Notes to the Editor

Orientation effects on a high *cis*-1,4-polybutadiene induced by shear rate in a capillary rheometer

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INTRODUCTION

It is known that the bulk crystallization kinetics of high polymers is influenced by the thermomechanical history.

In particular, it has been reported[1] that a high *cis*-1,4-polybutadiene shows faster crystallization kinetics after mechanical treatment in a laboratory mill. This has been attributed to a permanent orientation induced by the shear on the amorphous phase of the polymer or to an orientation on the 'impurities' that act as crystallization seeds.

In this study we have tried to take advantage of this phenomenon of mechanical memory of high *cis*-1,4-polybutadiene in order to detect, by crystallization kinetics, the degree of orientation induced on a high *cis*-1,4-polybutadiene by extrusion through a capillary, particularly when its rheological behaviour becomes anomalous.

In fact it has been found[2] that the flow through a capillary of crystallizable polymers, of *cis*-1,4-polybutadiene in particular[3], under certain conditions of temperature and shear rate becomes anomalous. In some cases the flow of the polymer stops on increasing the pressure above a certain level.

In the present study the *cis*-1,4-polybutadiene extruded under experimental conditions around the anomalous points, has been characterized by determining the crystallization kinetics in order to detect permanent orientation connected with the previous mechanical history.

EXPERIMENTAL

The high *cis*-1,4-polybutadiene was prepared by means of a tris (π-allyl) uranium halide catalyst.

The physical characteristics of the sample are: *cis*-1,4-content, 99%; intrinsic viscosity in toluene at 30°C, $[\eta] = 3.9 \times 10^2$ ml/g; polydispersity index, 4.3; half crystallization time, $t_{1/2}$ (at $-10°C$) = 85 min; Avrami exponent, 2.8; melting temperature, 2.7°C. The *cis*-1,4-polybutadiene was extruded by means of a capillary rheometer mounted on an Instron dynamometer. The capillary used had a diameter, $D = 0.151$ cm and length $L = 5.08$ cm; the entry angle was 90°.

The ratio $L/D = 33$ was sufficient to avoid entrance correction. The experimental results were represented by plotting the apparent viscosity η, against the shear stress τ. Apparent rates of shear and shear stresses were calculated from the well known relations: shear stress (at the wall), $\tau_w = R\Delta P/2L$, where ΔP is the pressure difference over the capillary; shear rate (at the wall), $\dot{\gamma} = 4Q/R^3$, where Q is the volumetric flow rate and apparent viscosity, $\eta_w = \tau_w/\dot{\gamma}_w$. The shear rates $\dot{\gamma}$ explored ranged from 10^{-1} to 10^3 sec^{-1}.

As well as the dilatometry, techniques used to obtain the crystallization parameters and melting points, are as already described elsewhere[4]. None of the extruded samples were submitted to any thermal treatment in order to avoid erasing part of the orientation. In fact, it is known for *cis*-1,4-polybutadiene[1] and for *cis*-1,4-polyisoprene[4] that thermal treatment at temperatures higher than that of fusion can reduce the orientation induced by mechanical treatments. All samples were examined dilatometrically within 24 h after extrusion from the capillary.

RESULTS AND DISCUSSION

Rheological data, crystallization parameters and melting points are reported in *Table 1*. The rheological curves log η_w vs. log τ_w are plotted in *Figure 1*.

The temperatures were so chosen because of the fundamental behaviour here of so-called shear induced crystallization. The curve obtained at 60°C is a typical non-Newtonian behaviour

Table 1 Rheological and dilatometric data

	$T = 60°C$				$T = 50°C$				$T = 40°C$			
$\dot{\gamma}_w$ (sec^{-1})	$\eta_w \times 10^{-4}$ (Pa sec)	$t_{1/2}$ (min)	T_m (°C)	n	$\eta_w \times 10^{-4}$ (Pa sec)	$t_{1/2}$ (min)	T_m (°C)	n	$\eta_w \times 10^{-4}$ (Pa sec)	$t_{1/2}$ (min)	T_m (°C)	n
0.181	23.7	70	2.5	2.0	42.5	65	1.4	2.0				
0.363	21.0	72	2.5	2.0	29.8	60	2.0	1.6				
0.725	13.8	70	2.6	2.2	20.0	60	1.5	2.0	24.2	68	1.3	1.7
1.81	8.4	78	2.4	2.0	11.4	62	2.5	1.8	13.2	64	1.2	1.7
3.63	5.5	74	2.7	2.0	7.25	60	1.4	1.7	8.25	62	1.5	2.0
7.25	3.4	74	2.5	2.5	4.38	60	1.7	2.0	5.50	66	1.7	2.3
18.1	1.78	70	2.7	2.2	2.26	64	1.7	1.8	4.26	80	2.5	2.8
36.3	0.99	70	2.5	2.0	1.44	72	2.7	2.3				
72.5	0.56	78	2.5	3.2	0.93	90	2.1	1.8				
181					0.43	96	2.6	1.7				
363					0.24							

