polymer communications

Chain folding in melt crystallized polyethylene: 2. Low molecular weight polymers

James N. Hay** **and Pauline A. Fitzgerald***
The Department of Chemistry, The University of Birmingham, Birmingham B15 2TT, UK
(*Received* 16*th March* 1981)

Introduction

In recent publications[1-4], the analysis of the melting points of linear monodisperse low molecular weight polyethylenes has been advocated to determine the equilibrium thermodynamic parameters of melting. The procedure involves the measurement of the melting points, $T_m(n)$, of extended chain lamellae in which the lamellae thickness is limited by the degree of polymerization, n, since the corresponding melting point depression equation is,

$$T_m(n) = T_m^0(\infty)\{1 - 2RT_m^0(\infty)\ln(n)/n\Delta h - 2\sigma_e/n\Delta h\} \quad (1)$$

in which R is the gas constant, Δh the heat of fusion per monomer repeat unit (in this case $-CH_2-$ unit), σ_e the lateral surface free energy, and $T_m^0(\infty)$ the equilibrium melting point of the infinitely extended chain. Plots of T_m against $\ln(n)/n$ are invariably linear, since σ_e is small compared with Δh, with intercepts at $\ln(n)/n = 0$ of $T_m^0(\infty)$ and slopes of $2RT_m^0(\infty)^2/\Delta h$ within the standard error of the accepted values of these parameters[1-4].

Monodisperse polyethylenes of low molecular weight crystallize with an extended chain conformation, analogous to the n-alkanes[1,2], and exhibit a separate dependence of the melting points on $\ln(n)/n$ from that of either solution crystallized single crystals or the cyclic-alkanes which are known to have a regular adjacent re-entry chain fold, see *Figure 1*. The extended chain crystals can be distinguished from chain folded crystals by this means, and using this procedure it was observed previously[5] that melt crystallized high molecular weight polyethylene fractions crystallized with extended chain lamellae under conditions of slow crystallization at the higher crystallization temperatures.

Kovacs *et al.*[6] and Booth *et al.*[7], however, have given detailed evidence for both extended and chain folded lamellae forming during the melt crystallization of low molecular weight polyethylene oxide, in the range 1–10 × 10^3, and accordingly the present communication is made on the application of equation (1) to low molecular weight systems in which chain extended and folded lamellae would be expected to form from the melt during slow crystallization. The general conclusions that a clear separation between these two distinct types of lamellae can be made from the melting point dependence on stem thickness can then be considered further.

Results and discussion

Narrow distribution polyethylene fractions crystallize with an extended chain configuration[4] and their molecular chain lengths limited the observed melting point

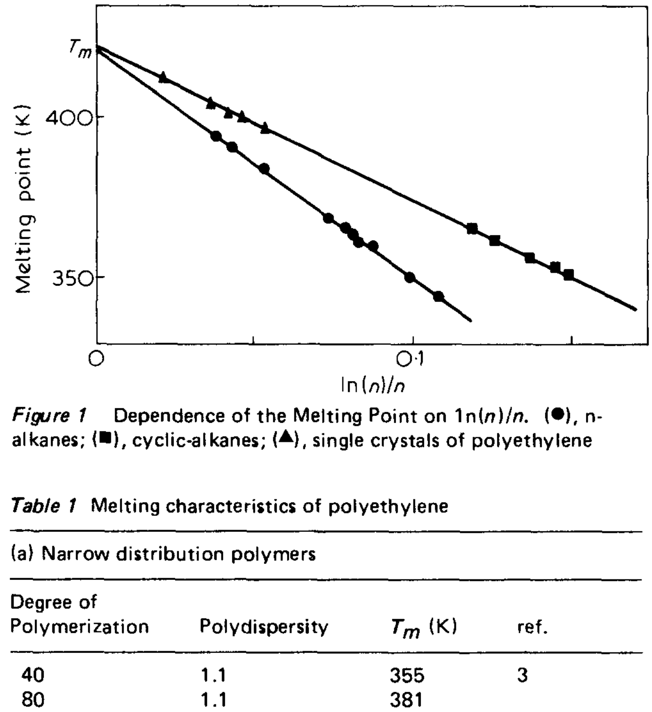

Figure 1 Dependence of the Melting Point on ln(n)/n. (●), n-alkanes; (■), cyclic-alkanes; (▲), single crystals of polyethylene

