reduce tendencies toward crosslinking. On heating, this stabilization is overcome and crosslinkage becomes a predominant feature in the absence of dimethyl sulphoxide. The contribution by hydrogen bonding may explain the lack of solubility of the methylolated celluloses in solvents other than dimethyl sulphoxide since the formation for hydrogen bonds will be less likely.

Regeneration of the methylolated celluloses and drying of the films produced samples of good tensile characteristics, good dimensional stability but reduced flexibility. Certain of our objectives have been achieved. These include the production of methylolated cellulose in a range of commercially acceptable solvents. The methylolated celluloses are sufficiently substituted to allow solution in dimethyl sulphoxide and subsequent regeneration in a desirable form whether as films or fibres. The main restriction is that the methylol derivative must not be allowed to become dry before regeneration is completed. The complete system of cellulose solution and regeneration, presented here, offers many advantages when compared to the xanthation process which is in use. Examples include greater ease of recovery of non-aqueous solvents for recycling and a much reduced corrosion problem.

Work is continuing, aimed at a more complete characterization of the intermediate and final products of this type of reaction, and an extension of the range of solvents for the methylol derivatives.

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(Received 25 October 1976; revised 19 November 1976)

References

1 Schweiger, R. G. *Tappi* 1974, 57, 86
2 Williams, M. D. US Pat. 3 236 669 (1966)
3 Hata, K. and Yokata, K. *J. Soc. Fibre Sci. Technol. Japan* 1968, **24**, 420
4 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *Eur. Polym. J.* 1972, 8, 747
5 Johnson, D. L. US Pat. 3 508 941 (1970)

Melting behaviour of stress crystallized high density polyethylene

Introduction

The relation between the observed melting point of polymers and their crystalline morphology is of topical interest. The purpose of the present Letter is to draw attention to past work in our laboratories on the melt extrusion of high molecular weight linear polyethylenes which gave discrete melting points of over 150°C.

Most of this work was carried out on experimental polyethylene grades with a weight-average molecular weight of about 300 000 and a melt flow index $\simeq 0.008$: (measured at 190°C/ 2.16 kg ASTM D/238 6S-T). The polymer was extruded through different die geometries at various melt temperatures. At melt temperatures of 160°C, the polymer could be readily extruded in a normal fashion and on solidification became opaque. When the melt temperature was reduced to about 148°C, the melt swelled up excessively on leaving the die, and a very high haul-off load was required to draw it back to the same cross-section as the die. Although the extrudate had a poor surface, it was more transparent and considerably stiffer than that made at 160°C. There was a gradation in the degree of transparency across the cross-section, the exact pattern of transparency depending on the configuration of the die design. It was the more transparent parts of the section that showed the melting point curiosity with which we are concerned. With the simplest die geometries, such as a slot die having a 1 mm gap, 10 mm width with a 10 mm land length, there was a tendency for the process to be unstable and, in particular, for the die to block after a short period. Special die configurations were therefore developed in order to eliminate this tendency to instability. These included dies which accelerated the inside layers of the melt more rapidly than the outside layers and those in which the central layers were held at lower temperatures than the outside layers. Details of these dies are given in refs 1 and 2. All these dies gave extrusions at about 148°C which contained transparent regions with a high melting component.

Experimental

Thin samples of about 2 mg were cut from the extrudates and examined in a Perkin–Elmer DSC2 scanning calorimeter operating with a helium quench gas. In most cases the samples were scanned with a heating rate of 80°C/min to above their melting point.

Some of the 148°C extrudate was treated in fuming nitric acid for 74 h at 65°C using the method of Palmer and Cobbold[3]. After thoroughly washing in distilled water and drying under vacuum, the embrittled solid was disintegrated ultrasonically and the debris was examined in an electron microscope.

