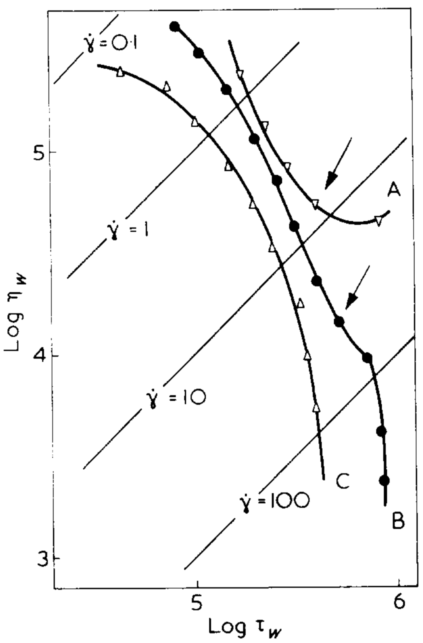

Figure 1 Apparent melt viscosity as a function of the shearing stress for *cis*-1,4-polybutadiene at various temperatures: A, 40°C; B, 50°C; C, 60°C

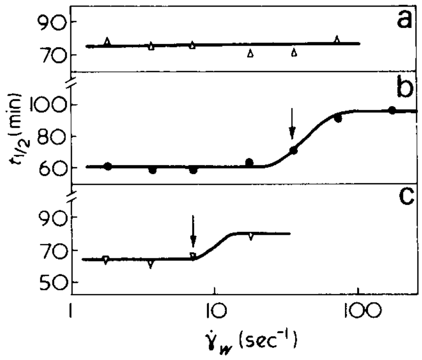

Figure 2 Half crystallization times *versus* apparent shear rates for *cis*-1,4-polybutadiene extruded at different temperatures: (a) 60°C; (b) 50°C; (c) 40°C

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

where[3]. Molecular weights (gel permeation chromatography) and melting points (dilatometry) are listed in *Table 1*: we denote the hydroxy-ended polymer 3000H and the ethoxy-ended polymer 3000E.

Crystal growth rates were measured as follows. Thin films of polymer (thickness 0.01 mm) held between glass cover slips (18 x 18 x 0.15 mm^3) were seeded by melting the samples on a hot plate controlled (to ±1K) at a temperature in the range 75°–85°C, crystallizing the sample at room temperature (~20°C), and then holding the samples on a second hot plate controlled (to ±0.05K) at 58.6°C (3000 H) or 58.8°C (3000E) for 35 min. Samples so seeded were crystallized by rapidly transfering them to a third hot plate controlled (to ±0.05K) at the appropriate crystallization temperature (T_c). After the required time (t_c) crystallization was stopped by quenching the samples in a mixture of dry ice and acetone. Each sample was used only once. Crystals prepared in this way are decorated at the edges by birefringent fibrilla outgrowths (~3 to 5 μm thick), while excess melt is homogeneously nucleated to a structure of low birefringence. Consequently the crystals are easily seen with a polarizing microscope: examples are shown in *Figure 1*. Growth rates were calculated from the variation in crystal height (H) or width (W) with time t_c, e.g. the growth rate G_H is defined as $H/2t_c$. Radial growth rates of spherulites (G_S) were measured as described elsewhere[4]. The hot plates, and the hot stage of the polarizing microscope used for spherulite growth, were calibrated by means of eight melting point standards (range 35° to 69°C). The melting points of

