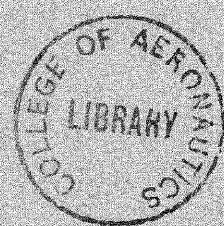


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THE TEMPERATURE DEPENDENCE OF PHOTO-ELASTIC
PROPERTIES OF CROSS-LINKED AMORPHOUS POLYETHYLENES

by

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The temperature dependence of photo-elastic properties of
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S U M M A R Y

Cross-linked samples of polyethylene were prepared by electron irradiation of both high and low density polymers in the crystalline state. A further cross-linked sample was obtained by curing a high density polyethylene by reaction with dicumyl peroxide at 180°C. The stress-strain birefringence relations were obtained, on specimens cut from these samples, at temperatures between 130 and 250°C.

All samples showed a substantial decrease in stress-optical coefficient with increasing degree of cross-linking and with increasing temperature. The stress-optical properties at each temperature were extrapolated to zero degree of cross-linking to give quantities characteristic of the Gaussian network. Comparison of these properties with Gaussian theory of the network leads to a value of ca. 1150 cal/mole for the difference in energy between trans and gauche conformations of successive links of the polyethylene chain and also indicates that the optical anisotropy of a - CH₂ - group in the elastomeric state is more nearly given by Denbigh's than by Bunn and Daubeny's polarisabilities.

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Introduction

The well-known kinetic theory of rubber-like elasticity may be extended to describe the photo-elastic properties of cross-linked networks, if the valence-optical scheme involving the principle of tensorial additivity of optical polarisabilities is accepted. The photo-elastic theory and this valence-optical scheme have been discussed in some detail by Treloar (1958) and Volkenstein (1963).

By making use of the rotational-isomeric model of a polyethylene chain, Saunders (1957) derived a tentative value for the difference in energy, U , between the trans and gauche conformations of successive links of the chain from photo-elastic measurements on cross-linked polyethylene at a single temperature above the crystal-melting point. The derivation involved the assumption of a particular value for the optical anisotropy of the monomeric unit of the chain and the actual value chosen is now open to some criticism. The value obtained for U was 2,300 cal/mole, which suggested the polyethylene chain was considerably 'stiffer' than might have been expected from estimates of U for short chain paraffin.

Ciferri, Hoeve and Flory (1961) obtained an independent estimate of $U = 500$ cal/mole from stress-temperature measurements on cross-linked polythene above its melting point.

In this paper, results of measurement of the temperature dependence of the photo-elastic properties of cross-linked polyethylene above their crystal melting point are presented. It is shown that these can be described by the theory if a value of $U = 1150$ cal/mole is adopted. This result does not depend on the assumption of a particular value for the optical anisotropy of a monomeric unit, indeed it is shown that an independent estimate of this quantity can be obtained from the measurements.

Theoretical background

In its classical form the kinetic theory of rubber-like elasticity (see Treloar, 1958) was developed for a network of long chains of randomly-jointed links. The resulting load-deformation relation in simple tension may be expressed in terms of the tensile stress t and the extension ratio λ as

$$t = \frac{\lambda f}{A_0} = NkT \left(\lambda^2 - \frac{1}{\lambda} \right) = \rho \frac{RT}{M_c} \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (1)$$

in which f is the applied tensile force acting on a cross-sectional area of magnitude A_0 when undeformed. N is the number of active network chains per unit volume of the network, k is Boltzmann's constant, T is the absolute temperature, ρ is the density of the cross-linked network, R the gas constant and M_c the number average network chain molecular weight.

If each link is assumed to be optically anisotropic with uniaxial

symmetry about the link direction, so that its properties may be characterised by optical polarisabilities α_ℓ and α_m respectively for light polarised with electric vector parallel and perpendicular to the link direction, then the birefringence of the stretched network Δn , may be computed from the distribution of link directions predicted by the theory by assuming the usual tensorial additivity of bond polarisability as discussed elsewhere, see for example Volkenstein (1963). This leads to

$$\Delta n = n_1 - n_2 = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \frac{2\pi N}{45} (\alpha_\ell - \alpha_m) \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (2)$$

in which n_1 and n_2 are respectively the refractive indices for light polarised with electric vector parallel and perpendicular to the direction of extension and \bar{n} is the mean refractive index of the network, which in a deformation at constant volume is taken to be independent of deformation.

The stress optical coefficient is thus given by

$$\frac{\Delta n}{t} = \frac{(\bar{n}^2 + 2)^2}{\bar{n}} \frac{2\pi}{45kT} (\alpha_\ell - \alpha_m) \quad (3)$$

This is independent of degree of cross-linking except insofar as cross-linking results in volume changes or changes in chemical composition. Since these are usually taken to be small the stress-optical coefficient is usually taken to be sensibly independent of degree of cross-linking.

The behaviour of real molecular networks may be more nearly approximated by considering networks of chains in which there is some correlation in direction of successive links due to valence angle restrictions and variations of internal energy during rotation about single bonds. A simple form of such a chain may be taken to consist of n_m rigid identical links each of length ℓ_m (Saunders, 1957) (Volkenstein, 1963) when, within the limitations of n_m large and the end-to-end vector r_m small so that $r_m \ll n_m \ell_m$, the distribution of r_m vectors for the free chain may be taken to be Gaussian and we may write the following relations for the mean square length $\overline{r_m^2}$, the fully extended length R_m , the optical anisotropies $\delta\gamma_m$ (difference between principal polarisabilities for the whole free chain, which can be shown to have uniaxial optical symmetry about the r_m direction) at length r_m , and $\delta\Gamma_m$ at length R_m .

$$\left. \begin{aligned} \overline{r_m^2} &= K_1 n_m \ell_m^2 & (a) \\ R_m &= K_2 n_m \ell_m & (b) \\ \delta\gamma_m &= K_3 \frac{r_m^2}{n_m \ell_m^2} (\beta_\ell - \beta_m) & (c) \\ \delta\Gamma_m &= K_4 n_m (\beta_\ell - \beta_m) & (d) \end{aligned} \right\} \quad (4)$$

in which $(\beta_l - \beta_m)$ is the difference in principal optical polarisabilities for a single link, taken to be parallel and perpendicular to the link direction respectively and K_1, K_2, K_3 and K_4 are parameters describing the link-to-link correlation in direction. In general these will be functions of valance angle, the form of the potential energy distribution for rotation about each link and temperature. When $K_1 = K_2 = K_3 = K_4 = 1$ the expressions reduce to those for a chain of randomly-jointed links as considered in the classical theory.

It has been shown, Volkenstein and Ptitsyn (1955), Flory, Hovee and Ciferri (1959), that for a network of such chains equation (1) above is replaced by

$$t = \frac{\lambda^2}{A_0} = NkT \left(\frac{\overline{r_i^2}}{\overline{r_m^2}} \right) \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (5)$$

in which $\overline{r_i^2}$ is the mean square end-to-end distance for the N active chains per unit volume of the network in the isotropic, force-free, condition and $\overline{r_m^2}$ is as given in equation (4a) for the free chain. This modification to equation (1) makes an allowance for the intramolecular change in internal energy in the sample during deformation and also obviates the assumptions, made in the classical form of the theory, concerning the distribution of end-to-end vector lengths in the undeformed network. It should be noted

that the factor $\left(\frac{\overline{r_i^2}}{\overline{r_m^2}} \right)$ is temperature dependent; $\overline{r_i^2}$ can be taken to depend on the thermal expansion of the isotropic network whereas $\overline{r_m^2}$ will have a temperature dependence determined by the form of K_1^2 for the particular type of chain considered.

