

Melting of Linear Polyethylene Crystallized From the Melt Under Shear Stress

INTRODUCTION

A stretched rubber crystallizes much faster than an unstretched rubber. Early experiments conducted by Treloar¹ and others^{2,3} show this effect clearly.

Stretching has also been found to have a marked effect on the nature of the crystallites formed in rubber.⁴ When an unstretched rubber is crystallized, the axes of the crystallites are oriented randomly in all directions; when a rubber is stretched and then crystallizes, the crystallites have the chain axes parallel to the direction of extension. The latter crystalline state is comparable to that of a typical fiber.

Recently, there has been renewed interest in the stress-induced crystallization of polymers.⁵ Primary emphasis has been on crystallization from a stressed melt or solution.⁵⁻¹⁴ Of particular note is the two-stage "row orientation" model proposed by Keller and Hill,^{5,10} which can be used to unify these new results with the classical effects of rubber. In this communication, some results obtained by determining the melting behavior of linear polyethylene crystallized under shear stress as reported in a previous publication¹³ are examined in light of the two-stage model.

EXPERIMENTAL

The melting behavior of samples of linear polyethylene, Table I, crystallized under shear stress and under quiescent conditions¹³ was determined using the Perkin-Elmer differential scanning calorimeter (Model DSC-1). All samples were unconstrained and heated at a rate of 10°C/min.

Owing to the small sample size (~0.7 mg), the apparent heat of fusion could not be accurately determined. However, in all cases it was of the order of 50-55 cal/g.

TABLE I
Properties of Polymers Used

Designation	Melt index* g/10 min	Viscosity-Average mol wt
HMW polyethylene	0.9	1.2×10^5
VHMW polyethylene	0.2	2.3×10^5
UHMW polyethylene	0.0	~ 10^6

* ASTM D1238, Measuring Flow Rates of Thermoplastics by Extrusion Plastometer, 1970 Book of Standards published by ASTM, Philadelphia, Pa. 19103.

RESULTS AND DISCUSSION

Keller and Hill have proposed a model for the crystallization of polymers under stress.⁵ The model is characterized by lamellar crystal growth occurring in planes perpendicular to a central nucleating axis.

The crystallization has been shown to be a two-stage process.¹⁰ First, fibrous (extended-chain) crystals form which are highly *c*-axis oriented, then the fibrous crystals induce transversely growing lamellar (folded-chain) crystals. Stress affects the number of the nuclei and the orientation of the lamellae. The nucleation process is intrinsic to the polymer and not the result of adventitious nucleating sources. Previously, it was reported that spherulites and/or impurities in a deforming melt cause a disturbance which results in the formation of similar nucleation lines.¹³ However, these are macroscopic observations whereas Keller's mechanism is molecular. The macroscopic lines are merely lines of high nucleation density which, depending upon the stress, may contain fibrous and/or lamellar crystals.

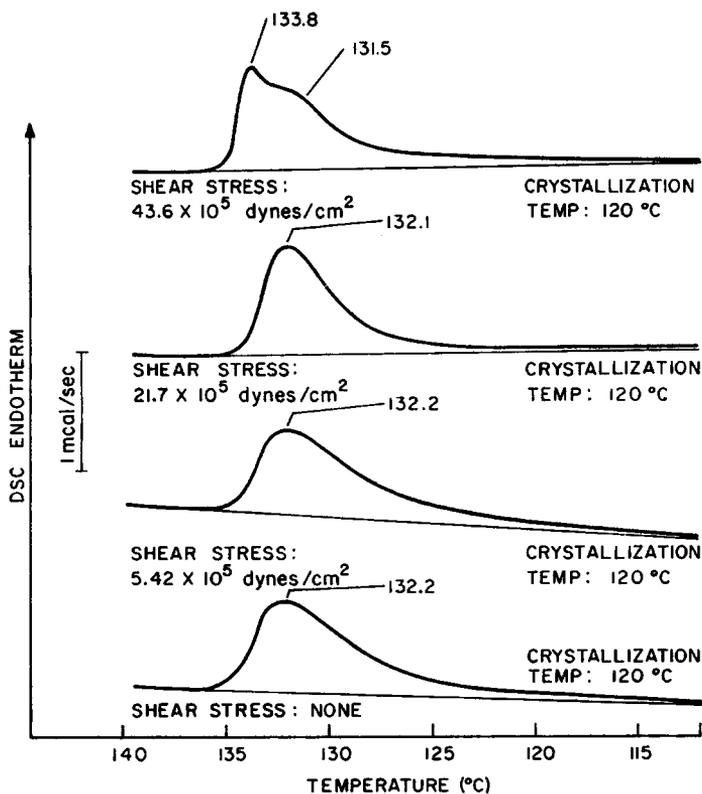


Fig. 1. DSC endotherms of HMW linear polyethylene crystallized at 120°C under various shear stresses.