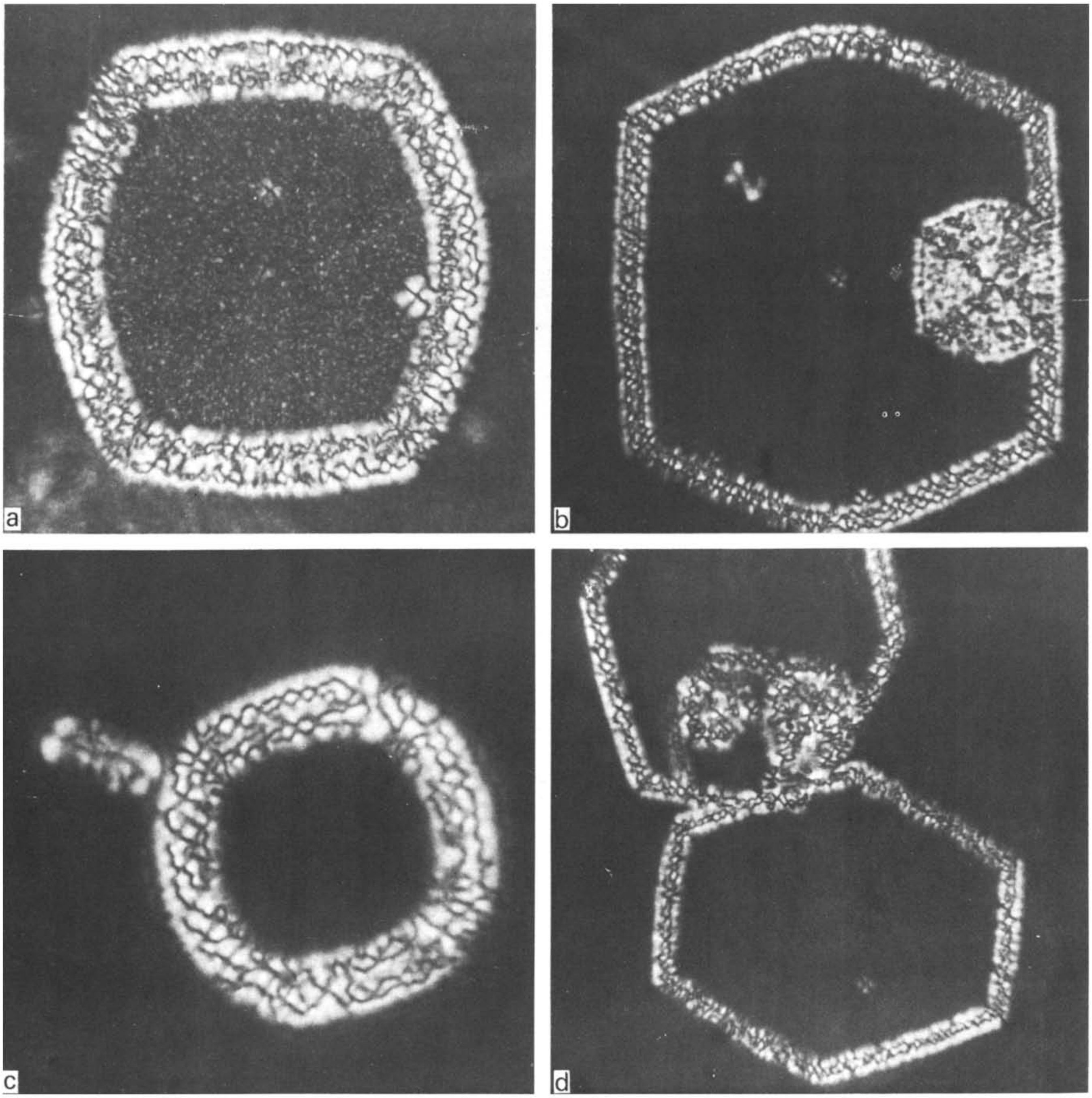

Figure 1 Self-decorated crystals of poly(ethylene oxide) 3000H: (a) T_c = 48.0°C; (b) T_c = 50.1°C; (c) T_c = 51.1°C; (d) T_c = 56.0°C. Magnification 500 X

the standards were checked against standardized thermometers (National Physical Laboratory).

Growth rates G_H (for crystals) and G_S (for spherulites) are plotted against crystallization temperature T_c in *Figure 2*. The curves so obtained exhibit major cusps at 51.1°C (3000H) and 51.6°C (3000E), i.e. at temperatures some 7.7°C below the dilatometric melting points of the samples. A second minor cusp is apparent in $G(T)$ of sample 3000E at 50.6°C. Following Kovacs and Gonthier[1] we denote these temperatures T_e (major) and T_{1f} (minor): T_e being associated with the transition from extended-chain to once-folded-chain lamella crystallization, and T_{1f} with the transition from once-folded-chain to twice-folded-chain lamella crystallization.