Following the method for calculating the birefringence of the network established by Treloar (1947), but using equations (5) rather than those for randomly-jointed chains, and further not making any assumptions concerning the value of the mean square length of the end-to-end vectors in the undeformed network, it is easy to show that the birefringence of the deformed network may be written

$$\Delta n = \frac{(\overline{n^2} + 2)^2}{\overline{n}} \cdot \frac{2\pi N}{45} K_3 K_1^2 \left(\frac{\overline{r_i^2}}{\overline{r_m^2}} \right) (\beta_l - \beta_m) \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (6)$$

From (5) and (6) the stress-optical coefficient therefore becomes

$$\frac{\Delta n}{t} = \frac{(\overline{n^2} + 2)^2}{\overline{n}} \frac{2}{45kT} K_3 K_1^2 (\beta_l - \beta_m) \quad (7)$$

which is identical with the expression given by Saunders (1957) in which the

factor $\left(\frac{\overline{r_i^2}}{\overline{r_m^2}} \right)$ in expressions (5) and (6) was not considered. The fundamental

importance of this factor has been stressed by Flory et al (1959); its inclusion in equation (5) represents the most rigorous method yet devised of allowing for internal energy effects in calculating the free energy of deformation of the network. It will be noted that it modifies the temperature dependence of stress in the deformed network from the near proportionality to absolute temperature suggested by equation (1). Equation (7) shows that by considering chains involving energetic effects the temperature dependence of the stress optical properties of the deformed network is also modified.

It is convenient to define a quantity A by the relation

$$A = \frac{\Delta n}{t} \frac{\bar{n}}{(\bar{n}^2 + 2)^2} \frac{45kT}{2\pi} \quad (8)$$

which includes only universal constants and properties of the network which are directly available to measurement. We may now re-write equation (7) in the form

$$A = K_3 K_1^2 (\beta_l - \beta_m) \quad (9)$$

in which we note that the right hand side contains only quantities describing the properties of a free chain. We can thus infer properties of the free chain from suitable measurements on the network. We further note that since $(\beta_l - \beta_m)$ is essentially independent of temperature, the observable temperature dependence of A is given by the temperature dependence of $K_3 K_1^2$, a combination of parameters describing the link-to-link correlation in the free chain.

Information obtained from a study of the temperature dependence of stress-optical properties should therefore be complementary to information obtained by Flory, Hove and Ciferri (1959), Ciferri, Hove and Flory (1961) from experiments on the temperature dependence of stress in deformed networks which gives information on K_1^2 via equations 4(a) and 5.

Experimental

Materials: Experiments were carried out on samples of three different types polyethylene. These were 1) a low density polyethylene designated DYNK obtained from Bakelite Limited, 2) a high density polyethylene designated HIFAX 1600 obtained from the Hercules Powder Co. Ltd., and 3) a high density polyethylene Hostalen G.S. obtained from Hoechst Chemicals Ltd.

The DYNK AND HIFAX polymers were pressed into sheets 1 to 2 mm thick, annealed, and subsequently cross-linked by exposure to electrons from a 2 m.e.V. linear accelerator. Irradiation was carried out at room temperature and samples were subjected to nominal doses of 20, 40, 80 and 160 m.rad. The results reported refer, therefore, to polymers free from such additives as antioxidants.

The Hostalen samples were prepared from polymer obtained in powder form. Up to ten parts by weight dicumyl peroxide per hundred parts of polymer was incorporated in the powdered polymer by a solution technique and cross-linked sheets between 1 and 2 mm thick were prepared by pressing for 8 mins. at 180°C. The sheets were subsequently annealed by heating in nitrogen.

Samples were prepared for the experiments in the form of dumbbells cut from the cross-linked sheets.

Determination of the stress-strain birefringence relations

The stress-strain-birefringence relations were determined for each sample at various deformations during one complete cycle of loading and unloading at constant known temperatures in the range 130°C to 240°C, i.e. at temperatures above the crystal melting point for the cross-linked materials. Simple tensile deformations were used throughout and the extension ratios were restricted to values less than those likely to induce crystallisation. The extension ratios rarely exceeded a value $\lambda = 2$.

The specimens were enclosed in a small furnace in which the temperature could be controlled to better than $\pm 1^\circ\text{C}$. The furnace was kept filled with oxygen-free nitrogen to minimise oxidative degradation. Extension ratios were derived from the separations of two ink marks on the specimen surface as determined using a cathetometer. The tensile loads were applied via a calibrated spring system. The birefringence was determined from measurement of optical path difference in the specimen using either a Babinet or Senarmont compensator.

In order to calculate the stress, strain and birefringence it was necessary to know the relevant dimensions of the samples in the unstrained state at the temperature of each experiment. The distance between the marks in the unstrained state was determined, in each case, by a suitable extrapolation of load-length measurements at the required temperature. The widths and the thicknesses of the specimens at each temperature were calculated from the widths and thicknesses measured at room temperature and the measured overall expansion of each sample between room temperature and the required temperature. This latter quantity was determined by observing the separation of two marks on a sample as a function of temperature using a cathetometer. In subsequent calculations it was assumed that the samples were isotropic, this assumption was substantially borne out by the results of subsidiary experiments on samples bearing marks in various orientations.

Samples were pre-conditioned by taking them through a complete cycle of loading and unloading at the required temperature prior to making measurements. During measurements the following sequence was used (i) deformation applied (ii) separation of marks observed (iii) path difference observed (iv) load observed. A rigorous time pattern of measurement was not imposed throughout but in each case sufficient time was allowed for the measured path difference and loads to have achieved substantially constant values.

Stresses and birefringence were calculated from the measured quantities on the assumption that the volume of the sample remained constant during deformation at constant temperature.

Determination of densities and refractive indices

It is necessary to know the density and the refractive index of each sample in the undeformed state at each temperature. The densities were obtained from the densities determined at room temperature, by hydrostatic weighing and flotation measurements, and the linear expansions determined as described above.

Refractive indices were calculated from the densities using the value of 0.3285 cc/gm for the specific refractivity of polyethylenes as given by Bianchi, Luetzel and Price (1958).

Results

In all cases the relation between the birefringence, Δn , and the tensile stress, t , was linear and reversible within the accuracy of the measurements. The measurements for the load-increasing part of the cycle were on the same line as those for the load decreasing part of the cycle. The slope of the line was taken as the stress-optical coefficient and designated $\frac{\Delta n}{t}$.

