

Heterogeneous reactions of polymers:

4. Melting behaviour of heterogeneously chlorinated and sulphonated polyethylenes

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The melting behaviour of heterogeneously chlorinated and sulphonated high-density polyethylene was studied by differential scanning calorimetry. It was found that an increase in T_m takes place at high degrees of substitution in the amorphous phase. For sulphonated polyethylenes the increase in T_m was also dependent on the type of the counterion. The effect is interpreted as a decrease in configurational entropy upon fusion due to the restraints that the highly chlorinated and sulphonated amorphous regions impose on the adjacent crystallites.

Keywords Entropy; fusion; differential scanning calorimetry; melting point; sulphonated polyethylene; chlorinated polyethylene

INTRODUCTION

The heterogeneous chlorination and chlorosulphonation of polyethylenes was recently investigated in this laboratory¹⁻⁴. It was found that, under the prevailing experimental conditions, only the amorphous regions of the polymer were susceptible to chemical attack. The crystalline phase remained chemically unchanged, though the perfection of the crystalline phase was affected by the extensive modification of the adjacent amorphous regions.

Polyhaloalkane-polyethylene, phase-separated, block copolymers are obtained by heterogeneous chlorination of polyethylene. The heterogeneously chlorosulphonated polyethylenes can be converted into polyethylene sulphonates by hydrolysis. Ion exchange materials prepared by this procedure are also of a block copolymer type and their structure is predetermined by the method of their preparation.

The peculiarities of the melting behaviour of the heterogeneously sulphonated and chlorinated high-density polyethylenes are discussed in this paper.

EXPERIMENTAL

The high-density polyethylene (HDPE) films used in the experiments were 9 μm thick. Sample A was prepared by blow extrusion from HDPE HiZex, 7000F, Mitsui Japan ($d=0.955\text{ g cm}^{-3}$; MFI 0.04). Sample B was prepared from Sample A by submitting it to compression in a press at 200°C, and 1.4×10^6 Pa, followed by quenching in cold water (20°C). The sulphonated polyethylenes (SPE) were prepared from the sulphonylchloride intermediates by hydrolysis in 1 N NaOH at room temperature for 8 h. Prolonged hydrolysis can induce irreversible changes in the samples' morphology⁵. The sulphonylchloride intermediates were prepared by bringing the polyethylene films in contact with carbon tetrachloride solution

saturated with sulphur dioxide-chlorine gaseous mixture as described previously⁴.

The sulphonated polyethylenes were converted by equilibration (for 24 h at room temperature) in 1 M solutions of HCl or MgCl_2 into the acid or the Mg^{2+} form, respectively. Samples were washed with deionized water and dried for 24 h at 40°C in high vacuum (10^{-3} Torr) prior to d.s.c. measurements.

The heterogeneously chlorinated polyethylenes (CPE) were prepared from Sample A by bringing it in contact with carbon tetrachloride solution saturated with chlorine as described elsewhere². After completion of the reaction, films were rinsed and soaked in diethyl ether for 24 h. Ether was changed every 8 h in order to remove traces of the absorbed carbon tetrachloride. They were subsequently dried at room temperature in vacuum (0.1 bar).

D.s.c. measurements were performed on a Perkin-Elmer DSC A-1 instrument as described previously². The temperature corresponding to the maximum of the endotherm is reported as the melting temperature. A clamping arrangement analogous to that described by Clough⁶ was used for d.s.c. measurements performed under isometric conditions. The heating rate was 8°C min^{-1} .