Results

Figure 1 shows a superposition of the d.s.c. scans for extrudates drawn from melts of 160° and 148°C respectively. The 160°C extrudate gave a single melting peak at 135°C, whereas the 148°C extrudate gave a double peak, one centred at 132°C and another at 152°C. The relative areas of these peaks varies with position in the extrudate. In the most transparent parts we have found that up to about 10% of the total area of the melting endotherm can be associated with the high temperature peak.

The precise shape of the melting endotherm varies with the heating rate. At rates lower than 80°C/min an inter-

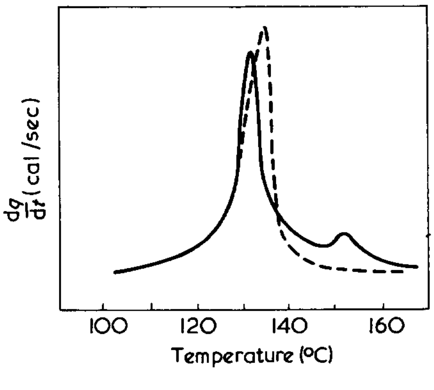

Figure 1 D.s.c. melting endotherms of extrudates: ——, extruded at 148°C; – – – –, extruded at 160°C

Table 2 Estimates of viscosities and relaxation times of polyethylene grades used

	Polymer	Experiment	Low shear viscosity at 150°C* ($Nsec/m^2$)	Relaxation time at 150°C† (sec)
(1)	Marlex 6050 (*MFI* ~ 5.0)	Stirred solution (ref 9)	10^4	1
(2)	Marlex 6009 (*MFI* ~ 1)	Stirred solution (ref 4)	10^5	10
(3)	*MFI* 0.16	Melt extrusion (present work)	10^6	10^2
(4)	*MFI* 0.008	Melt extrusion (present work)	10^7	10^3
(5)	Holstalen GUR (*MFI* ~ zero)	Stirred solution (ref 9)	$>10^8$	$>10^5$

*Viscosity under shear stress of 10^3 N/m^2; †Ratio of shear viscosity/shear modulus at low shear[11]

mediate peak at about 140°C often becomes visible between the high (T_2) and low (T_1) temperature peaks mentioned above. However in this Letter we will not dwell on this third peak since melting points around 140°C in solid extrusions have already been widely reported. *Table 1* illustrates how the positions of the two main peaks can vary with heating rate. It will be noted that, whereas T_1 shows an increased superheating effect as the rate is increased, the position of T_2 appears to be independent of heating rate.

When samples of extrudate were heated in the d.s.c. to 140°C for 2 min, then cooled to room temperature and then reheated, the T_2 peak was retained. It could only be removed by prior heating in excess of 150°C.

After samples of extrudate had been degraded with nitric acid, the T_2 peak was no longer visible. Electron microscopy of the debris revealed two morphological components. First there were irregular fragments of lamellar crystals similar to those obtained by degrading unoriented melt crystallized polymer[3]. Secondly there were crossbanded fibres very similar to the structure described by Keller and Willmouth as 'microshishkebabs' which are produced by crystallizing from rapidly stirred solutions of polyethylene in xylene[4]. The extrusion phenomenon of high extrusion pressure and excessive die swell, that occurred at 148°C in the above example, is very dependent on the molecular weight of the polymer. When the molecular weight was reduced, the unusual extrusion behaviour occurred at progressively lower temperatures. Coupled with this the proportion of high melting point material also decreased. With *MFI* = 0.16, the largest 150°C peak obtainable was only equivalent to ~1% of total endotherm. By the time one had reached normal molecular weight material (e.g. *MFI* ~ 1.0), a melt temperature of 136°C and very high extrusion pressures were required. At this point the extrusion was seemingly similar to the experiments of Southern *et al.*[5]. We have found that such materials no longer have a melting peak at 150°C, but have an enhanced main melting process at about 140°C.