The relation between the stress, t , and extension-ratio, λ , was such that plots of

$$t \text{ vs } \left(\lambda^2 - \frac{1}{\lambda} \right)$$

were substantially linear and reversible. There were some systematic departures from linearity and reversibility, particularly in the most lightly cross-linked samples, but these were relatively small. It should be noted that invariably the amplitude of the imposed strain cycle increased as the degree of cross-linking decreased and vice versa for the amplitude of the stress cycle. No investigation of the departures from reversibility and linearity will therefore be undertaken. Values of

$$\left(\frac{t}{\lambda^2 - \frac{1}{\lambda}} \right)_{\lambda=1}$$

were taken from the graphs.

The values of A and $\frac{1}{M_c}$ were calculated from the measured quantities according to equations (8) and (1) respectively. The significance of A has already been explained. The values of $\frac{1}{M_c}$ will be used as a simple comparative index of degree of cross-linking for each sample. No attempt has been made to

obtain a more sophisticated value of $\frac{1}{M_c}$ by a more detailed analysis such as has been carried out for natural rubber, see Mullins and Thomas (1963) and attempted for polyethylene by Vickroy and Gent (1966).

The full results are given in Tables 1, 2 and 3.

There are two sets of results for Hifax 1600 given in parts (a) and (b) of the table respectively. These results all relate to samples of the same polymer but the conditions of irradiation varied between parts (a) and (b) and the nominal doses are therefore not comparable. This is borne out in figure 5 in which it will be seen that the 8OMR sample of part (b) corresponds more closely with the 4OMR sample than with 8OMR sample of part (a).

Dependence of stress-optical properties on degree of cross-linking

Inspection of Tables 1, 2 and 3 shows that for all three sets of samples the stress-optical coefficient, and hence the value of A, decreases as the degree of cross-linking increases. This is shown more clearly in Figures 1, 2 and 3 in which the values of A are plotted against $\frac{1}{M_c}$. Despite a pronounced scatter it is evident that A decreases substantially as $\frac{1}{M_c}$ increases for all samples. This result is in agreement with the earlier work of Saunders (1956, 1957), in which such an effect was first noted. It was suggested there that such behaviour could be attributed to short-chain non-Gaussian behaviour in the network, but quantitative agreement with non-Gaussian theory could only be obtained if the polyethylene chain was taken to be relatively stiff compared with, say, the rubber and gutta percha chains, so that 'short-chain' effects became more important.

In a recent publication Gent and Vickroy (1966) state that the decrease of A with increasing cross-linking does not occur in samples cross-linked in the molten state. Careful inspection shows, however, that this statement is not sustained by the results which they present. In fact, their results on samples cross-linked in the amorphous state do show the effect to a similar extent to the result reported here and previously. Their tentative suggestion as to the cause of the effect therefore loses its point.

From the earlier work of Saunders (1956, 1957) the quantity A_{∞} , obtained by extrapolating A to $\frac{1}{M_c} = 0$ will be taken to be characteristic of the Gaussian network.

Because of the scatter in Figures 1 and 2 the extrapolation is not easy and has been made by eye treating, as far as possible, the whole group of points as a family. In the case of Hostalen G.S., Figure 3, the scatter was similar in magnitude but in view of the larger number of points the best straight lines were fitted through the points according to the method of least squares.

The values for A_{∞} at the various temperatures are given for each of the

three polymers in Table 4. In the previous publication a value of $A_{\infty} = 7.5 \times 10^{-24} \text{cm}^3$ was suggested for irradiated samples of a low density polyethylene (Alkathene) at 130°C and a linear polymer, polymethylene, at 180°C. These values compare well with the values presented here for the irradiated DYNK, low density, and HIFAX 1600, high density, samples (see figure 6).

Dependence of stress-optical properties on temperature

The temperature dependence of A for the DYNK and HIFAX samples is shown in Figures 4 and 5. With the exception of the 20 m.rad. sample of HIFAX, the results show a systematic decrease of A with increasing temperature. The behaviour of the 20 m.rad. Hifax sample cannot be explained. It has been taken to be a gross experimental error and the offending results have been ignored in discussion. Unfortunately a repeat of the measurements on that sample was not possible. It is felt that the two offending points do not invalidate the general results.

Figure 6 shows the variation of A_{∞} with temperature for all three polymers.

Also incorporated are the earlier results, Saunders (1956, 1957) for a low density polyethylene and polymethylene and some results on a linear polyethylene quoted by Gent and Vickroy (1966). These last results are obtained on samples cross-linked in the amorphous state and it is interesting to note that the dependence on temperature agrees well with that shown by our Hostalen samples; it should be noted, however, that these values of A have not been extrapolated to zero cross-linking

$$\left(\frac{1}{M_c} = 0\right)$$

so that the agreement in magnitude of A must be regarded as of limited quantitative significance. Inspection of Gent and Vickroy's other results suggests that extrapolation would increase the values at all temperatures by about 10%.

Discussion

According to equation (9) the experimentally observable quantity A is given by

$$A = K_3 K_1^2 (\beta_l - \beta_m)$$

in which K_3 and K_1 are functions of the parameters describing link-to-link correlation in direction in the 'free' polymer chain and $(\beta_l - \beta_m)$ is the difference in principal optical polarisabilities for a single link in that chain.

Previous workers have compared the values of A obtained experimentally with values of $(\beta_l - \beta_m)$ calculated for monomeric units of known structure

using tables of bond polarisabilities given in the literature. The calculation involves the assumption that bond polarisabilities may be added tensorially to yield a value of $(\beta_l - \beta_m)$, the optical anisotropy of the monomeric unit. Since for a chain of randomly joined links $K_3 K_1^2 = 1$. A has been regarded as the optical anisotropy of 'the equivalent random link' and the quantity

$$\frac{A}{(\beta_l - \beta_m)}$$

as the number of monomers per equivalent random link, a measure of chain 'stiffness' or 'flexibility'.

The best value to be assigned to $(\beta_l - \beta_m)$ has been a matter of some discussion. Denbigh (1940) published a table of values of bond polarisabilities, based on measurements made in the gaseous phase, which are the usual basis for calculation of $(\beta_l - \beta_m)$. However, there are grounds for criticism of Denbigh's values and a good general discussion has been given by Volkenstein (1963, p.391). In particular, doubt has been cast on the large anisotropy attributed by Denbigh to the C - C single bond. Bunn and Daubeny (1954), as a result of measurements on paraffin single crystals, suggested a much reduced value for this quantity and discussion has ensued on which value was the most appropriate for use in work on polymers in the elastomeric state. Saunders (1957) argued in favour of the lower value whilst more recently Volkenstein (1963) and other workers have favoured the higher values. The two different values lead to significantly different values for $(\beta_l - \beta_m)$ for the $-\text{CH}_2-$ unit. Denbigh's values give $(\beta_l - \beta_m) = 14.4 \times 10^{-25} \text{cm}^3$ whilst Bunn and Daubeny's value gives $(\beta_l - \beta_m) = 3.1 \times 10^{-25} \text{cm}^3$. In both cases the same values of bond polarisabilities of the C-H bond are adopted. It would, therefore, be desirable to have an independent method of estimating $(\beta_l - \beta_m)$ from measurements on polymers in the rubber-like state. Such an estimate can, in the case of polyethylenes, be obtained in principle from the results presented here.