Normally, linear polyethylene shows evidence of melting to temperatures of 135°–136°C. However, crystals comprised of fully extended chains are expected to exhibit unusually high melting points.⁵

Having now a qualitative description of the stress-induced crystallization process, consider the melting behavior of the HMW polyethylene (Table I) crystallized under various shear stresses and quiescent conditions at temperatures between 120° and 135°C (Figs. 1 and 2). The sample crystallized at 135°C fractured under the high shear stress of 43.0×10^6 dynes/cm² and was immediately cooled to room temperature. This sample exhibited a melting peak at the lowest temperature of all the samples (130.5°C) and, therefore, indicates that fracture had relieved the stress so that the major portion of the crystals formed upon cooling to room temperature. However, there was a long tail, or shoulder, toward much higher temperatures, i.e., to approximately 145°C, which is indicative of the melting of extended-chain crystals. The extended-chain crystals are expected to support the major portion of the load in a stress-crystallized sample.¹⁰ Moreover, the general shape of the fusion curve closely resembles that obtained from solution-stirred crystals.¹⁵

When examining the results obtained from samples crystallized under the same high shear stress ($\sim 43.0 \times 10^6$ dynes/cm²) but at lower temperatures, there is the familiar dependance of the melting on the crystallization temperature, i.e., the higher the crystallization temperature, the higher the melting temperature. In theory, this result could be considered as simply a reflection of the dependance of the critical size nucleus on the supercooling. In this case, however, it may be that at the lower crystallization tem-

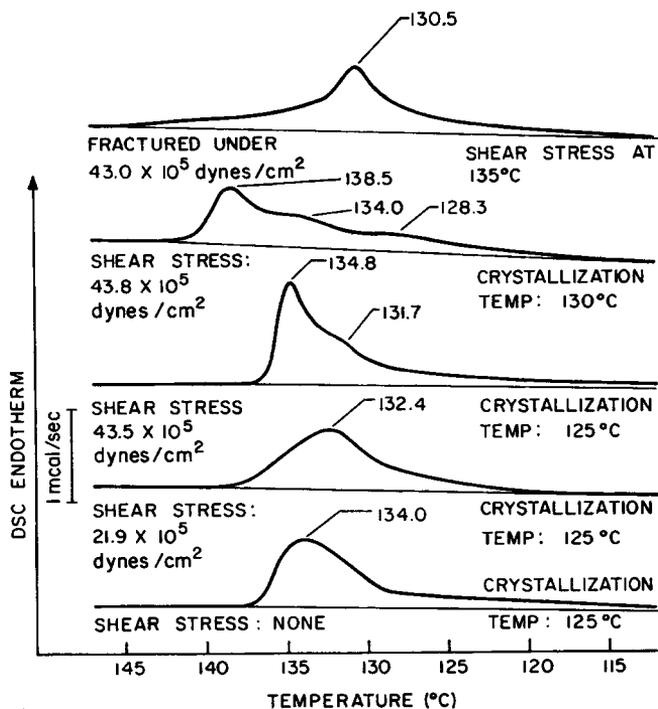


Fig. 2 DSC endotherms of HMW linear polyethylene crystallized at 125°, 130°, and 135°C under various shear stresses.

peratures, there is a decreasing number of fibrous crystals formed that can be detected in the calorimeter. Indeed, Keller has reported that large amounts of stress-crystallized melt polyethylene samples were required to detect a very small shoulder up to 141°C in a laboratory-built DTA apparatus and that the effect was not observable in the commercial Perkin-Elmer DSC instrument.⁵ Except for the shoulder, the endotherms of the samples crystallized at 125°C under 43.5×10^6 dynes/cm² shear stress and at 120°C under 43.6×10^6 dynes/cm² shear stress are markedly similar in shape to the one reported by Keller. However, because of the apparent high nucleation density (high transparency to visible light and lack of resolution of any morphology under the microscope) and similarity in crystallization kinetics of all of the high stress samples, it may be more reasonable to argue that large concentrations of fibrous crystals exist in *all* samples crystallized under high shear stress.

Another possibility for the temperature dependence of the melting of the samples crystallized under high stress, then, is the existence of degrees of order in the fibrous crystals themselves. Recent evidence indicates that fibrous crystals are a composite structure of both chain-folded and extended-chain crystals.^{5,10} A similar temperature dependence has been observed in the melting of polyethylene samples crystallized under stress at these temperatures in a capillary rheometer^{11,14} and has been shown to be associated with increasing *c*-axis orientation. Furthermore, such dependence is associated with the unconstrained melting of stretched natural rubber ("racked" rubber) in which the existence of fibrous crystals has been well established.^{1,4} Therefore, decreasing order of the fibrous crystals with decreasing crystallization temperature is a plausible explanation for the observed decrease in melting temperature with decreasing crystallization temperature of the samples crystallized under high shear stress.

