a]		PE[b]		PP[b]		PB1[c]		PP1[c]		P4MP1[c]	
	T^* (K)	7569		6363		5952		6174		5997		6049	
Solvent[e]		$c_1\tau^2$	*LCST*[d]	$c_1\tau^2$	*LCST*	$c_1\tau^2$	*LCST*	$c_1\tau^2$	*LCST*	$c_1\tau^2$	*LCST*	$c_1\tau^2$	*LCST*
4	3990	0.214	269	0.133	368	0.104	389	0.120	378	0.107	387	0.111	359
5	4215	0.208	295	0.121	399	0.0902	420	0.1070	410	0.0935	418	0.0973	416
6	4441	0.198	327	0.106	432	0.0748	451	0.0914	442	0.0781	449	0.0820	447
7	4665	0.186	363	0.0899	465	0.0590	481	0.0754	473	0.0623	480	0.0661	465
8	4864	0.174	397	0.0756	494	0.0455	506	0.0614	500	0.0487	505	0.0523	504
9	5097	0.155	443	0.0574	526	0.0299	535	0.0442	531	0.0327	534	0.0359	533
10	5273	0.142	475	0.0455	549	0.0201	555	0.0329	552	0.0225	554	0.0255	554
6b	4397	0.199	322	0.108	426	0.0775	445	0.0940	436	0.0808	444	0.0847	441
7a	4460	0.216	298	0.115	428	0.0804	450	0.0987	439	0.0841	448	0.0883	446
7b	4567	0.189	350	0.0958	452	0.0651	468	0.0814	460	0.0683	467	0.0721	465
7e	4703	0.164	397	0.0779	476	0.0504	488	0.0649	482	0.0533	487	0.0566	486
8a	4801	0.164	405	0.0741	488	0.0460	500	0.0608	494	0.0489	499	0.0523	497
8b	4747	0.185	371	0.0857	476	0.0544	491	0.0709	484	0.0577	490	0.0615	488
7f	4699	0.173	384	0.0828	473	0.0534	486	0.0688	480	0.0565	485	0.0601	484
7g	4650	0.188	359	0.0915	463	0.0604	479	0.0770	471	0.0637	477	0.0676	476
8d	5010	0.150	442	0.0592	516	0.0328	525	0.0466	521	0.0355	524	0.0386	523

[a] Experimental *LCST* are not reported in this work and can be found in ref. 17

[b] As stated in part I the equation of state parameters predict a 20°C difference only between the *LCST* for PE and PP, while the experimental one can reach 90°C

[c] Experimental data in *Table 3*

[d] As is common with this model, the *LCST* are predicted 40°–60° lower than the experimental ones

[e] Identification of the solvents is in *Table 3*

Gas liquid chromatography

PB1 was fraction T with the transparent aspect of an atactic polymer. PB1 was deposited on columns (I) and (II) and the 33%E EP copolymer on column (III). They were coated onto chromosorb W (60–80 mesh AW DMSC treated) from a petroleum ether (I–II) or toluene (III) solution. The coated support was packed in $\frac{1}{4}$ inch outer diameter copper tubing (petroleum ether washed).

Column characteristics: The three columns had the following parameter lengths (ft): 6.0 (I), 3.5 (II) and 3.0 (III). Wt coated support: 8,814 (I), 5.090 (II) and 4.863 (III). Total wt of polymer (g): 0.393 (I), 0.4074 (II) and 0.3412 (III). Weight % of polymer: 4.19 (I), 7.99 (II) and 5.22 (III). Retention volumes were measured at two pressures (5 and 4 psi) for (I) and (II) and one pressure (2 psi) for (III).

Retention volumes were taken at 115°C and 135°C for (I), 120°C for (II) and 110°C for (III). The g.l.c. apparatus and the procedures used to measure retention times and volumes have been described elsewhere[17b].

Theory of the LCST

The following general expression was derived for the χ parameter at low polymer concentration and at zero pressure[12].

$$\chi = \frac{-U_s}{RT} v^2 + \frac{C_{p,s}}{2R} \tau^2 \qquad (1)$$

or in the reduced form where the tilde superscript indicates a reduced quantity:

$$\frac{\chi}{c_1} = \frac{-\tilde{U}_s}{\tilde{T}_s} v^2 + \frac{\tilde{C}_{p,s}}{2} \tau^2 \qquad (2)$$

U_s is the configurational energy of the solvent, essentially the negative of the energy of vaporization, and $C_{p,s}$ is the configurational heat capacity or temperature derivative of U_s. The second term of the right hand side of equation (1) reflects the difference in free volume between the two components through the parameter:

$$\tau = 1 - \frac{T_s^*}{T_p^*} \qquad (3)$$

T_s^* and T_p^* are the temperature reducing parameters obtainable either from a corresponding state theory or from a model. In the first term v^2 (equivalent to X_{12}/P_s^* in the Flory theory) is a measure of the relative weakness of the polymer–solvent contacts to the average of the solvent–solvent and polymer–polymer contacts. According to equation (1), χ can go through a minimum when the temperature increases due to the importance of the first term at low temperatures and of the second at higher temperatures. Consequently, two phase separations can occur, one at low temperature which is the usual θ temperature and one at high temperature namely the *LCST* when χ reaches 0.5, the critical value for an infinite molecular weight. For the solutions of polyolefins in non-polar solvents, the difference in force field between the two components is sufficently small to justify the approximation $v^2 = 0$, leaving only the second term or equation of state term to contribute to χ.

$$\chi = \frac{C_{p,s}}{2R} \tau^2 = \frac{\tilde{C}_{p,s}}{2} c_1 \tau^2 \qquad (4)$$

In volatile solvents, the critical value of χ can be obtained at low enough temperatures since τ^2 is large. For higher molecular weight solvents for which τ^2 is small, the *LCST* also occurs when the critical value of χ is reached due to the rapid increase of C_p near the critical solvent temperature T_c.