In order to achieve this it is necessary to have information on the form of $K_3 K_1^2$ in equation (9). Adopting the rotational isomeric model for the polyethylene chain and taking the angles to be tetrahedral (see Volkenstein (1963) for a detailed discussion) one can take $K_1 = \sqrt{2(2\epsilon+1)}/3$ in which $\epsilon = \exp U/RT$, U being the energy difference between gauche and trans conformations of successive links of the chain. This expression has been obtained by many workers and is well authenticated. The form of K_3 is, however, in some doubt. Kubo (1949) first obtained the relation

$$K_3 = \frac{3}{8} \frac{10\epsilon^2 + 14\epsilon - 9}{(2\epsilon + 1)^2}$$

whilst a recalculation by Sack (1956), according to Kubo's method, yielded

$$K_3 = \frac{3}{8} \frac{8\epsilon^2 + 8\epsilon - 1}{(2\epsilon + 1)^2}$$

Volkenstein (1963) p. 413 quotes results of calculations by Gotlib which may be reduced to the form $K_3 = \frac{3}{8} \frac{12\epsilon^2 + 12\epsilon + 1}{(2\epsilon + 1)^2}$ for our particular model.

There is thus some doubt as to the best form for the quantity $K_3 K_1^2$ in equation (9). For convenience we will write $D = K_1^2 K_3$ and further

$$D_K = \frac{10\epsilon^2 + 14\epsilon - 1}{4(2\epsilon + 1)}, \quad D_S = \frac{8\epsilon^2 + 8\epsilon - 1}{4(2\epsilon + 1)} \quad \text{and} \quad D_V = \frac{12\epsilon^2 + 12\epsilon + 1}{4(2\epsilon + 1)}$$

which are the expressions for D according to the results of Kubo, Sack and Volkenstein respectively.

We may now write:

$$\log_{10} 10^{24} A = \log_{10} D + \log_{10} 10^{24} (\beta_L - \beta_m)$$

and since $(\beta_L - \beta_m)$ is essentially independent of temperature, the temperature dependence of A occurs in the terms involving D which may take one of the forms quoted above.

In figure 7 the experimental values of $\log_{10} 10^{24} A$ are plotted versus $\frac{1}{T}$ and compared with the calculated values of D for the three forms quoted for each of three chosen values of U, the gauche - trans energy difference. The values of U chosen are 2,300; 1,150 and 540 cal/mole respectively. The large value corresponds approximately with that suggested by Saunders (1957) from stress-optical work at a single temperature. The small value corresponds to that suggested by Flory, Hove and Cifferi (1959) from stress-temperature measurements. The intermediate value is that best fitting the results here quoted. It can be seen in Figure 7 that the calculated relations between $\log_{10} D$ and $\frac{1}{T}$ are sensibly linear over the range covered, in all cases. The three different forms of D give, for each value of U, a set of essentially parallel lines but the slope of that set varies with U. It will be seen also that the experimental results may be taken to be on lines sensibly parallel to the lines for D with U = 1,150 cal/mole. They cannot be nearly so well represented by lines parallel to those for D with U = 2,300 or 540 cal/mole. It is suggested therefore that the approximate value for the trans - gauche energy difference is ca 1,150 cal/mole.

The vertical separations between the lines through the experimental points and the parallel calculated lines for $\log_{10} D$ i.e. those for U = 1,150 cal/mole, gives therefore the value $\log_{10} 10^{24} (\beta_L - \beta_m)$ in each case, and hence the optical anisotropy for a single monomeric unit. Since in Figure 7 the experimental points do not all lie on the same line there will be a different value of $(\beta_L - \beta_m)$ for each polymer. There will also be different values according to which of the three expressions for D is used. The full set of nine values of $(\beta_L - \beta_m)$ is given in Table 5. These values range from $10 \times 10^{-25} \text{cm}^3$ to $19.5 \times 10^{-25} \text{cm}^3$ and are to be compared with the values $14.4 \times 10^{-25} \text{cm}^3$ according to Denbigh's values of bond polarisabilities and $3.1 \times 10^{-25} \text{cm}^3$ according to the values of Bunn and Daubeny.

It is unfortunate that the theoretical form of D is not better established but it may be taken, at least from the results on the two linear polyethylenes, that Denbigh's values, involving the high C-C anisotropy, are to be preferred to those of Bunn and Daubeny for polyethylene in the elastomeric state.

Conclusions

We may conclude therefore that accepting any of the quoted forms for D gives a value for U considerably greater than that suggested by Flory and co-workers from stress-temperature measurements. The method of obtaining U described here has the merit that one does not need so rigorously to approach the equilibrium state during measurement as in the stress-temperature measurements since it is well established, and was confirmed in supplementary measurements during this work, that the value for $\frac{\Delta n}{t}$ remains constant during the approach to equilibrium and also during the early stages of degradative breakdown of the sample. This latter effect is important in measurements which have to be made at temperatures above the melting point.

Neither this work nor the stress-temperature work takes account of 'Mooney-type' deviations from the behaviour predicted by simple theory. Such deviations undoubtedly exist in cross-linked polyethenes as reported by Gent and Vickroy (1966) and as found by us in subsidiary experiments not reported here. It is found, however, that $\frac{\Delta n}{t}$ is sensibly independent of extension ratio and one must conclude therefore that both the Δn vs λ and t vs λ relations are similarly affected. It is tempting therefore to infer that the results based on stress-optical measurements will be less affected by these departures than those based on direct stress-strain measurements.

The uncertainty in the form of D detracts from the analysis of the stress-optical measurements but it should be noted that all the forms of D give essentially similar values for U. In contrast they give a range of values for $(\beta_l - \beta_m)$ which in general favour the bond polarisability values of Denbigh rather than Bunn and Daubeny. It is interesting to note that whatever the form of D the values of $(\beta_l - \beta_m)$ for the linear chains (Hostalen and Hifax) are greater than that for the branched chain (DYNK) although there are significant differences between the linear polymers.

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TABLE 1

Stress-optical properties of DYNK low density polyethylene cross-linked by electron irradiation

Nominal sample dose m.rad.	$10^4 \frac{\Delta n}{t}$ cm ² /kg	$\left[\frac{t}{\lambda^2 - \frac{1}{\lambda}} \right]_{\lambda=1}$ kg/cm ²	ρ gm/cm ³	$\frac{\bar{n}}{(\bar{n}^2+2)^2}$	$10^{24}A$ cm ⁵	$\frac{10^4}{M_c}$ gm ⁻¹
<u>130°C</u>						
20	2.01	1.45	0.856	0.0846	6.90	0.50
40	1.89	3.75	0.849	0.0849	6.51	1.29
80	1.90	7.00	0.846	0.0850	6.55	2.42
160	1.69	14.10	0.845	0.0851	5.83	4.89
<u>145°C</u>						
20	1.72	1.70	0.853*	0.0847 ⁵	6.14	0.56
40	1.77	3.86	0.840	0.0853	6.35	1.29
80	1.65	7.45	0.842	0.0852	5.92	2.66
160	1.47	15.50	0.843	0.0851	5.25 ⁵	5.18
<u>160°C</u>						
20	1.56	2.64	0.820	0.0861	5.86	0.88
40	1.61	3.80	0.825	0.0859	6.03	1.25
80	1.59	7.20	0.829	0.0857	5.94	2.37
160	1.35	15.80	0.838	0.0853 ⁵	5.02	5.15
<u>190°C</u>						
20	1.42	2.58	0.786	0.0874	5.79	0.84
40	1.35	3.50	0.797	0.0870	5.47	1.12
80	1.29	7.33	0.813	0.0863	5.19	2.30
160	1.11	16.40	0.832	0.0856	4.43	5.02
<u>220°C</u>						
20	1.30	3.00	0.753	0.0887	5.72	0.95
40	1.27	3.95	0.776	0.0878	5.49	1.22
80	(1.04)* (.95)	8.14	0.793	0.0871	(4.50)* (4.11)	2.45
160	.97	17.10	0.824	0.0859	4.13	4.97

