temperature to be made, it is clear that K decreases with increasing temperature, as expected. Since, at any temperature, initiation occurs exclusively by the complex when the rate has attained its plateau value, these experiments allow estimation of the difference in the activation energies (E) and the ratio of the frequency factors (A) for initiation by AZO and complex. It turns out that:

$$\left.\begin{aligned} E_{\text{AZO}} - E_{\text{complex}} &= 2{\cdot}7 \text{ kcal mole}^{-1} \\ A_{\text{AZO}} / A_{\text{complex}} &= 12{\cdot}5 \end{aligned}\right\} \qquad (1)$$

Models show that it is easily possible to obtain a conformation of the AZO molecule (with a *trans* azo group) in which both nitrile groups can be bonded to a single silver ion. The azo group would appear to be too far from the silver to permit effective bonding. Formation of a cyclic complex in this way would introduce strain into the C—N═N—C linkages; relief of this strain in the transition state would tend to reduce the activation energy for decomposition. Further, it seems possible that in the transition state restrictions are imposed by the CN··Ag···NC bonds, so that degrees of freedom which develop in the transition state for the AZO decomposition are inoperative with the complex. The lower frequency factor for initiation by the complex is therefore understandable. The data in *Table 1* of ref. 1 suggest that the efficiency of initiation of the polymerization of methyl methacrylate at 70°C may be slightly higher for the complex than for AZO. This could arise from a reduction in the probability of recombination of two primary radicals brought about by their unfavourable disposition when coordinated to a silver ion.

We are extending these investigations to other related systems. Professor J. M. Robertson, F.R.S., of the Chemistry Department, University of Glasgow, has kindly undertaken a determination of the crystal structure of the AZO–$AgClO_4$ complex.

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Crystal Density, Crystallinity and Heat of Fusion of Poly (tetramethylene oxide)

THE determination of crystallinity in polymers from specific volume data is subject to a large error unless the crystal and amorphous phase values are known to high accuracy. The purpose of this communication is to give an early presentation of these constants for poly (tetramethylene oxide) and thus prevent the acceptance of less accurate values by default[1,2]. We consider that the information given below establishes 1·12 g cm^{-3} as the crystal density, 0·982 g cm^{-3} as the amorphous density, both at 25°C, and a heat of fusion of the crystal phase of approximately 200 J g^{-1} at the melting point (~ 44°C) [N.B. 1 calorie = 4·18 J].

A full presentation of the experimental details, crystallization kinetics and theoretical treatment will be published later[3]. For the present purposes it suffices to say that the cell dimensions of poly (tetramethylene oxide) were determined by conventional X-ray techniques on oriented samples of $\bar{M}_v = 570 \times 10^3$, prepared using PF_5 catalyst. The cell dimensions were obtained with an estimated probable error of ±0·02Å and are compared with other recently published values in *Table 1*.

Table 1. Comparison of crystallographic data at 25°C

Source ref.	*c (Å)*	*b (Å)*	*a(Å)*	d_{100}*(Å)*	ρ_{100}*(g cm⁻³)*
4, 6, 7	12·07	8·73	5·48	3·93	1·155
5	12·25	8·92	5·61	4·00	1·095
Present work	12·15	8·89	—	3·97	1·116

The crystal density, evaluated on the basis of four complete monomer units per unit cell, is shown in the last column. With the stated probable error in cell dimensions the error in the density term will be about 0·01 g cm^{-3}.

Before considering crystallinity values, let us first establish an acceptable value for the amorphous specific volume. The situation here is summarized in *Table 2*.

Table 2. Amorphous specific volume and expansion coefficient at 25°C

Ref.	*Sample details*		V_A *(25°C)* cm^3g^{-1}	$(\partial V/\partial T) \times 10^4$ *(25°C)*
2	SbF_5 cat.	$\bar{M}_n = 12·2 \times 10^3$	1·019	6·9
		$\bar{M}_w = 17·2 \times 10^3$		
1	PF_5 cat.	$\bar{M}_n = 130 \times 10^3$	1·021	7·3
		$\bar{M}_n = 6·8 \times 10^3$	1·020	
Present work	PF_5 cat.	$\bar{M}_v = 570 \times 10^3$	1·019	7·0

As these are the results of completely independent determinations we can have high confidence in the value $V_A = 1·019 \pm 0·001$ cm^3 g^{-1} at 25°C. Certainly for present purposes the error involved in the amorphous specific volume term is trivial compared to that in the crystal term.

It is common practice to determine the *weight* percentage crystallinity (X_w) via

$$X_w = 100\,(V_A - V_x)/(V_A - V_c) \qquad (1)$$

where V_A, V_x and V_c are the specific volumes of the amorphous, partially crystalline and perfect crystal phases respectively. The absolute crystallinity (X_x) can be determined from the integrated intensity of X-ray scattering due to the amorphous phase in a partially crystalline sample (I_x) and in the completely amorphous sample (I_A) from the equation

$$X_x = 100\,(I_A - I_x)/I_A \tag{2}$$

This of course defines the percentage of material with crystallographic packing. All other packing, including defects and chain folds, is counted as amorphous on this scheme.