Since the polyethylene samples used have a broad molecular weight distribution, the entanglement density and therefore the extent of the melt orientation under stress may

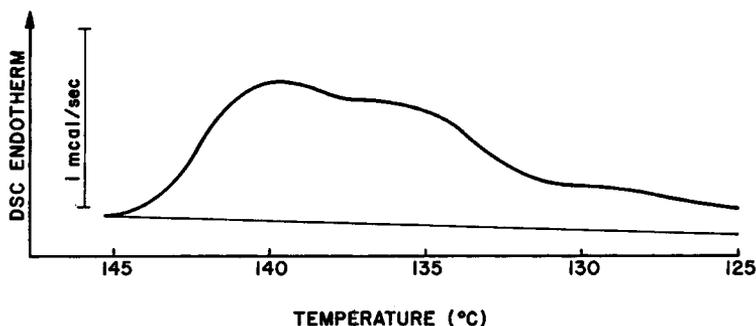


Fig. 3. DSC endotherms of VHMW linear polyethylene crystallized at 130°C under 43.4×10^6 dynes/cm² shear stress.

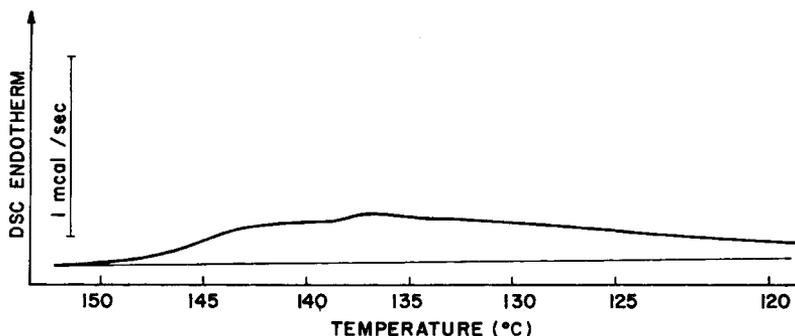


Fig. 4. DSC endotherms of UHMW linear polyethylene crystallized at 145°C under 53.9×10^6 dynes/cm² shear stress.

vary widely in a sample. The melting at lower temperatures in individual samples apparently represents the melting of crystals formed from less oriented molecules the majority of which are lamellar and, especially at the higher crystallization temperatures, formed upon cooling the sample to room temperature.

Examination of the endotherms of polyethylene samples crystallized under various shear stresses and quiescent conditions at 125° and 120°C reveals that the apparent maximum melting temperatures are essentially independent of the applied shear stress, again in accord with results obtained with stretched natural rubber.¹ At 125°C, the lower temperature melting peaks shift toward lower temperatures apparently owing to decreased time at the crystallization temperature. At 120°C, the effect was not observed because of the large initial supercooling.

The melting of a sample of VHMW polyethylene which was crystallized at 130°C under a high shear stress of 43.4×10^6 dynes/cm² is shown in Figure 3. The broad endotherm is generally similar in appearance to that of the HMW polyethylene crystallized under similar conditions, but the entire endotherm is shifted toward higher melting temperatures. In polyethylene, there is evidence that the amount of superheating is dependent upon the molecular weight, i.e., the higher the molecular weight, the more the superheating.¹⁵ It has been shown that extended-chain crystals are more superheatable than chain-folded crystals.¹⁵

In previously described crystallization experiments¹³ it was observed that there was always a limiting crystallization temperature at which failure of the polymer samples occurred under all stresses employed. This temperature was found to be molecular weight dependent, increasing with increasing molecular weight, e.g., 135°C with the

HMW polyethylene and 125°C with the LMW polyethylene. Therefore, in order to demonstrate shear stress-induced crystallization above the quiescent equilibrium melting temperature, a number of experiments were conducted at high temperatures with a UHMW polyethylene.

The endotherm of a UHMW sample crystallized at 145°C under 53.9×10^6 dynes/cm² shear stress, shown in Figure 4, exhibits a very broad melting range containing several poorly defined melting peaks. The melting process was observed to continue to temperatures as high as 150°C, which indicates that at least some of the crystals must have superheated several degrees. The melting at these higher temperatures may be taken as evidence of the melting of crystals comprised of fully extended chains.

These studies are continuing and will be reported at a latter date.

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