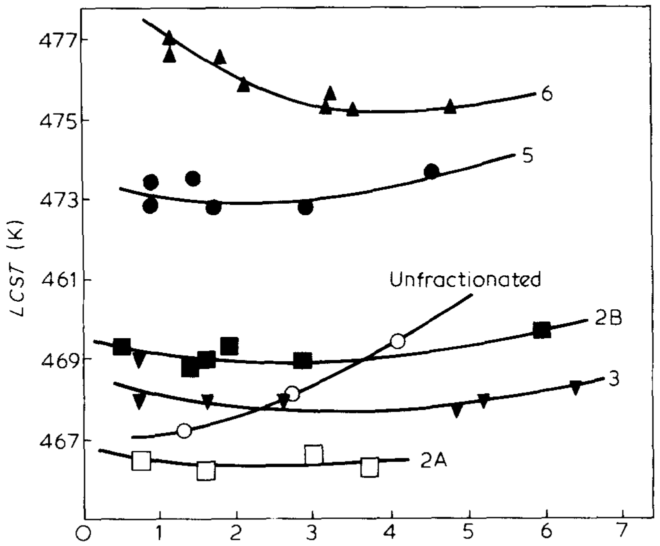

Figure 1 Phase diagrams in n-hexane of 6 isotactic PB1 samples (identified in *Table 1*): 5 fractions (2A, 3, 2B, 5 and 6) and one unfractionated sample

Parameters for the equation of state term: Temperature reduction parameters:

The polymer and the reference system (n-C_8) parameters, are obtained from the expansion coefficients and the van der Waals model[13]. The T^* for the other solvents have been taken from the corresponding state calculations of Patterson[14] and de Ligny and collaborators[15] and reported in *Table 2*.

Degrees of freedom

$3c_1$, The number of degrees of freedom of the solvents has been obtained from reference 15. c_1 is related to the pressure, volume and temperature reduction parameters by $3c_1 = P^*V^*/RT^*$.

Van der Waals model

Values of C_p necessary to obtain χ for equation (4) are given by a model since experimental data are not available. With the Van der Waals model $\tilde{U} = -\tilde{v}^{-1}$ where $\tilde{v}$ is the reduced volume and $\tilde{C}_p = [(4/3\tilde{v}^{-1/3} - 1]$. The corresponding temperature is $\tilde{T} = \tilde{v}^{-1}\ (1 - \tilde{v}^{-1/3})$. Further details can be found in previous work[13,16]. Values of $c_1\tau^2$ and of the predicted $LCST_\infty$ are lised for PIB, PE, PP, PB1, PP1 and P4MP1 in *Table 2*.

RESULTS AND DISCUSSION

Figure 1 gives a selection of the phase-diagrams in n-C_6 conducted on 12 samples of PB1. The *LCST*, the minimum temperature of each of these curves, is plotted in *Figure 2 versus* the inverse square root of the polymer molecular weight. It is usual to plot the inverse of the temperature rather than the temperature itself when this type of diagram corresponds to a *UCST*. However since χ increases with temperature at the *LCST*, the direct dependence with $M^{-1/2}$ is preferred although the two plots give similar values[17] for the extrapolation at the infinite molecular weight, $LCST_\infty$. The entropy of dilution parameter ψ_1 has been calculated and found to be -1.85. This value is similar to that found on a comparable system at the *LCST* (ref 23 of Part 1). In *Figure 2*, the *LCST* for an unfractionated polymer with $M_v = 5.3 \times 10^5$ is on the general curve and 2°C higher than the $LCST_\infty$. By generalizing the present results, one can assume that for the unfractionated samples with $M_v \simeq 2 \times 10^5$, used in part 1 or here, the difference between the *LCST* and $LCST_\infty$ is likely to be less than 5°C. Since the slope of $LCST\ (M^{-1/2})$ is known to diminish when the *LCST* increases[18], the difference between the listed values in *Table 3* and the *LCST* is going to be even smaller for higher molecular weight compounds.