* Difficult to assess

TABLE 2(a)

Stress-optical properties of HIFAX 1600 high density
polyethylene cross-linked by electron irradiation

Nominal sample dose m.rad.	$10^4 \frac{\Delta n}{t}$ cm ² /kg	$\left[\frac{t}{\lambda^2 - \frac{1}{\lambda}} \right]_{\lambda=1}$ kg/cm ²	ρ gm/cm ³	$\frac{\bar{n}}{(\bar{n}^2+2)^2}$	$10^{24}A$ cm ³	$\frac{10^4}{M_c}$ gm ⁻¹
<u>130°C</u>						
20	2.16	1.75	0.860	0.0845	7.40 ⁶	0.59 ⁸
40	2.14	4.20	0.843	0.0849	7.37 ³	1.45 ⁰
80	2.14	7.15	0.846	0.0850	7.38 ²	2.47 ⁰
160	1.86	14.50	0.842	0.0852	6.43 ²	5.05 ⁴
<u>145°C</u>						
20	2.16	0.85	0.832	0.0856	7.78 ²	0.28 ⁹
40	2.06	3.95	0.835	0.0855	7.41 ²	1.33 ⁸
80	1.96	6.60	0.840	0.0853	7.03 ⁷	2.22 ⁰
160	1.61	13.00	0.844	0.0851	5.76 ⁶	4.35 ⁰
<u>160°C</u>						
20	1.88	1.55	0.818	0.0861	7.05 ⁹	.51 ⁷
40	1.84	4.35	0.810	0.0864	6.93 ²	1.46 ⁵
80	1.68	8.25	0.833	0.0850	6.21 ⁷	2.70
160	1.35	16.00	0.828	0.0854	5.02 ⁷	5.28
<u>190°C</u>						
20*	2.16	1.31	0.771	0.0880	8.86 ²	.43 ⁴
40	1.62	4.25	0.778	0.0877	6.62 ⁴	1.39 ³
80	1.46	7.40	0.805	0.0867	5.90 ²	2.34 ²
160	1.12	19.00	0.809	0.0865	4.51 ²	6.00
<u>220°C</u>						
20*	2.00	1.10	0.723	0.0899	8.92 ⁷	.46 ⁴
40	1.31	3.60	0.742	0.0891	5.79 ⁴	1.16
80	1.15	10.50	0.779	0.0877	5.00 ⁵	3.24
160	0.45	20.80	0.796	0.0870	4.10 ⁴	6.24

*Difficulties in measurement experienced - also non-typical points.

TABLE 2(b)

Stress-optical properties of HIFAX 1600 high density
polyethylene cross-linked by electron irradiation

Nominal sample dose 80 m.rad.

Temp. °C	T °K	$10^4 \frac{\Delta n}{t}$ cm ² /kg	ρ gm/cm ³	$\frac{\bar{n}}{(\bar{n}^2+2)^2}$	$10^4 T \frac{\Delta n}{t}$	$10^{24} A$ cm ³
140	413	2.16	.864	0.0843	8.92	7.57
150	423	2.00	.858	0.0846	8.46	7.21
160	433	1.89	.850	0.0849	8.18	6.99
170	443	1.73	.844	0.0851	7.66	6.57
180	453	1.61	.837	0.0854	7.29	6.27
190	463	1.54	.832	0.0856	7.13	6.14
200	473	1.53	.825	0.0858	7.24	6.25
210	483	1.45	.819	0.0861	7.00	6.07
220	493	1.34	.812	0.0864	6.61	5.75
230	503	1.32	.806	0.0866	6.64	5.79
240	513	1.20	.800	0.0868	6.16	5.39
250	523	1.12	.794	0.0871	5.86	5.14

TABLE 3

Stress-optical properties of Hostalen G.S. high density polyethylene cross-linked by curing with dicumyl peroxide

Nominal parts per hundred dicup.	$10^4 \frac{\Delta n}{t}$ cm ² /kg	$\left[\frac{t}{\lambda^2 - 1} \right]_{\lambda=1}$	ρ gm/cm ³	$\frac{\bar{n}}{(\bar{n}^2+2)^2}$	$10^{24}A$ cm ³	$\frac{10^4}{M_c}$ gm ⁻¹
<u>156°C</u>						
10	2.19	9.60	0.791	0.0872	8.19	3.34
5	2.37	4.83	0.792	0.0872	7.90	1.68
5	2.29	4.79	0.800	0.0869	8.37	1.65
5	2.12	4.52	0.800	0.0869	8.43	1.56
3	2.22	2.73	0.768	0.0881	8.19	0.98
3	2.13	2.39	0.783	0.0876	8.12	0.84
3	2.37	2.23	0.768	0.0881	8.74	0.80
<u>182°C</u>						
10	1.79	12.66	0.796	0.0870	7.15	4.12
10	1.81	11.72	0.786	0.0874	7.27	3.87
7.5	1.54	6.28	0.792	0.0872	6.16	2.06
7.5	1.69	6.01	0.792	0.0872	6.77	1.97
5	1.95	1.95	0.792	0.0872	7.79	0.64
3	2.00	0.93	0.784	0.0875	8.03	0.31
3	1.82	0.87	0.778	0.0877	7.32	0.29
<u>193°C</u>						
10	1.56	12.31	0.782	0.0876	6.40	3.99
10	1.40	11.54	0.791	0.0872	5.75	3.69
10	1.46	11.50	0.782	0.0876	6.05	3.73
7.5	1.48	8.41	0.790	0.0873	6.06	2.70
7.5	1.50	8.18	0.790	0.0873	6.14	2.62
5	1.52	4.48	0.779	0.0877	6.27	1.46
5	1.60	4.38	0.766	0.0882	6.61	1.45
3	1.72	2.08	0.790	0.0873	7.05	0.67
3	1.73	1.76	0.790	0.0873	7.07	0.58

TABLE 3 (Contd.)