Table 1 Melting characteristics of polyethylene

(a) Narrow distribution polymers

Degree of Polymerization	Polydispersity	T_m (K)	ref.
40	1.1	355	3
80	1.1	381	
100	1.1	389	
110	1.4	394	
300	1.7	405	
400	1.9	406	

(b) Broad distribution polymers		$T_{m,1}$ (K)	$T_{m,2}$ (K)
132	2.7	397.5	393
133	2.6	399.3	391.5
118	1.3	395.5	390

(c) Data from Kawai[9]

Degree of Polymerization			Folded or extended	$T_m(n)$ (K)
Calculated	Observed	*LAXS*		
78	64–78	71	extended	376.9
128	nd	75	extended	383
157	nd	77	folded	388
185	nd	83	folded	392
272	nd	82	folded	392
331	nd	85	folded	395
446	290–561	94	folded	397

---

* Present address: Boots Ltd., Nottingham

** To whom all communications should be addressed

0032-3861/81/081003-03$02.00

rather than the crystallization temperature. Their molecular weight dependence on ln(n)/n was identical to that of the n-alkanes[4]. Broader distribution low molecular wt. samples, whose characteristics are listed in *Table 1*, exhibited multiple melting point behaviour, see *Figure 2*, with at least two distinct melting point regions characterized by m.pts. $T_{m,1}$. The higher melting point was independent of crystallization temperature, T_c, and as such was similar to that observed with the narrow distribution samples. The lower melting point, $T_{m,2}$, increased progressively with T_c according to the relationship[8],

$$T_{m,2} = T_m^0/(1-2B) + T_c/(2B) \qquad (2)$$

see *Figure 3*. B was observed to be unity, consistent with equilibrium conditions during the crystallization, and $T_{m,2}$ being nucleation dependent. This is consistent with $T_{m,1}$ being molecular chain length dependent and hence associated with the extended chain, and $T_{m,2}$ with the once folded chain as described by Kovacs *et al.*[6]. Using the stem lengths associated with the extended and once folded chains as n, it was observed that $T_{m,1}$ followed the same dependence on ln(n)/n as the n-alkanes and $T_{m,2}$ as the cyclic-hydrocarbons, and single crystals, see *Figure 4*, in total agreement with the general conclusions above.