Table 1 Peak positions in d.s.c. scans of material extruded at 145°C

Scan speed (°C/min)	Peak positions (°C)	
	T_1	T_2
10	131	150
20	131	150
40	132	150
80	132	150.5
160	134	151

Discussion

The most notable feature of the 148°C extrudate is the presence of a discrete component with a melting point above 150°C. This is approaching 10°C above theoretical estimates of the equilibrium melting point and is much higher than had previously been reported for extruded polyethylenes.

Reports in the literature show two distinct morphologies that have given such marked superheating. The first is the 'chain extended' morphology that is produced by crystallizing from unoriented melts under high pressures. Hellmuth and Wunderlich[6], when using very high molecular weight polymethylenes, have found that the melting point increased from 148° to 154°C as the heating rate was increased from 10° to 65°C/min. This superheating was presumed to occur because the progress of the melt front through the chain extended crystals was slow compared with the heating rate[7]. Such behaviour is in contrast to our 150°C peak, which appears to be unaffected by heating rate.

The second type of morphology in which superheating has been found is the fibrous structure that is formed by crystallizing from rapidly stirred xylene solutions[8]. In the case of ultra high molecular weight polyethylene (Hostalen GUR), Pennings and van der Mark[9] have found a shoulder at about 150°C which is broadly similar to our melting curves, and also occasionally found discrete peaks at 180°C. Unlike our extrusions, they found that their melt memory was such that the 150°C peak was still present after cooling and reheating. They associated the 150°C shoulder with the central core of the fibres. Keller and Willmouth[4] have studied this system using normal molecular weight polymer (Marlex 6009). Although no discrete peak or shoulder was present, they found the melting range extended well above 150°C. Unlike high pressure crystallized chain extended crystals, the melting behaviour was not appreciably altered by changing the heating rate. Keller and Willmouth described the fibres as microshishkebabs and deduced that they had a composite structure consisting of a chain extended core surrounded by lamellar crystals interconnected by a high density of tie molecules. They suggested that the high superheating could be associated with a phenomenon suggested by Zachmann[10] in which normal thickness crystalline lamellae are connected by a high concentration of tie molecules and where superheating is the result of local entropy restrictions in the melt.

It is now known that microshishkebabs from stirred solutions form in regions of elongational flow and that such structures can act as nuclei for the subsequent growth of lamellae. Since regions of high elongational flow exist in our dies one can presume a similar phenomenon will take place during our melt extrusions. In view of the d.s.c. and electron microscope evidence it is therefore attractive to associate our 150°C melting component with microshishkebab structures and to associate the main 132°C peak with conventional lamellar crystals that have possibly been nucleated by the microshishkebabs.

Our experiments and the experiences reported in the literature show that the occurrence of the 150°C peak is a phenomenon closely associated with high molecular weight material. This is illustrated by *Table 2* which gives estimates of the viscosities and relaxation times of the polymers that have been used. It is the last two which have given significant peaks at 150°C and it is only Hostalen GUR that also has a sufficiently long relaxation time for the melt to retain a memory to enable the material associated with the 150°C peak to be reconstituted on cooling. Hostalen GUR is not melt-processable by conventional extrusion technology and could not be used in our extrusion experiments. This molecular weight dependence could be a direct reflection of the fact that the formation of microshishkebabs in elongational flow fields is very sensitive to molecular weight. The absence of a 150°C peak in low molecular weight extrudates may be due to the very small proportion of microshishkebabs that form. Alternatively the 150°C peak may be the result of a Zachmann type of phenomenon where high molecular weight molecules can be expected to exacerbate the occurrence of entangled tie molecules and hence produce a greater proportion of superheatable material.