RESULTS

The melting behaviour of the heterogeneously chlorinated polyethylenes is rather complicated. Some typical melting endotherms are shown in *Figure 1*. The T_m during the first melting cycle can differ from the melting temperature in subsequent remeltings. The later experiments were conducted by repeating the d.s.c. runs without removing samples from the pan. The heating and cooling rates were identical within the cycle. Samples of CPE with high chlorine content melt at substantially lower temperatures during the second melting cycle than during the first one. The T_m of CPE samples with low chlorine content is virtually unaffected by the subsequent

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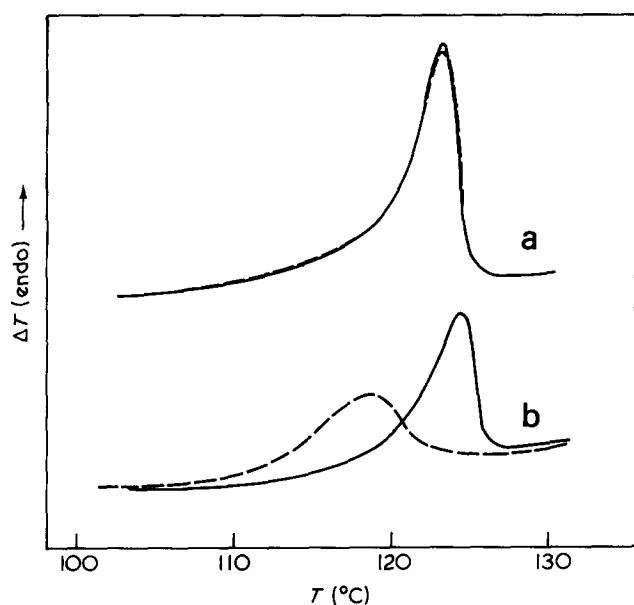


Figure 1 Typical fusion endotherms of the heterogeneously chlorinated polyethylenes: (a) CPE, chlorine content 16.7%; (b) CPE, chlorine content 37.1%. Full and dashed lines denote the first and second melting cycles, respectively

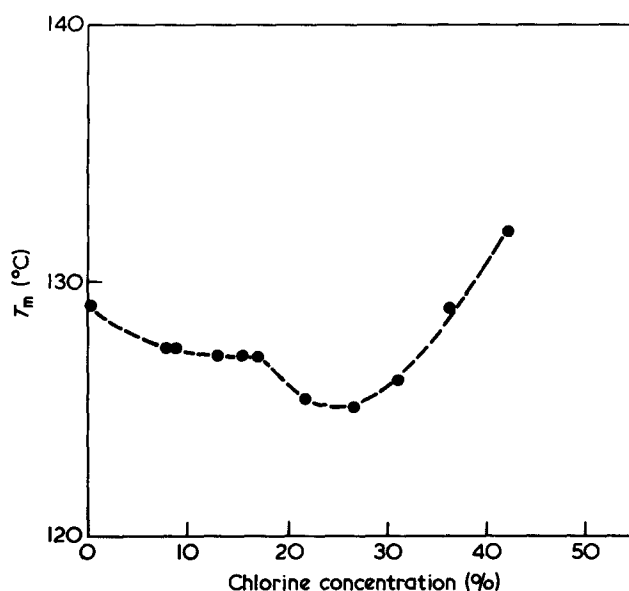


Figure 2 Melting points of the heterogeneously chlorinated polyethylenes as function of chlorine content

melting cycle. Similar behaviour is also observed for samples of SPE. The decrease in the melting temperatures that is usually observed for the heterogeneously modified polyethylene samples during a repeated melting cycle is analogous to that reported for the heterogeneously modified single crystals of polyethylene⁷. The melting temperatures of the remelted CPE and SPE samples are dependent on the crystallization conditions, thermal history and their specific morphologies. However, only the thermal behaviour corresponding to the first melting cycle is discussed here.

The melting temperature of CPE films is plotted as a function of the chlorine content of the samples in Figure 2. The T_m of the CPE samples decreases first with increase in chlorine contents; however, at high degrees of

substitution, a subsequent increase in T_m is observed.

Melting temperatures and the heats of fusion were found to be identical for CPE films that were melted under the isometric and at dimensionally unrestricted conditions.

The melting endotherms of the SPE samples are shown in Figure 3, and the thermal properties are summarized in Table 1. As can be seen from Figure 3 and Table 1, the sulphonated polyethylenes melt at temperatures significantly higher than the parent polyethylenes. Their T_m are influenced by the concentration of the ionic sites, the nature of the counter-ion and the orientation of the polyethylenic precursor.