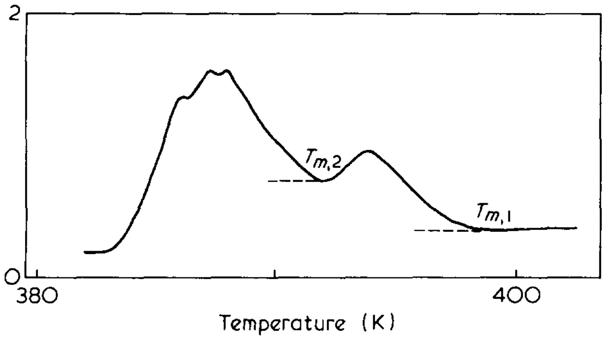

Figure 2 Melting exotherm of polyethylene

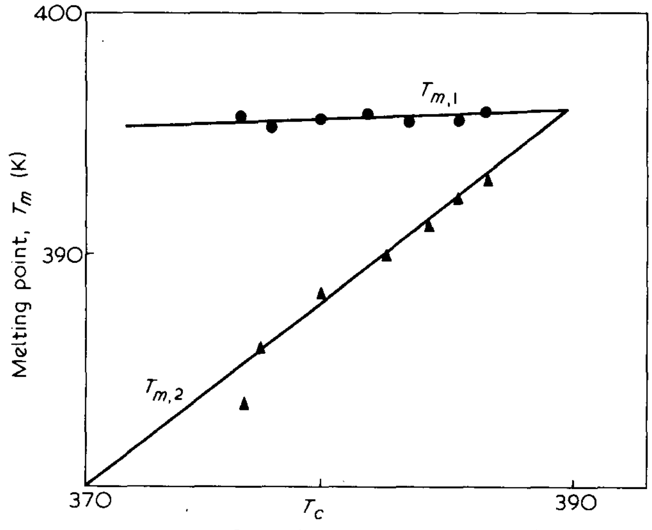

Figure 3 Variation of melting points with crystallization temperature

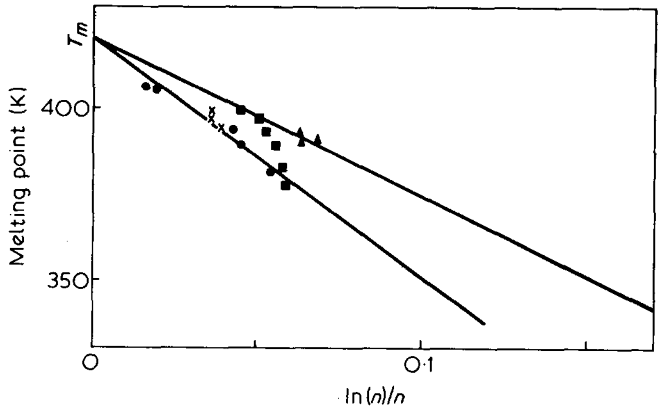

Figure 4 Dependence of the melting point of polyethylene on ln(n)/n. (●), Narrow distribution polymers; Broad distribution polymers; (▲), folded; (x), extended; Kawai's data, (■)

Table 2 Variation of final crystallization extent with crystallization temperature

Degree of polymerization n	Crystallization temperature Tc (K)	Crystallization extent
133	381	0.45
–	382	0.36
–	383	0.31
–	384	0.24
–	386	0.07
118	377	0.51
–	387	0.08
132	378	0.40
–	387	0.1

Similarly, the melting points of the low molecular weight fractions listed by Kawai, for which he had measured the stem length by *LAXS* also confirmed these conclusions. Kawai estimated the number average molecular weight of each fraction from the weight loss data of the solution fractionation assuming a Tung distribution[9]. It was thus possible to determine which of the fractions had crystallized as extended and which folded chain lamellae, see *Table 1*. This data is also included in *Figure 4*, from which it can be seen that as the molecular weight of the fractions increase chain folding sets in, and this is accompanied by a change in the melting point/ln(n)/n dependence. This change, however, is progressive and not as sudden as would be expected, since it is either an extended or folded chain, but this may be an artefact of the method of estimating the number average molecular weight. The two extremes in molecular weight exhibit the two different dependences, and so the general conclusions observed with the high molecular weight fractions have to be somewhat modified. Chain folded crystallization does occur with the low molecular weight fractions, especially during rapid crystallization at the higher degrees of supercooling. This difference may reflect the increased mobility of the smaller chains, and the lower viscosity of the melt. However, it may also reflect the fact that the polydisperse low molecular weight sample does not crystallize to the same extent as the higher molecular weight fractions in an isothermal crystallization, see *Table 2*, and the lower molecular species may be acting as solvent for the higher species in their crystallization. Melt crystallization should then be considered as a solution crystallization.

The conclusion that chain extended and chain folded lamellae can be separated by the stem length dependence of their melting points is, however, sustained by this communication. These differences arise from differences in the lateral surface energies between chain extended and regular folded conformations.