Correlation of the LCST *data*

Comparing *Tables 2* and *3* for the three polyolefins PB1, PP1 and P4MP1, it can be seen that the predicted *LCST* by this model are 40°–60°C lower than the experimental. However, the trend of χ with the solvent volatility is well described by the van der Waals model which also that the liquid–vapour critical temperature takes at a single value of the reduced temperature $\tilde{T}_c = 0.119 = T_c/T^*$. Consequently, the ratio $LCST/T_c$ can be used as well as $LCST/T^*$ as a measure of the reduced *LCST*. From equation (4) this ratio plotted against $c_1\tau^2$ should give a single curve for all systems for which $\nu^2 = 0$ is valid since $\tilde{T}$ is a function of $\tilde{v}$ only. *Figure 3* gives the plot of $LCST/T_c$ for the six polyolefins *versus* the calculated $c_1\tau^2$. The copolymers have not been included. The physical picture of *Figure 3* is essentially identical to that obtained from previous work using the same approximation[17]. Except for PE, the polyolefins follow a single curve reasonably well. Due to its high density and low expansion coefficient, PIB is singled out, but its *LCST* data are predicted with the same accuracy as that of the other polyolefins. The 4 polyolefins P4MP1, PB1, PP1 and PP have *LCST* near the T_c of the corresponding solvent, this result was found for another expanded polymer PDMS[19]. The *LCST* of PE are found to be lower than expected from their $c_1\tau^2$ discussed in part 1. For a given polymer, the *LCST* in different solvents follw the same curve, the reduced *LCST* (or $LCST/T_c$) being lower for the volatile solvents.

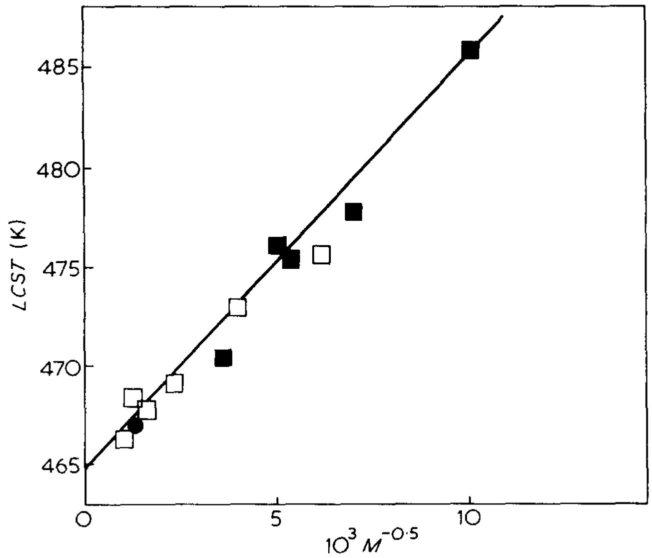

Figure 2 *LCST* (in K) of 12 samples of PB1 in n-hexane plotted against the inverse square root of the molecular weight: (■), five atactic; (□), six isotactic and (●), one unfractionated isotactic sample

Table 3 *LCST* of PB1, PP1 and P4MP1 in linear, branched and cyclic alkanes, and values of interaction parameter $\chi(\phi_2 \rightarrow 1$ where ϕ_2 is the polymer volume fraction) for PB1 and the 33%E EP copolymer

		LCST (K)			χ	
		PB1	PP1	P4MP1	PB1	33%^{d}
n-Butane	4			388		
n-Pentane	5	421^a	433	441		
n-Hexane	6	464^a	482	487		0.29
n-Heptane	7	509	522	522	0.38	0.23
n-Octane	8	540	556	553	0.36	0.19
n-Nonane	9	564^a		579	0.32	0.16
n-Decane	10				0.30	
n-Dodecane	12					
2-Methyl butane	5a	416	422	431		
2,2-Dimethyl butane	6a	444	457	462		
2,4-Dimethyl pentane	7a	480	493	499	0.40	0.26
2,2-Dimethyl pentane	7b		502	499		
2-Methyl hexane	7c				0.39	0.25
3-Methyl hexane	7d				0.38	
2,2,3-Trimethyl butane	7e	507		521		
2,2,4-Trimethyl pentane	8a		527		0.35	0.23
2,5-Dimethyl hexane	8b	519			0.36	0.23
2,3-Dimethyl pentane	7f	517	529		0.35	0.19
3-Ethyl pentane	7g	523	537	532	0.34	0.19
2,4-Dimethyl hexane	8c					
3,4-Dimethyl hexane	8d	559	>569			
Cyclopentane	5b	498	502	505		
Cyclohexane	6d				0.20^c	0.15
Benzene					0.49^c	0.31
Toluene					0.47^c	0.24
m-Xylene						0.16
p-Xylene						0.14
Mesitylene						0.11

[a] Extrapolated to infinite molecular weight
[b] Average for 2 or 3 temperatures between 115°C and 135°C
[c] Values at 135°C. χ diminish by 0.08 between 105°C and 135°C
[d] At 110°C

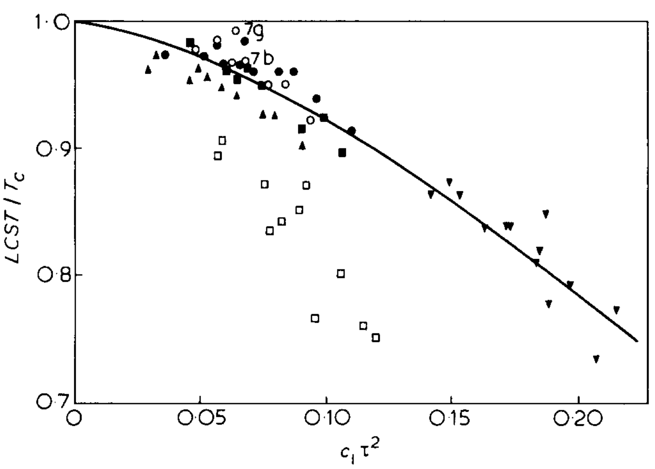

Figure 3 Reduced *LCST*, *LCST*/T_c, for 6 polyolefins in linear and branched alkanes plotted against $c_1\tau^2$, a parameter characterizing the difference in free volume between polymer and solvent: (▼), PIB; (□), PE; (▲), PP; (■), PB1; (○), PP1 and (●), P4MP1. The *LCST* are well correlated with $c_1\tau^2$ except for PE due to *CMO* destruction