DISCUSSION

The melting temperature T_m for crystals formed from high molecular weight chains in the pure state is given^{8,9} by:

$$\frac{1}{T_m} = \frac{1}{T_m^0} + \frac{2\sigma_{ex}}{T_m\zeta\Delta H_u}$$

where ζ is the thickness of the crystal, σ_{ex} is the excess free energy characteristic of each crystalline sequence which emerges from the basal plane, ΔH_u is the heat of fusion per unit volume and T_m^0 for polyethylene is 145.5°C.

Considerable increase in the thickness of the crystals or a decrease in the interfacial basal free energy would have to take place to account for a 15°–20°C increase in the melting temperatures. Moreover, chemical modification of the surface of polyethylene crystals tends to increase the surface energy⁷, leading to a decrease in T_m .

Heterogeneous chlorination and chlorosulphonation of polyethylene were shown to take place solely in the amorphous regions² and it can be assumed that the thickness of the crystallites is not altered significantly during the chemical reaction or during the subsequent

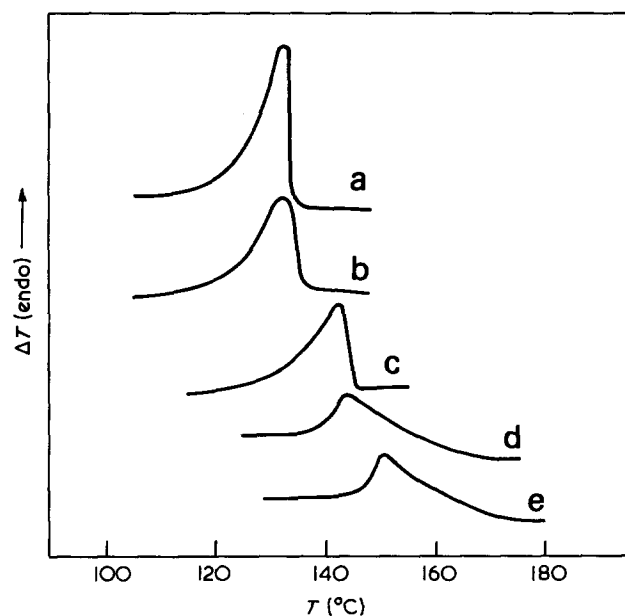


Figure 3 Fusion endotherms of the parent polyethylene and of its sulphonated products: (a) Compression moulded HDPE film, Sample B; (b) SPE-B/1, 1.2 mEq g⁻¹, counter-ion H⁺; (c) SPE-B/2, 2.0 mEq g⁻¹, counter-ion H⁺; (d) SPE-B/2, 2.0 mEq g⁻¹, counter-ion Na⁺; (e) SPE-B/2, 2.0 mEq g⁻¹, counter-ion Mg²⁺

Table 1 Heats of fusion and melting points of sulphonated polyethylenes (SPE) and their polyethylenic precursors

Sample ^a	Cation exchange capacity (mEq g ⁻¹)	Counter-ion	Melting point (°C)	Heat of fusion of crystalline phase ^b , ΔH_u		Entropy of fusion of crystalline phase, ΔS_u (cal °C ⁻¹ mol ⁻¹)
				(cal g ⁻¹)	(cal mol ⁻¹)	
A	—	—	129	37.6	877	2.18
SPE-A	2.0	H ⁺	133	16.8	523	1.29
		Na ⁺	136	15.0	467	1.14
		Mg ²⁺	139	12.4	385	0.93
B	—	—	131	38.5	900	2.23
SPE-B/1	1.2	H ⁺	131	25.7	713	1.76
		Na ⁺	135	24.4	677	1.66
		Mg ²⁺	139	19.6	543	1.32
SPE-B/2	2.0	H ⁺	142	21.5	635	1.53
		Na ⁺	144	20.5	538	1.30
		Mg ²⁺	150	17.7	523	1.24

^a SPE-A and SPE-B denote samples obtained by heterogeneous chlorosulphonation of polyethylene films A (blow extruded) and B (compression moulded), respectively

^b Calculated on the assumption that polyethylene crystallites were not destroyed during chlorination (*cf. ref. 2*). The decrease in thus calculated values of ΔH_u is attributed to the distortion of crystallites

hydrolysis of the SO₂Cl groups. Thus, other factors should be considered in order to account for the increase in the melting temperatures. Since the melting temperature is uniquely described by the heat and the entropy of fusion⁹:

$$T_m = \Delta H_u / \Delta S_u$$

(ΔH_u and ΔS_u per chain repeating unit), attention must be focused on these two quantities.