References

1 Hay, J. N. *J. Polym. Sci., Chem. Edn.* 1976, **14**, 2845
2 Hay, J. N. *Makromol. Chem.* 1976, **177**, 2559
3 Hay, J. N. and Wiles, M. *Makromol. Chem.* 1977, **178**, 623
4 Hay, J. N. and Wiles, M. *J. Polym. Sci., Chem. Edn.* 1979, **17**, 2223
5 Hay, J. N. *Polymer* 1981, **22**, 718
6 Kovacs, A. J. and Buckley, C. P. *Prog. Coll.* 1975, **58**, 44; *Polym. Sci.* 1976, **254**, 46
7 Ashman, P. C. and Booth, C. *Polymer* 1972, **13**, 459
8 Hoffmann, J. D. and Weeks, J. J. *J. Res. Nat. Bur. Stand.* 1962, **A66**, 13
9 Kawai, T. *Koll. Zeit. Polym.* 1965 **201**

A pair of high molecular weight compatible polymers showing upper critical solution temperature behaviour

D. J. Walsh, Shi Lainghe[*] and Chai Zhikuan[*]
Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, London SW7, UK

(*Received* 16 *January* 1981; *revised* 23 *March* 1981)

Introduction

The study of polymer compatibility has received considerable attention both industrially and academically over the last few years[3]. The subject can be conveniently split into two areas, the compatability of low molecular weight polymers (oligomers), and that of high molecular weight polymers.

For oligomers the entropy of mixing ΔS_m can be given by the combinatorial entropy[1]

$$\Delta S_m = -R(n \ln \varphi_1 + n_2 \ln \varphi_2) \qquad (1)$$

(where n_i is the number of molecules of component i with volume fraction (φ) which is relatively large and favours mixing. For systems where there are no specific interactions, the heat of mixing ΔH_m may be of the same order and is unfavourable for mixing. Mixing is controlled by the free energy of mixing given by

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Mixing, therefore, is favoured by high temperatures and we might expect the possibility of finding upper crutical solution behaviour.

For high molecular weight polymers the combinatorial entropy, which depends on the number of molecules is expected to be small. They are therefore only compatible if ΔH_m is very small or negative which can occur if there is a volume change (contraction) on mixing or a specific interaction. Each of these will have an unfavourable entropy change associated with them which could make ΔS_m negative. Then mixing will be favoured by low temperature and we could expect lower critical solution behaviour. The heat of mixing may also vary markedly with temperature which could in principle cause either sort of critical behaviour. So far, in practice, high molecular weight compatible polymers have only been found to show lower critical solution temperatures.

In this communication we describe results with mixtures of poly(methyl methacrylate) (PMMA) and solution chlorinated polyethylene (SCPE) having varying degrees of chlorination. This system has been found to give both lower and upper critical solution behaviour.

Experimental

Materials. Poly(methyl methacrylate) (PMMA). A sample of pure suspension polymerized PMMA was used (supplied by ICI Plastics Division). This was dissolved in acetone (AR), reprecipitated into distilled water and dried under vacuum for 14 days at 50°C. The molecular weight was measured by g.p.c. in tetrahydrofuran relative to polystyrene standards and found to be, $\bar{M}_w = 11.7 \times 10^4$, $\bar{M}_n = 5.6 \times 10^4$.

Solution chlorinated polyethylene (SCPE). This was prepared from a commercial high density polyethylene (nominal $\bar{M}_n = 1 \times 10^4$). This was dissolved in chlorobenzene (AR) at 140°C to give a 5% w/v solution. It was photochlorinated using irradiation from a 60 watt tungsten lamp. The chlorine was bubbled through the solution which was kept under a nitrogen blanket. By adjusting the conditions, products with different degrees of chlorination were obtained. The reaction products were cooled and precipitated into a 10 times excess of AR methanol, washed with methanol and dried for 14 days at 50°C in a vacuum oven.

The degree of chlorination was determined by elemental analysis and the results shown in *Table 1*. The molecular weights and distributions were examined by g.p.c. in tetrahydrofuran and the results also given in *Table 1* as above. The molecular weights found are difficult to interpret because the nature of the polymer changes with chlorination. Chlorination increases the molecular weight

---

[*] Institute of Chemistry, Academia Sinica, Beijing

0032-3861/81/081005-03$02.00