Use of d_s *and* d_p *in the equation of state term*

The correlation shown in *Figure 3* while reasonably good, has some weaknesses. For instance, the reduction of the *LCST* by T_c has a tendency to make the points for all the solvents gather around $LCST/T_c = 1$ so that the correlation with $c_1\tau^2$ is hardly visible. Some calculated $c_1\tau^2$ may not be reliable due probably to the uncertainty of some of the experimental data necessary to obtain c_1 and τ. For instance, the two isomers 3-ethylpentane (7g) and 2,2-dimethylpentane (7b) have a *LCST* with all the polyolefins which are far apart (35°C for PP1) although their $c_1\tau^2$ are similar, (0.0637 and 0.0683). Expressions more elaborate than that given by equation (4), where the pressure reduction parameter of the solvent and polymers is included in the equation of state term, would improve the correlation. However, the fact that the densities 0.694 and 0.669 are quite different for the two isomers mentioned above suggests that this parameter can be used to correlate the *LCST* of a single polymer in different solvents.

In *Figure 4*, the *LCST* for PP1, P4MP1 and PB1 in (a) linear and (b) branched alkanes have been plotted against the solvent density. The correlation of the *LCST* with d_s, particularly for the branched alkanes, is rather better than with $c_1\tau^2$ and has the advantage of being simple. Due to the difference in scale between *Figure 3* and *Figure 4*, the improved quality of the d_s correlation is not apparent. However, it can be better visualized in PE solutions by comparing the smooth curve of *Figure 1* of part 1 and *Figure 3*.

In *Figure 5*, the *LCST* for different polyolefins are compared by using the ratio d_s/d_p (d_p being the polymer density at 25°C) instead of $c_1\tau^2$ to describe the difference in the state of expansion between the two components. The data for PE with order-breaker solvents (volatile and

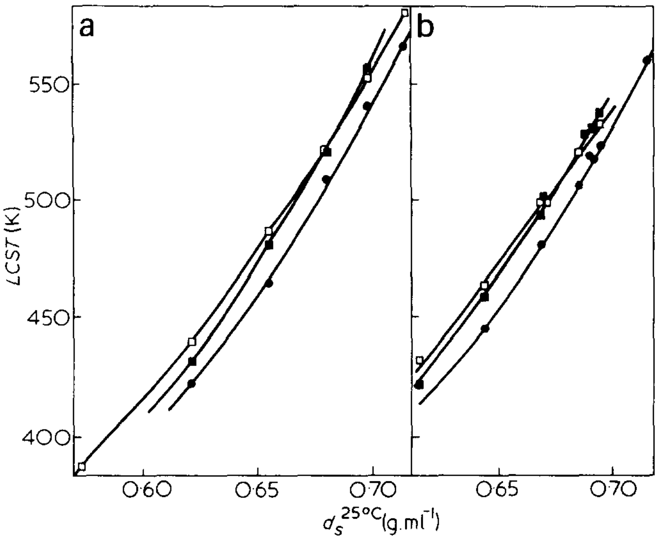

Figure 4 *LCST* (in K) of PB1 (●), PP1, (■) and P4MP1, (□) in linear alkanes (*Figure 4a*) and branched alkanes (*Figure 4b*) plotted against d_s (g. ml^{-1}), the solvent density. These curves show that even at high temperature, the free volume term generating the *LCST*, is better described for a given polymer by the solvent density than by $c_1\tau^2$ (*Figure 3*)

branched solvents) have not been inserted in the graph because the contribution to χ which does not come from the equation of state lowers the *LCST*. Three points have been added corresponding to experimental data of *LCST* at higher pressure (a) PE + n-C_4[20], (b) PE + n-C_5[20], and (c) PIB + n-C_5[21]. The *LCST* of PE fall on the general curve although it is not the case at $P = 0$, because the lower free volume of the solvent under pressure diminishes its order-breaking ability as in the case of the longer alkanes. The densities at these pressures have been calculated from compressibility data in the literature[22]. The feature of the *LCST* for the cycloalkanes not falling on the same general curve due to their higher cohesive energy is common to the two representations.

PARAMETER IN CONCENTRATED SOLUTIONS AND *CMO*

Comparison of *LCST* data for a number of polyolefins having about the same expansion coefficient (PE, PP, PB1, and P4MP1) showed that the *LCST* in PE solutions were lower than with the 4 other polymers due to the destruction of *CMO* of PE by the solvent. Furthermore, the χ parameter in dilute solution is found to be smaller (or the *LCST* higher) in linear alkane solutions compared with the branched alkane having the same density. This feature is present, , but to a much lesser extent in solutions of branched polymers.