For both samples crystals grown below T_e were hexagonal with H/W = 1.15 ± 0.15 (*Figures 1a* and *1b*); those grown at or just above T_e were roughly circular (*Figure 1c*); and those grown much above T_e were hexagonal with H/W = 0.93 ± 0.05 (*Figure 1d*). Crystals grown at or below T_e had a finely decorated inner region and a coarsely decorated surround (*Figures 1a* and *1c*). Crystals grown above T_e were essentially undecorated (*Figure 1d*): however at $T_c > 56$°C crystals were entirely coarsely decorated. No change in shape or decoration of the crystals of sample 3000E could be detected at or about T_{1f}. All these morphological observations agree with those reported by Kovacs and Gonthier[1] for samples of molecular weight 3000 or lower (e.g. see ref 1, Figures 6, 10, 19, 29). They have assigned the distinct inner region to crystal thickened by a rapid chain unfolding process. The coarse decoration at high T_c is thought to be due to chain fractionation during slow crystallization.

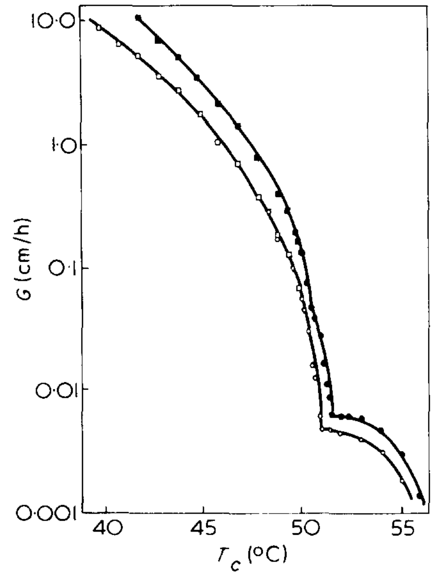

Figure 2 Semi-logarithmic plot of growth rate *versus* crystallization temperature (T_c) for poly(ethylene oxide) fractions 3000H (○, □) and 3000E (●, ■). ○, ● Crystal growth rates (G_H) and □, ■, spherulite growth rates (G_S).

These results serve to show that the differences in crystallization behaviour between hydroxy- and ethoxy-ended poly(ethylene oxide) fractions are slight: the only significant difference being an increased propensity for the formation of twice-folded-chain lamella crystals of 3000E compared with 3000H. This close correspondence of behaviour seems to rule out any model of the growth and thickening processes which assigns a specific role to hydrogen bonding interactions involving the hydroxy-end-group.

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Infra-red spectra of the copolymer(β-benzyl D- and L-aspartate) obtained by the polymerization of the *N*-carboxylic anhydride

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INTRODUCTION

Poly(α-amino-acid) obtained by the polymerization of α-amino-acid *N*-carboxylic anhydride (NCA) has played an important role as a model for protein. Little attention has been paid to the initiator used for the polymerization. However, the sequential distribution of D- and L-residues in the copolymer(D- and L-amino-acid) from NCA may vary depending upon the nature of the initiator. For example, poly(γ-benzyl-DL-glutamate) obtained from racemic NCA with butylamine as initiator has an infra-red spectrum similar to those of sequential polymers such as $(DL)_n$ or $(DLLL)_n$, while the spectrum of the polymer obtained from racemic NCA with sodium methoxide substantially retains the characteristics of the L-polymers, indicating higher stereoselectivity in the sodium methoxide initiated system[1].

On the other hand, in the copolymerization of D- and L-NCA of alanine[2] and of γ-benzyl glutamate[3,4] with primary amine type initiator, α-helical conformation of the growing polymer chain has been considered responsible for the selection of one of the NCA antipodes. In contrast, no selection of the antipode of NCA was observed in the copolymerization of D- and L-NCA of valine initiated by primary amine, where the polymer formed assumes β-conformation[5,6]. However, the effect of the secondary conformation of the polymer being formed in the NCA polymerization initiated by sodium methoxide has not been clearly elucidated.

Since poly(β-benzyl-L-aspartate) is known to assume a left handed α-helical conformation which is much less stable than the right handed α-helical conformation of poly(γ-benzyl-L-glutamate)[7], it is of interest to study the copolymerization of D- and L-NCA of β-benzyl aspartate with different initiators. In the present report the infra-red spectra of the copolymer(β-benzyl D- and L-aspartate) obtained with butylamine and sodium methoxide as initiators are described.

RESULTS AND DISCUSSION

The infra-red spectra of cast film from a chloroform solution of the copolymer