Nominal part per hundred dicup.	$10^4 \frac{\Delta n}{t}$ cm ² /kg	$\left[\frac{t}{\lambda - \frac{1}{\lambda}} \right]_{\lambda=1}$	ρ gm/cm ³	$\frac{\bar{n}}{(\bar{n}^2+2)^2}$	$10^{24}A$ cm ³	$\frac{10^4}{M_c}$ gm ⁻¹
<u>220°C</u>						
10	1.44	10.66	0.772	0.0880	6.30	3.30
10	1.49	9.32	0.794	0.0889	6.57	2.98
10	1.51	8.84	0.749	0.0889	6.65	2.82
5	1.42	5.35	0.729	0.0896	6.32	1.76
7.5	1.50	2.84	0.742	0.0891	6.62	0.92
7.5	1.53	2.84	0.744	0.0891	6.77	0.91
7.5	1.52	2.77	0.742	0.0891	6.72	0.89
7.5	1.51	2.67	0.744	0.0891	6.70	0.86
5	1.56	1.50	0.734	0.0894	6.94	0.49
<u>238°C</u>						
10	1.31	11.56	0.7331	0.0895	6.09	3.61
10	1.27	11.49	0.7331	0.0895	5.93	3.58
3	1.39	10.89	0.7337	0.0894	6.45	3.39
3	1.31	10.71	0.7337	0.0894	6.07	3.34
10	1.35	10.55	0.7518	0.0887	6.22	3.21
3	1.31	9.84	0.7262	0.0898	6.12	3.10
5	1.44	6.27	0.7193	0.0900	6.76	1.99
7.5	1.36	3.68	0.7330	0.0895	6.34	1.15
7.5	1.40	3.40	0.7330	0.0895	6.52	1.06
7.5	1.44	2.61	0.7371	0.0893	6.69	0.81
5	1.28	1.38	0.7282	0.0897	6.29	0.43
5	1.57	1.32	0.7282	0.0897	7.30	0.41

TABLE 4

The temperature dependence of A_{∞} for all three polymers

T °K	$\frac{10^3}{T}$	HIFAX 1600		DYNK		T °K	$\frac{10^3}{T}$	HOSTALEN GS	
		$10^{24}A_{\infty}$ cm ³	$\log_{10}10^{24}A_{\infty}$	$10^{24}A_{\infty}$ cm ³	$\log_{10}10^{24}A_{\infty}$			$10^{24}A_{\infty}$ cm ³	$\log_{10}10^{24}A_{\infty}$
403	2.48	7.9	.8976	7.1	0.8513	429	2.33x	8.4	.9243
418	2.39	7.9	.8976	6.6	0.8195	455	2.20	8.2	.9138
433	2.31	7.45	.8722	6.3	0.7993	466	2.16	7.2 ⁵	.8603
463	2.16	7.0	.8451	5.9	0.7709	493	2.03	6.95	.8420
493	2.03	6.2	.7924	5.65	0.7521	511	1.96	6.9	.8389

TABLE 5

The optical anisotropy ($\beta_l - \beta_m$) for a single

- CH₂ - monomeric unit computed from figure 7.

Polymer	$10^{25}(\beta_l - \beta_m)$ cm ³		
	from Ds	from Dk	from Dv
DYNK	15.1	11.9	10.0
HIFAX 1600	17.4	13.3	11.5
HOSTALEN GS	19.5	15.1	12.9