The next question raised was the effect of *CMO* in concentrated solutions. Comparison of the χ parameter in linear and branched polymer in solution with linear and branched alkanes should give the answer. The concentration dependence of χ has been measured on some polyolefin solutions[23] by vapour sorption but the data are not sufficiently complete for a meaningful comparison between the solvents of different shape. However, the g.l.c. route to the χ determination at high polymer concentration has been followed extensively[24] for a large variety of polymers including the polyolefins[24,25], the results being in good agreement with the static method[23b,26].

In the present work, g.l.c. determination of χ was pursued on a non-ordered polyolefin, PB1, in linear and branched alkanes and some other solvents and on the 33%E EP copolymer in the same solvents. The χ results will be compared with those available in the literature on linear and branched PE, on a long linear alkane $C_{24}H_{50}$ and on the 52%E EP copolymer.

Interaction parameter

The relation between χ and the specific retention volumes is that developed in ref 24a. The approximations (neglect of the third term and, in equation 1 of ref 24b, of the interaction between the molecule in the vapour phase and the carrier gas) are the same as in ref 24b. The parameters needed in the equation for χ, are derived from data and equations in the literature. The temperature variation of d_p was calculated from *Table 1* in part 1. The specific retention volumes ascertained from the familiar expression of Littlewood and coworkers[27] have not been listed but can be given on request.

The PB1 values listed in *Table 3* are, for the linear alkanes the average of the χ values at 115°C column I), 120°C (column II) and 135°C (column I) and for the

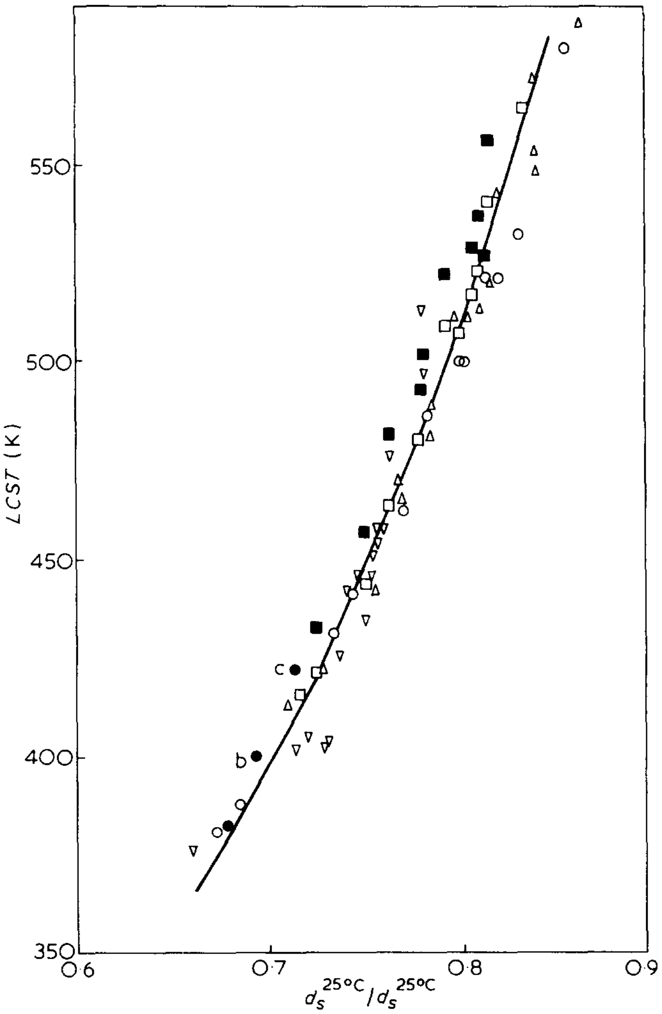

Figure 5 General correlation of the *LCST* of polyolefins in linear and branched alkanes using the ratio of the solvent to polymer density to characterize their free volume difference. PIB, (▽); PP, (△); PB1, (□); PP1, (■); P4MP1, (○). Three points (●) have been added for *LCST* under pressure (a) PE in n-butane at 204 Atm[20a], (b) PE in n-pentane at 80.5 Atm[20a] and (c) PIB in n-pentane[20b] at 100 Atm

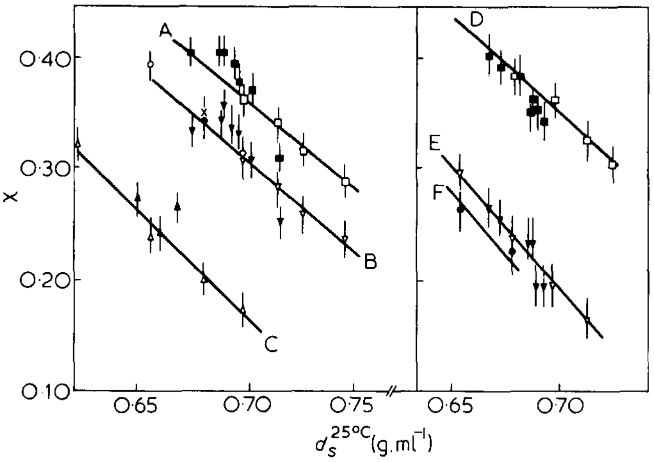

Figure 6 Gas liquid chromatography χ parameter for some polyolefins and n-$C_{24}H_{50}$ + linear (open) and branched (full) alkanes. Curve A (□) linear PE[24b] at 145°–152°C; curve B (▽, ○) branched PE[24b,25b] at 150°C; curve C (△) n-$C_{24}H_{50}$ [25d] at 65°C; curve D (□) PB1 at 115°–135°C; curve E (▽) 33%E copolymer at 110°C; curve F (●) 52%E copolymer[25b] at 150°C. χ for branched PE[23b] – n-heptane, determined by a vapour sorption method, is also reported (X). The lines are drawn through the values for the linear alkanes. For all systems, χ is represented with an uncertainty of ±0.015. χ values in the PE and the long alkanes (A, B, C) appear to be significantly lower in linear alkanes than in branched ones having the same density. This does not occur in the branched polymers (D, E)

branched alkanes at 115°C (I) and 135°C (I). The values over the 115°–135°C temperature range were found to lie inside a 0.015 interval.