Throughout this work a rounded-off value of $\rho_c = 1{\cdot}12$ g cm^{-3} ($V_c = 0{\cdot}893$) has been used in density determination and we find that this has consistently given precise correspondence between crystallinity determinations via equations (1) and (2). A comparison of X_w and X_x for a sample of $\overline{M}_v = 570 \times 10^3$, crystallized over experimentally accurate temperature and time ranges is given in *Table 3*, using $\rho_c = 1{\cdot}12$ g cm^{-3} and also $\rho_c = 1{\cdot}09$ g cm^{-3} as has been previously used[1,2].

Table 3. Comparison of crystallinity estimates

*Crystallization conditions**	X_x (%)	$\rho_c = 1{\cdot}09$ g cm^{-3}		$\rho_c = 1{\cdot}12$ g cm^{-3}	
		X_w (%)	$X_x - X_w$	X_w (%)	$X_x - X_w$
Crystallized at 18°C 100 min	24·2	32·4	− 8·2	25·9	−1·7
Crystallized at 18°C 4 140 min	36·9	44·7	− 7·8	35·8	+1·1
Crystallized at 23·5°C 1 500 min	27·4	38·3	−10·9	30·5	−3·1
Crystallized at 23·5°C 10 000 min	38·6	46·3	− 7·7	36·8	+1·8

*For further details of crystallization conditions see ref. 8.

We see that in the final column the difference term ($X_x - X_w$) fluctuates in line with random experimental error, whereas the difference term using $\rho_c = 1{\cdot}09$ g cm^{-3} shows consistently large negative deviations. These data are typical of results we have obtained in many measurements on poly (tetramethylene oxide). We thus conclude that $\rho_c = 1{\cdot}12$ g cm^{-3} ($V_c = 0{\cdot}893$) is a more accurate estimate of the crystal density of poly (tetramethylene oxide) and combined with the amorphous specific volume $V_A = 1{\cdot}019$ cm^3 g^{-1} gives good agreement with X-ray determinations of crystallinity.

The importance of knowing the crystal density to high accuracy can be seen in the thermodynamic data recently reported by Clegg, Gee, Melia and Tyson[2]. Using $\rho_c = 1{\cdot}09$ g cm^{-3} yields $X_w = 69$ per cent and consequently from their thermal data a heat of fusion of the crystal phase $\Delta H_f = 172$ J g^{-1} is obtained. However, using $\rho_c = 1{\cdot}12$ g cm^{-3} we obtain $\Delta H_f = 198$ J g^{-1}. This latter value is in good agreement with 206 J g^{-1} which we have obtained by differential scanning calorimetry in the present work.

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*On the Surface Free Energy of the Crystallites in Drawn Polyethylene**

AS OBSERVED by some investigators[1-3] the melting point of drawn linear polyethylene is almost independent of the preparation and annealing conditions and also of the crystal thickness. With single crystals and melt crystallized polyethylene, on the other hand, a linear relationship between the reciprocal value of crystal thickness and melting point has been found in agreement with the Thomson equation. In the light of a model proposed by Fischer, Goddar and Schmidt[4,5] there seems to be a possibility of understanding the constancy of the melting point of drawn polyethylene.

The model mentioned above starts from the assumption that the structure of the unannealed drawn polymer is represented by a nearly homogeneous crystalline matrix with high defect concentration caused by chain folds, chain ends, and disarranged sequences. As a consequence of the annealing treatment the defects diffuse to the boundaries of the crystalline regions and a layer structure is created. To describe the thermal behaviour of the polymer, knowledge of the surface free energy between the crystalline and disordered regions is necessary. It is quite clear that this quantity depends on the colloidal structure of the polymer. Using a two-phase model the surface free energy, σ_e, can be calculated according to the Thomson equation

$$\sigma_e = \{(T_m^0 - T_m)/2\,T_m^0\}\,\Delta h\, l \tag{1}$$

where T^0_m is the equilibrium melting point, T_m the actual melting point, and Δh represents[6,7] the heat of fusion per volume unit ($2{\cdot}93 \times 10^9$ erg/cm^3). The crystal thickness, l, is given by the expression

$$l = \alpha\, L \tag{2}$$

Here L means the long period, and α signifies the degree of crystallinity which may be estimated from density or enthalpy measurements. Because of the difficulties in calculating the degree of crystallinity of drawn polyethylene (for further information see refs 5 and 6) this quantity was taken to be constant and a reasonable value of 0·85 was chosen. A deviation

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