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(Received 18 October 1976;
revised 8 November 1976)

References

1 Cogswell, F. N. and Jukes, A. W. UK Pat. Appl. 16291/73 (1973)
2 Cogswell, F. N. UK Pat. Appl. 26252/74 (1974)
3 Palmer, R. P. and Cobbold, A. J. *Makromol. Chem.* 1964, **74**, 174
4 Keller, A. and Willmouth, F. M. *J. Macromol. Sci. (B)* 1972, **6**, 493
5 Southern, J. M., Weeks, N., Porter, R. S. and Crystal, R. G. *Makromol. Chem.* 1972, **162**, 19
6 Hellmuth, E. and Wunderlich, B. *J. Appl. Phys.* 1965, **36**, 3039
7 Wunderlich, B. *Thermochim. Acta* 1972, **4**, 175
8 Pennings, A. J. and Kiel, A. M. *Kolloid-Z* 1965, **205**, 160
9 Pennings, A. J. and van der Mark, J. M. A. *Rheol. Acta* 1971, **10**, 174
10 Zachmann, H. G. *Kolloid-Z.* 1967, **216–217**, 180
11 Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn, Wiley, New York, p 60

Unusual thermal energy transduction by means of a composite membrane system

Transport phenomena occurring across membranes separating two solutions of identical composition, kept at two different temperatures, have already been studied, and they are known as thermo-osmotic effects[1–5]. The temperature difference between the two semicelles of constant volume, separated by a membrane, causes a flow of matter which is called 'thermo-osmotic flow'. At the steady state a pressure difference between the two semicelles, called 'thermo-osmotic pressure', is established. Coupled to the flow of matter is a heat flow.

For a phenomenological description of such a non-isothermal system the thermodynamics of the irreversible processes[6,7] can be utilized.

The purpose of this Letter is to illustrate the experimental results obtained if a 'composite membrane' system is utilized instead of a simple cellulose membrane[11]. Our experimental set up is schematically shown in *Figure 1.* Two thermostatically controlled reservoirs R1 and R2, containing the same pure solvent, water, are separated by a chamber LM ('liquid membrane') filled up with an aqueous solution of poly(ethylene oxide) (PEO) having an average molecular weight of 20 000. The chamber LM is a plexiglass cylinder 4 mm thick, with an inner diameter of 30 mm, closed on the lower and upper sides by means of two pure cellulose dialysis membranes m_1 and m_2 (supplied by A. H. Thomas Co.), impermeable to the PEO.

If a temperature difference, measured by copper–constantan thermocouples placed on m_1 and m_2, is applied on the two sides of the composite membrane, a pressure difference is established as the steady state is reached. The pressure π^* on the hot side of our system was measured with a Bell and Howell pressure transducer, and it is plotted as a function of the PEO concentration inside the liquid membrane in *Figure 2*. In *Figure 3* is shown the dependence of π^* on the temperature difference applied to the composite membrane.

The more relevant points in these data are the values of the measured pressures, which are much higher than those previously obtained in thermo-osmosis experiments carried out on single membranes. In fact, a more than 300 fold amplification of the thermo-osmotic effect is now reached, as compared to the data quoted by Rastogi[5] and by Haase[8].

In order to account for the unusual pressures measured, the osmotic gradient established at the steady state within the 'liquid membrane', as a result of thermal diffusion effects, must be considered.

Such a kind of membrane can be

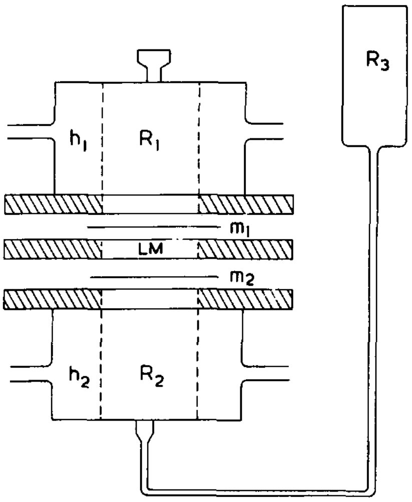

Figure 1 Experimental apparatus: R_1, R_2, R_3, solvent reservoirs; h_1, h_2, heating jackets; m_1, m_2, cellulose membranes; LM, plexiglass chamber containing the polymer solution