33%E EP copolymer. Three different runs were made at 110°C and averaged to establish the tabulated value.

Accuracy. The accuracy in χ is estimated to be ± 0.015. A more complete discussion, given in ref 24b, applies here since the experimental setting of the two series of measurements is the same.

In order to illustrate the influence of the free volume contribution, the parameters have been plotted in *Figure 6* against the solvent density, d_s, at 25°C. The lines have been drawn through the values for the linear alkanes. Lines D and E correspond to data obtained in this work for PB1 and the 33%E copolymer respectively, while A, B, C and F are literature values. The characteristic features of this graph are the following:

(1) The good correlation between χ and d_s supports the assumption that, in concentrated solutions, also, the variable contribution to the χ parameter in a series of chemically similar solvents, comes from the difference in free volume between the components.

(2) Values for branched PE and linear alkanes obtained in different laboratories[24b,25b] with this method or with the static method[23b] are seen to match well. The two EP copolymers, 33%E and 52%E[25b] are also found to have similar χ values.

(3) In the branched polymers, PB1 (curve D) and the 33%E EP copolymer (curve E) the values for the branched alkanes fall approximately on the line for the linear alkanes. However, in the linear PE (curve A), branched PE (curve B) and in n-$C_{24}H_{50}$ (curve C), the branched alkane solutions have χ values situated, on average, above the line for the linear alkanes. This can be taken as an indication of *CMO* between the ethylene segments of these polymers and the linear alkanes, *CMO* which do not exist in the branched PB1 and the 33%E EP copolymer. The lowering of χ when polymer and segment solvent segments can fit, is in agreement with the conclusions that Hammers and de Ligny[28] have drawn from their g.l.c. results at different temperatures (80°–100°C) using long alkanes (n-$C_{32}H_{66}$ and n-$C_{36}H_{74}$) as the stationary phase.

(4) In the approximation of no force-field difference in these polyolefin solutions, the difference of χ from one polymer to another, as seen from the position of the corresponding curves in *Figure 6* should be indicative of the magnitude of the free volume term or of the other contribution investigated here, namely that caused by the breaking of *CMO* in the pure polymers. It seems reasonable that the decrease of χ from the linear PE (curve A), the branched PE (curve B), the 33%E (curve E) and the 52%E (curve F) copolymers follows the expected decrease of *CMO* in the polymer melts. We feel this explanation has a more physical basis than that invoking the small difference of the state equation of state term[24b].

It is interesting to note the parallel between the small molecule mixtures and the polymer solutions. For instance, the heats of mixing of n-hexadecane with the order-breaker cyclohexane is 637 J mol^{-1}, a high value which corresponds to the destruction of *CMO* in n-hexadecane. However, with the same second component, the heat is only 407 J mol^{-1} if the long-chain alkane is replaced by the 6-methylpentadecane. A single methyl group in the middle of the chain diminished the *CMO* considerably in 6-methylpentadecane and consequently the heat of mixing. In the same way, the side chains along the main PE chain existing in the branched PE reduce the *CMO*, so that the contribution to χ due to the destruction of *CMO* by the solvent is lower. In a subsequent work, the χ result will be given for branched PE with increasing degree of branching and for EP copolymers of different ethylene content.

The thermodynamic properties of the polymers corresponding to curves A, B, E, F, for concentrated solutions follow those in dilute solutions (*LCST*). One would expect then that the line corresponding to the χ values for PB1 would be that of branched polyolefins. The experimental data where χ is as high for PB1 as for PE are quite surprising. The more so if one notes that a PE solution in n-heptane for instance is only 30°C below its *LCST* although for a PB1 solution in the same solvent it is 80°C below its *LCST*. One explanation could be that the concentration dependence of χ is different for the two polymers. In view of the experimental results by static measurements on non-polar systems where χ either increases gently over the concentration range (0.45 to 0.52 for PIB + cyclohexane)[23c] or increases sharply (0.50 to 0.90 for PIB + n-C_5)[23c] this is not an unlikely possibility. It is also possible that part of the lowering of χ in the case of the copolymer is due to an increase of the combinatorial entropy which does not occur in the homopolymer.