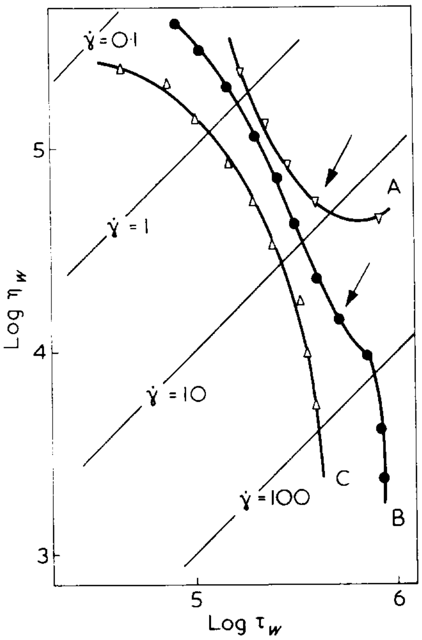

Figure 1 Apparent melt viscosity as a function of the shearing stress for *cis*-1,4-polybutadiene at various temperatures: A, 40°C; B, 50°C; C, 60°C

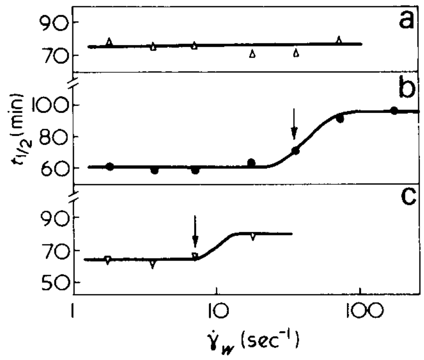

Figure 2 Half crystallization times *versus* apparent shear rates for *cis*-1,4-polybutadiene extruded at different temperatures: (a) 60°C; (b) 50°C; (c) 40°C

but different types of behaviour were obtained at 50° and 40°C. At higher values of τ_w there exists an anomalous behaviour due to flow-induced crystallization phenomena according to ref 2 or to high elastic phenomena according to ref 5. These critical points are indicated by arrows. These phenomena can be so strong as to stop any further flow of the elastomer through the capillary at lower temperatures. In *Figure 2* the $t_{1/2}$ measured at −10°C are plotted as a function of $\dot{\gamma}_w$.

It is possible to distinguish the following items.

(a) The samples extruded at 60°C always show a lower $t_{1/2}$ than the unprocessed sample. This means that an orientation was developed during extrusion, though not very high.

(b) At a temperature of 50°C the samples show low values of $t_{1/2}$ for small $\dot{\gamma}_w$. On increasing $\dot{\gamma}_w$ we observe a sharp increase of $t_{1/2}$ just when $\dot{\gamma}_w$ becomes critical, i.e. the rheological behaviour becomes anomalous. The $t_{1/2}$ approaches the value of the unprocessed sample.

(c) A further lowering of the extrusion temperature confirms and supports the phenomena exhibited in point (b).

The above mentioned experimental findings lead to the conclusion that at low shear rates a flow exists which orients the macromolecules in such a way as to develop nucleation sites which further act as an acceleration media. When the shear rate increases, the nature of the flow changes; orientation development decreases as revealed by lowering of crystallization rate. The absence of orientation in the extrudate, at high shear rate, can be explained assuming that there is a plug flow and critical region as described recently in the literature[5].

From *Table 1* it is easy to infer that for a small degree of orientation (data at 60°C) $t_{1/2}$, T_m and n are practically independent from $\dot{\gamma}_w$ and that there is no change of nucleation and growth habit.

This is not the case when the change of orientation degree becomes strongly $\dot{\gamma}_w$ dependent (data at 40°C). There are now different types of growth of the spherulites proceeding from rod-like (n = 1.5) to sphere-like (n = 2.5) habit, both with homogeneous nucleation. The melting temperatures seem to be slightly affected by this different type of spherulite habit.

The crystallinity level is independent of $\dot{\gamma}_w$ and no change of intrinsic viscosity of the processed samples was observed.

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Crystallization of α,ω-ethoxy-poly(ethylene oxide)

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Kovacs, Gonthier and Straupe[1,2] have described important effects in the crystallization of low molecular weight samples of α,ω-hydroxy-poly(ethylene oxide) which are attributable to stepwise changes in the degree of chain-folding of the chains in the growing crystalline lamellae and also to similar changes subsequent to the initial crystallization. There is some uncertainty[1,2] regarding the role of the hydroxy-end-groups in determining these effects, particularly in respect of lamella thickening[1]. Accordingly we have used the methods described by Kovacs and Gonthier[1] to compare the crystallization of ethoxy-ended and hydroxy-ended derivatives of the same poly (ethylene oxide) chain.

The α,ω-hydroxy-poly(ethylene oxide) of nominal molecular weight $\bar{M}_n$ = 3000 was obtained from Fluka AG. Its purification, ethoxylation and characterization are described else-

Table 1 Properties of the poly(ethylene oxide) samples

	Molecular weight		Melting point	
Sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_c (°C)	T_m (°C)
3000H	2800	1.06	35–49	58.8
3000E	2900	1.04	35–42	59.4