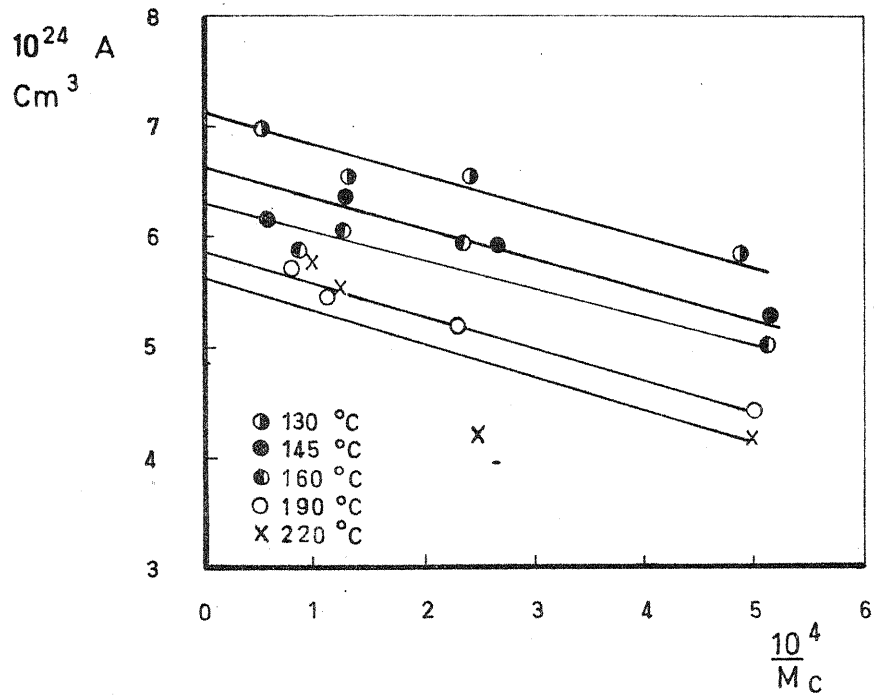


FIG. 1 THE DEPENDENCE OF A ON DEGREE OF CROSS-LINKING FOR DYNK AT VARIOUS TEMPERATURES

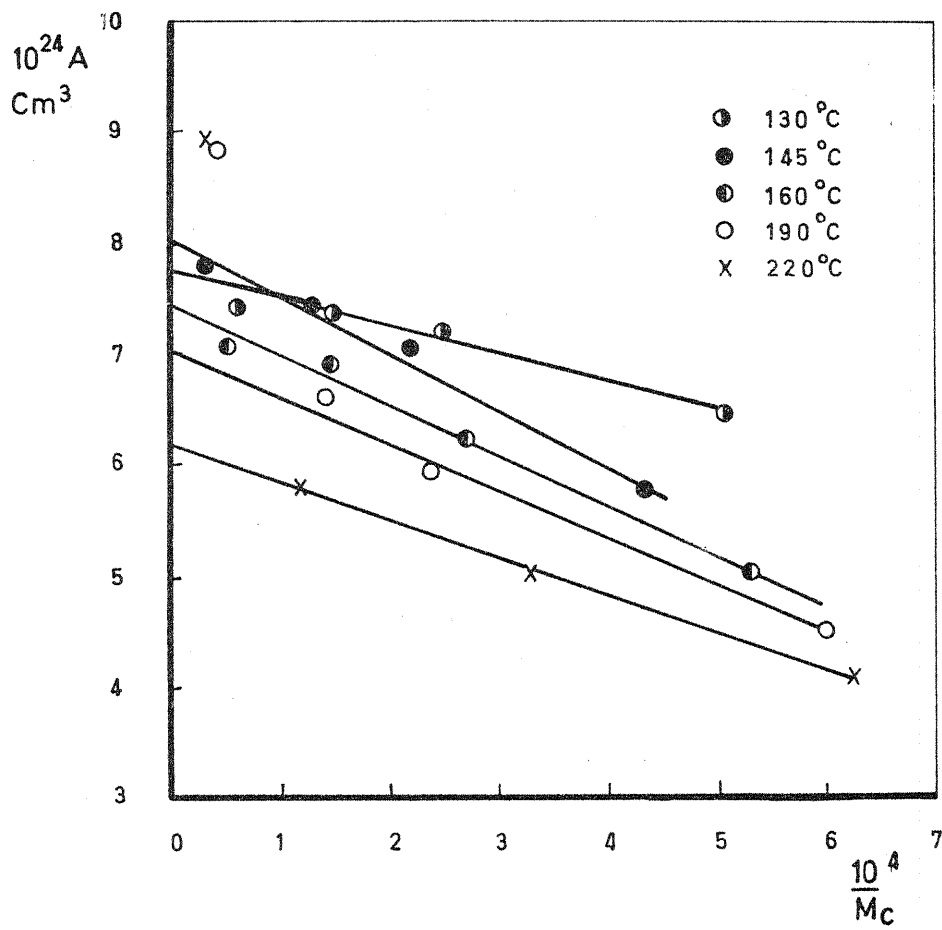


FIG. 2 THE DEPENDENCE OF A ON DEGREE OF CROSS-LINKING FOR HIFAX 1600 AT VARIOUS TEMPERATURES

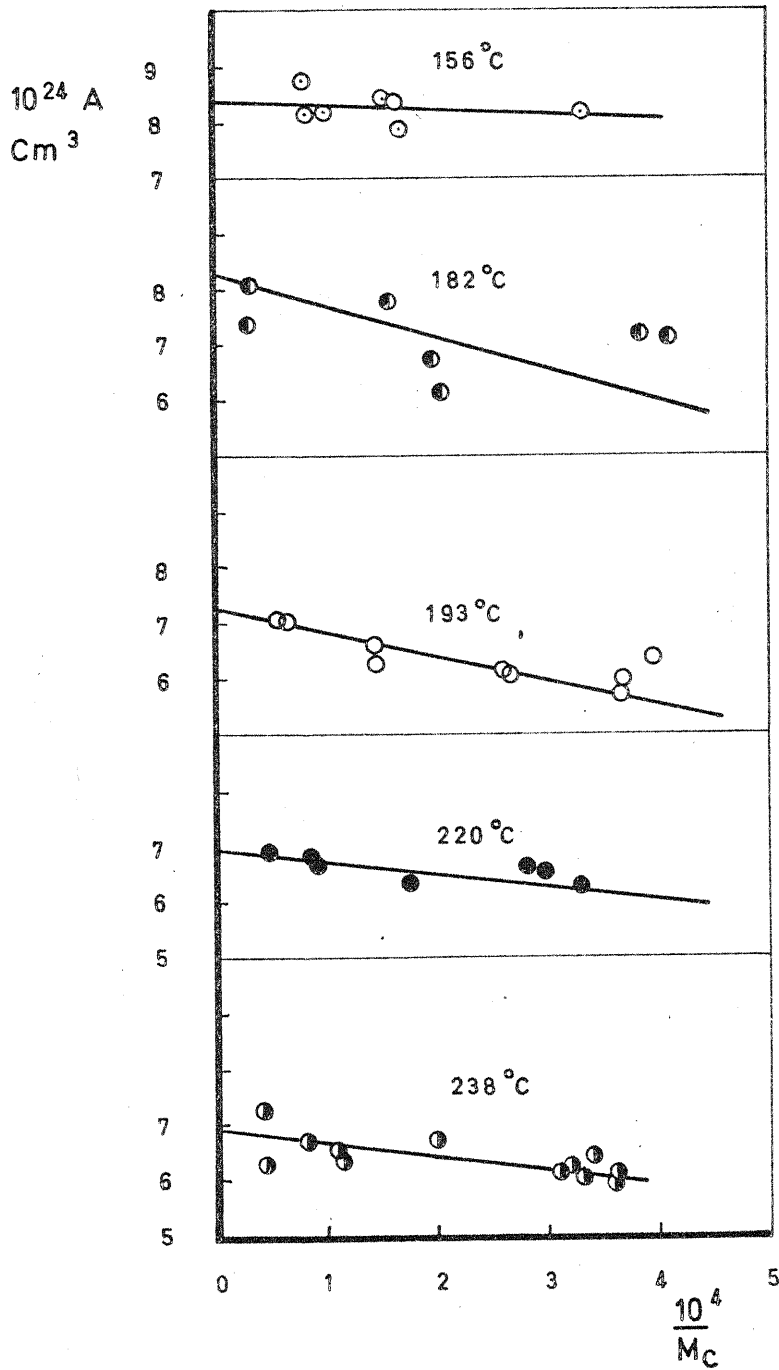


FIG. 3 THE DEPENDENCE OF A ON DEGREE OF CROSS-LINKING FOR HOSTALEN G.S. AT VARIOUS TEMPERATURES

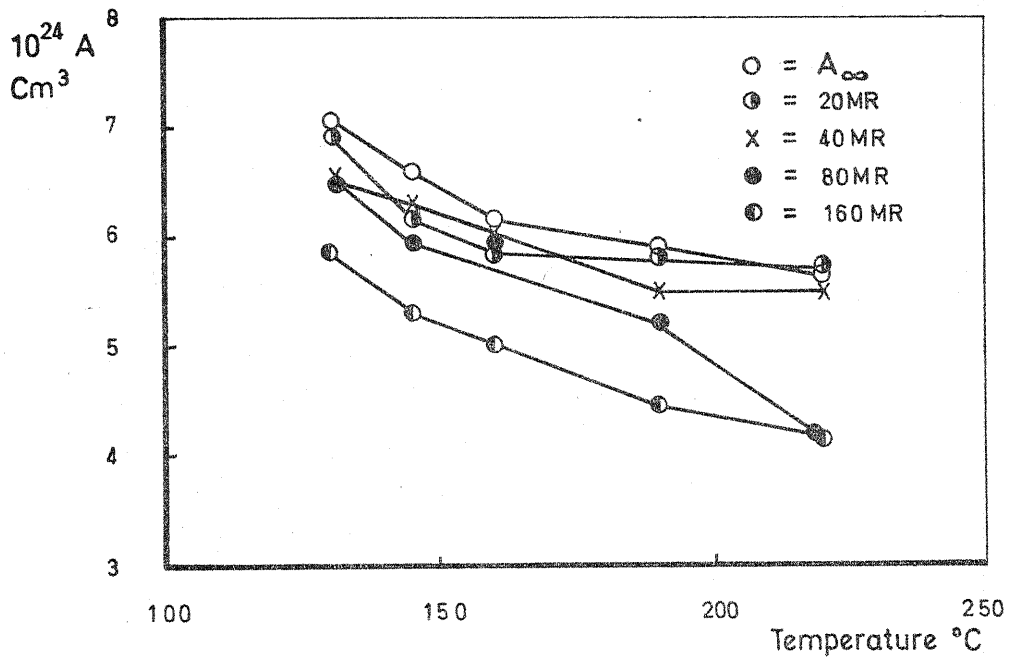