Effect of the solvent steric hindrance on the LCST *and on the* χ *parameter*

An unexpected result of the systematic study of solutions in which one of the components is a branched alkane has been to discover the importance of the position of the methyl groups along the chain on the thermodynamic properties of the mixture. For instance, the heat of mixing of a long-chain compound such as $NDodec_3$ with

2-methylhexane is 290 $\mathrm{J\,mol^{-1}}$ while it is 190 $\mathrm{J\,mol^{-1}}$ with its isomer 3-methylhexane[29]. This generally occurs with branched alkanes where the side groups are borne by neighbouring carbon atoms[30] or with tetra-substituted compounds such as 3,3-diethylpentane or $Sn(C_2H_5)_4$[31]. The crowding at the centre of the molecule increases the steric hindrance and the density as shown in *Table 2* of part 1. According to Mann[32], the steric hindrance of a compound can be defined by the number of *gauche* conformations, Z_g, which have been calculated for a series of branched alkanes up to the octanes[28b]. The steric hindrance effect associated with the sterically hindered molecules gives at room temperature an exothermic contribution to the heats (in the example quoted above, this contribution would be around -100 $\mathrm{J\,mol^{-1}}$) and lowers the free energy[29]. In polymer solutions, the steric hindrance of the solvent increases the solvent quality or lowers the free energy. In the sterically hindered 2,3-dimethylpentane, the intrinsic viscosity of the 63%E EP copolymers is 2.37 $\mathrm{dl.g^{-1}}$ while it is only 1.93 in 2,4 dimethylpentane which is not sterically hindered. The steric hindrance effect has been associated with a loss of mobility of the second component when it is mixed with the sterically hindered compound equivalent to an increased order in solution, hence the negative sign of the contribution to the heats of mixing and volume of mixing.

Another description of this effect, not clearly understood on the molecular level, is the coupling of the torsional oscillations of the two compounds[33]. The present data, established for sterically and non-sterically hindered solvents, can give information on the effect of high temperatures on this new interaction which gives greater effects at room temperature[34].

LCST

If the *LCST* for PB1 in three branched heptanes 2,4-dimethypentane 2,3-dimethylheptane and 3-ethylpentane are compared, it is found that they are 37°C and 43°C higher for the two sterically hindered compounds than for 2,4-dimethylpentane (which is not). The improved solvent quality due to steric hindrance is still apparent at temperatures as high as the *LCST*. However, in *Figure 4b*, the points corresponding to the *LCST* for these 3 compounds fall on the main curve of *LCST* versus d_s. This means that the difference in *LCST* can be a consequence of the difference in the equation of state term between the components as well. In other words, the *LCST* in a non-sterically hindered compound, having the same density as 2,3-dimethylpentane ($d_s = 0.691$ $\mathrm{g.ml^{-1}}$) such as 2,5-dimethylhexane ($d_s = 0.689$ $\mathrm{g.ml^{-1}}$), should have the same value as in 2,3-dimethylpentane. The difference is indeed small, 2°C for PB1 (*Table 3*, 8b and 7f) and 5°C for the 81% E copolymer (part 1 *Table 2*) and for PIB[17]. It therefore can be concluded that solution properties at the *LCST* are sensitive to the steric hindrance of the solvent but the effect cannot be separated from the free volume effect when the latter is measured by the solvent density at 25°C.

χ parameter

If the specific steric hindrance effect exists at high polymer concentration and at high temperature, one would anticipate a χ value for the sterically hindered compounds to be lower than that expected on the curve χ (d_s) for the branched alkanes. For the PB1 solutions, the more sterically hindered 2,3-dimethylpentane and 3-ethylpentane are not significantly outside of the general line so that one cannot conclude to an alternative effect other than that included in the free volume term. However, the three other polymers which contain ethylene sequences, PE, $C_{24}H_{53}$ and the 33%E EP copolymer, show lower χ values for the sterically hindered. This lowering due to steric hindrance can be estimated by the difference between the experimental and the expected value, the latter value being obtained by drawing a line through the other branched alkanes. For PE (*Figure 6* curves A and B) the point for 3,4-dimethylpentane is about 0.05 lower than expected. The points corresponding to 2,3-dimethylpentane and 3-ethylpentane appear to be 0.02 to 0.04 too low for the 33%E EP copolymer (*Figure 6* curve E) although there are not too many branched alkanes to ascertain the comparison.

In a recent work[35], χ has been obtained from intrinsic viscosity data and the Stockmayer–Fixman relation. The lowering of χ due to steric hindrance was calculated and found to be 0.05 for the 63%E copolymer and for the same two sterically hindered branched heptanes.

De Ligny and Hammers[36] have analysed their g.l.c. results of squalane and linear and branched alkanes. By substracting the calculated free volume contribution to the experimental data of the excess chemical potential, they obtained the interchange free energy parameter X_{12} for the series and find it constant between 27°–86°C. The X_{12} values calculated for sterically hindered branched alkanes are systematically lower than the others. This result is qualitatively similar to those discussed except the effects are larger. Probably at lower temperature the steric hindrance effect is more important as seen by intrinsic viscosities at room temperature[35]. It is probable too that part of the effect which caused the spread of X_{12} over the different branched alkanes could be absorbed in the free volume term if better equation of state parameters could be developed for branched alkanes.

ACKNOWLEDGEMENTS

We thank Professor D. Patterson (McGill University) for kindly letting us use the g.l.c. equipment in his laboratory and Dr Nga Ho Duc (Université de Montréal) for doing the g.p.c. measurements. One of us (G.C.) is thankful to the French and Quebec governments for a scholarship.