The distinctly different structural characteristics of a polymer molecule in the crystalline and in the liquid states must manifest themselves by increase of the configurational entropy of the system upon melting. A wide array of configurations in the liquid state of the polyethylene may be prohibited upon introduction of polar groups into the amorphous phase of the polymer. The segmental mobility depends upon the nature of the interchain forces. Thus, in the case of ionic polymers, it must be influenced by the concentration of ionic groups, by the degree of their dissociation and by the nature of the counter-ion. It was observed experimentally that the electrostatic forces between the bound ions in the polymer chain and the counter-ions reduce the segmental mobility and increase T_g ^{10,11}. The T_g of the amorphous phase may become higher than the melting point of its crystallites when the concentration of the ionic group is high. Consequently, the amorphous phase may restrict the mobility of the polymeric chains in the crystallites during their melting. Thus, the high value of the melting temperatures of the polyethylene-based cation exchange materials can be attributed to the decrease in configurational entropy.

Takamizawa *et al.*¹² reported an increase in melting temperatures for polyethylene crystals crosslinked by γ -radiation. These authors have also attributed the observed effect to a decrease in configurational entropy in the liquid state. An increase in T_m induced by an increase in the degree of crosslinking of the crystal surfaces was also observed for biopolymers¹³. Increase in T_m due to

crosslinking of polymeric segments adjacent to the highly ordered crystalline phase was also predicted by the theoretical calculations of Flory¹⁴.

The melting temperatures of samples of SPE increase with increase in the concentration of ionic groups. T_m is further influenced by the nature of the counterion. It increases from the acid to the salt form and further from the monovalent counterion to the bivalent one following the increase in T_g . The shape of the melting endotherm also changes and becomes asymmetric with a shoulder towards higher temperatures. Evidently, a considerable fraction of the crystallites melt at temperatures even higher than the temperature corresponding to the maximum of the endotherm. This introduces considerable uncertainty in the calculated entropy values. The changes in the melting temperatures are reversible and the original values are restored upon exchange of Mg²⁺ and Na⁺ and H⁺, respectively.

The decrease of the configurational entropy in the SPE samples prepared from the blow extruded polyethylene (Sample A) seems to be higher than in those prepared from the compression moulded film (Sample B). This may be expected in view of the irregular character of the interphase of the lamellae in the blow extruded polyethylene. However, differences in the interphases of the lamellae seem also to be responsible for considerable differences in the degree of distortion of the crystallites, due to ionic crosslinking. Consequently, for samples having identical overall ion exchange capacities, the experimentally determined increments in T_m are much larger for the SPE-B/2 than for the SPE-A series.

Introduction of chlorine into the amorphous phase of polyethylene may also cause a rise in the glass transition temperature, because of the induced dipole-dipole interactions. However, the resulting increase in T_g is smaller than in the case of sulphonated materials. Data reported in the literature on chain mobility of the chlorinated polyethylenes¹⁵ indicate that severe restrictions of the melting process may be expected only at very high levels of chlorination. An increase in T_m is indeed

observed only when the overall chlorine content is higher than 30%, i.e. the chlorine content in the amorphous phase is higher than 45%. The initial decrease in melting temperatures that takes place at low degrees of substitution can be related to an increase in the excess surface free energy, σ_{ex} , in complete analogy to chlorinated single crystals⁷. An additional decrease in melting temperatures that takes place at intermediate degrees of substitution (see *Figure 2*) can be related to the distortion of crystallites induced by the heterogeneous modification of the amorphous phase². However, at very high degree of chlorination, these effects are offset by entropy factors.

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