REFERENCES

1 Charlet, G. and Delmas, G. *Polymer* 1981, **22**, 1181

2a Campbell, T. W. *J. Appl. Polym. Sci.* 1960, **5**, 181

b Griffith, J. H. and Randy, B. J. *J. Polym. Sci.* 1960, **44**, 369

3 Aharoni, A., Charlet, G. and Delmas, G. *Macromolecules* 1981, **14**, 000

4 Moraglio, G., Zoppi, F. and Gianotti, G. *IUPAC* International Symposium on macromolecules, Leiden 1970, Abstracts I, 197

5 Kobayashi, M., Tsumura, K., Tadokoro, H. *J. Polym. Sci. A2*, 1968, **6**, 1493

6 Delmas, G. and Tancrede, P. *Eur. Polym. J.* 1973, **9**, 199

7 Moraglio, G., Gianotti, G., Zoppi, F. and Bonicelli, U. *Eur. Polym. J.* 1971, **7**, 303

8a Satyanarayana Sastry, K. and Patel, R. D. *Eur. Polym. J.* 1969, **5**, 79

b Stivala, S. S., Valles, R. J. and Levi, D. W. *J. Appl. Polym. Sci.* 1963, **7**, 97

9a Francis, P. S., Cooke, R. Jr., Elliott, J. H. *J. Polym. Sci.* 1957, **31**, 453

b Filiatrault, D., Phuong-Nguyen, H. and Delmas, G. *J. Polym. Sci. Polym. Phys. Edn.* 1981, **19**, 763, 773

c Delmas, G., Daviet, V. and Filliatrault, D. *J. Polym. Sci.* 1976, **14**, 1629

d Kinsinger, J. B. and Hughes, R. E. *J. Phys. Chem.* 1959, **63**, 2002

10 Moraglio, G. and Gianotti, G. *Eur. Polym. J.* 1969, **5**, 781

11a Hoffman, A. S., Frier, B. A. and Condit, P. C. *J. Polym. Sci.* 1963, **C4**, 109

b Tani, S., Hamada, F. and Nakajima, A. *Polymer J.* 1973, **5**, 86

12 Patterson, D. *J. Polym. Sci.* (*C*), 1968, **16**, 3379

13 Orwoll, R. A. and Flory, P. J. *J. Am. Chem. Soc.* 1967, **89**, 6814, 6823

14 Patterson, D. and Bardin, J. M. *Trans. Faraday Soc.* 1970, **66**, 32

15 Klunder, H., Hammers, W. E. and De Ligny, C. L. *J. Solut. Chem.* 1978, **7**, 475

16 Delmas, G. and Patterson, D. *Faraday Soc. Discuss.* 1970, **49**, 1

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

18 Delmas, G. and Patterson, D. *J. Polym. Sci.* 1970, **C30**, 1

19 Patterson, D., Delmas, G. and Somcynski, T. *Polymer* 1967, **8**, 503

20 Ehrlich, P. and Kurpen, J. J. *J. Polym. Sci.* (*A-1*) 1963, 3217

21 Zeman, L., Biros, J., Delmas, G. and Patterson, D. *J. Phys. Chem.* 1972, **76**, 1206

22 Francis, A. W. *Ind. Eng. Chem.* 1957, **49**, 1779

23a Briston, G. M. and Watson, W. G. *Trans. Faraday Soc.* 1958, **54**, 1567

b Van Der Waals, J. H. and Hermans, J. J. *Rec. Trav. Chim. Pays-Bas* 1950, **69**, 971

c Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035, 2053, 2060 and 2066

24a Patterson, D., Tewari, Y. B., Schreiber, H. P. and Guillet, J. E. *Macromolecules* 1971, **4**, 356

b Schreiber, H. P., Tewari, Y. B. and Patterson, D. *J. Polym. Sci., Polym Phys. Edn.* 1973, **11**, 15

25a Tewari, Y. B., Martire, E. D. and Sheridan, J. P. *J. Phys. Chem* 1970, **74**, 2345

b Newman, R. D. and Prausnitz, J. M. *Aiche Journal* 1973, **19**, 706

c Hammers, W. E. and De Ligny, C. L. *Rec. Trav. Chem. Pays-Bas*, 1971, **90**, 912

d Deshpande, D. D., Patterson, D., Schreider, H. P. and Su, C. S. *Macromolecules* 1974, **7**, 530

26a Tewari, Y. B. and Schreider, H. P. *Macromolecules* 1972, **5**, 12

b Summers, R., Tewari, Y. B. and Schreider, H. B. *Macromolecules* 1972, **5**, 12

27 Littlewood, A. B., Phillips, C. S. G. and Price, D. T. *J. Chem. Soc.* 1955, 1480

28a Klunder, H., Hammers, W. E. and De Ligny, C. L. *J. Solut. Chem.* 1978, **7**, 485

b ibid, 1978, 475

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

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

31 Delmas-Patterson, G. and Nguyen Thi Thanh, J. Phys. Chem. 1977, **81**, 1730

32 Mann, G. *Tetrahedron* 1967, **23**, 3375, 3393

33 Richon, D., Patterson, D. and Turrell, *G. Chem. Phys. Lett.* 1975, **36**, 492

34 Philippe, R., Delmas, G. and Phuong-Nguyen, H. *Can. J. Chem.* 1978, **56**, 2856

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

36 De Ligny, C. L. and Hammers, W. E. *J. Solut. Chem.* 1978, **7**, 155