FIG. 4 THE TEMPERATURE DEPENDENCE OF A AND A_{∞} FOR DYNK

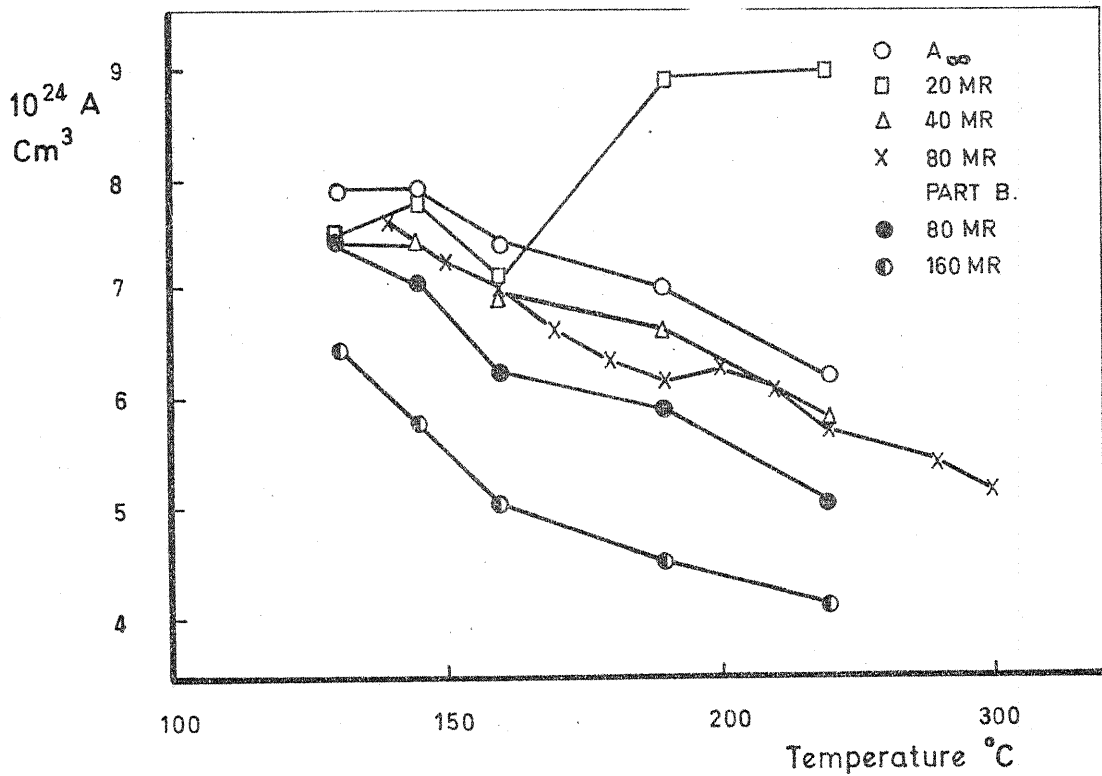


FIG. 5 THE TEMPERATURE DEPENDENCE OF A AND A_{∞} FOR HIFAX 1600

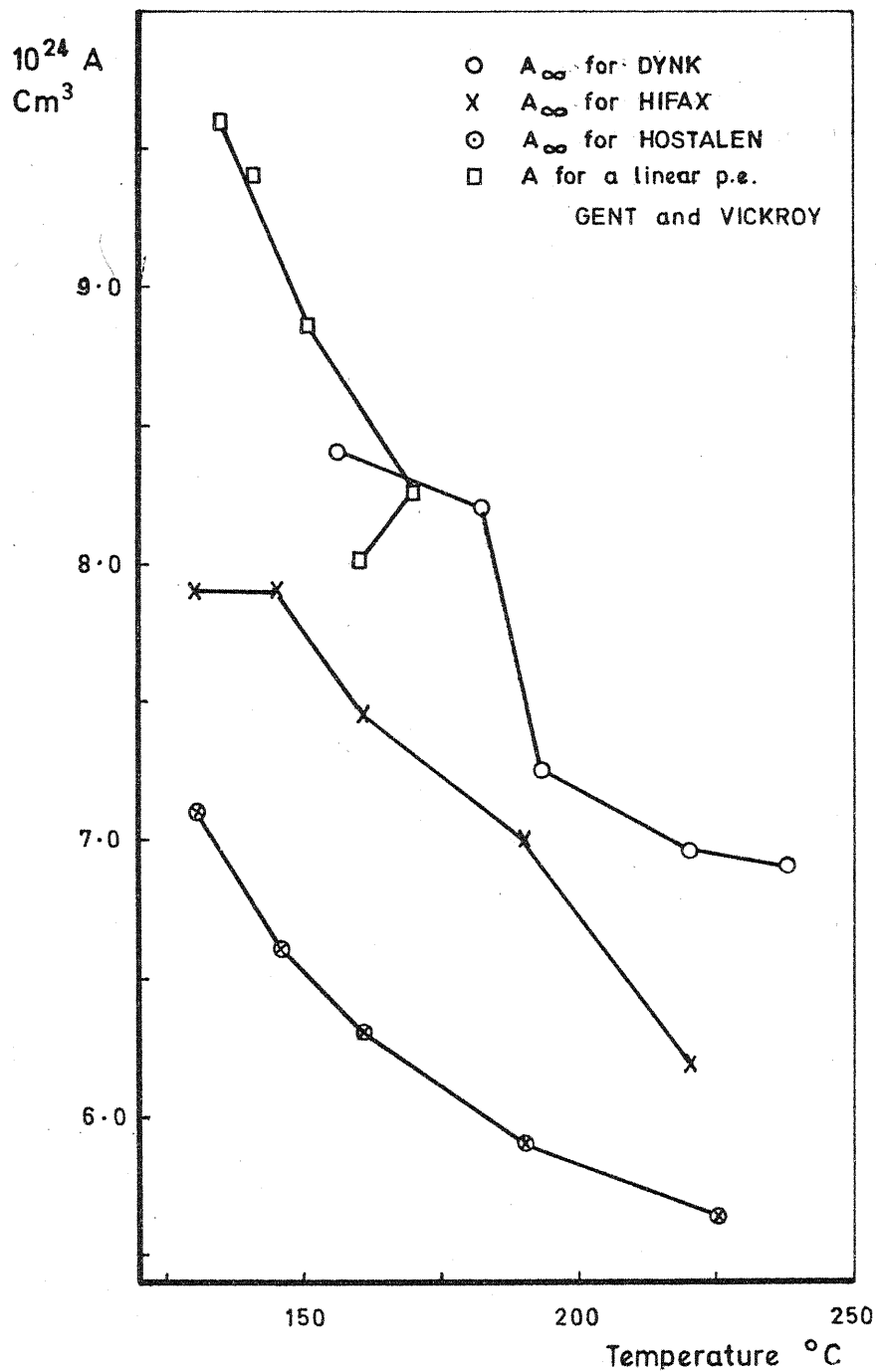


FIG. 6 THE TEMPERATURE DEPENDENCE OF A_{∞} FOR THE DYNK, HIFAX 1600 AND HOSTALEN G. S. ALSO INCLUDED ARE THE RESULTS OF GENT AND VICKROY (1966) ON A LINEAR POLYETHYLENE CROSS-LINKED IN THE AMORPHOUS STATE AND THE RESULTS FOR ALKATHENE, POINT 1, AND POLYMETHYLENE POINT 2 FROM SAUNDERS (1956)

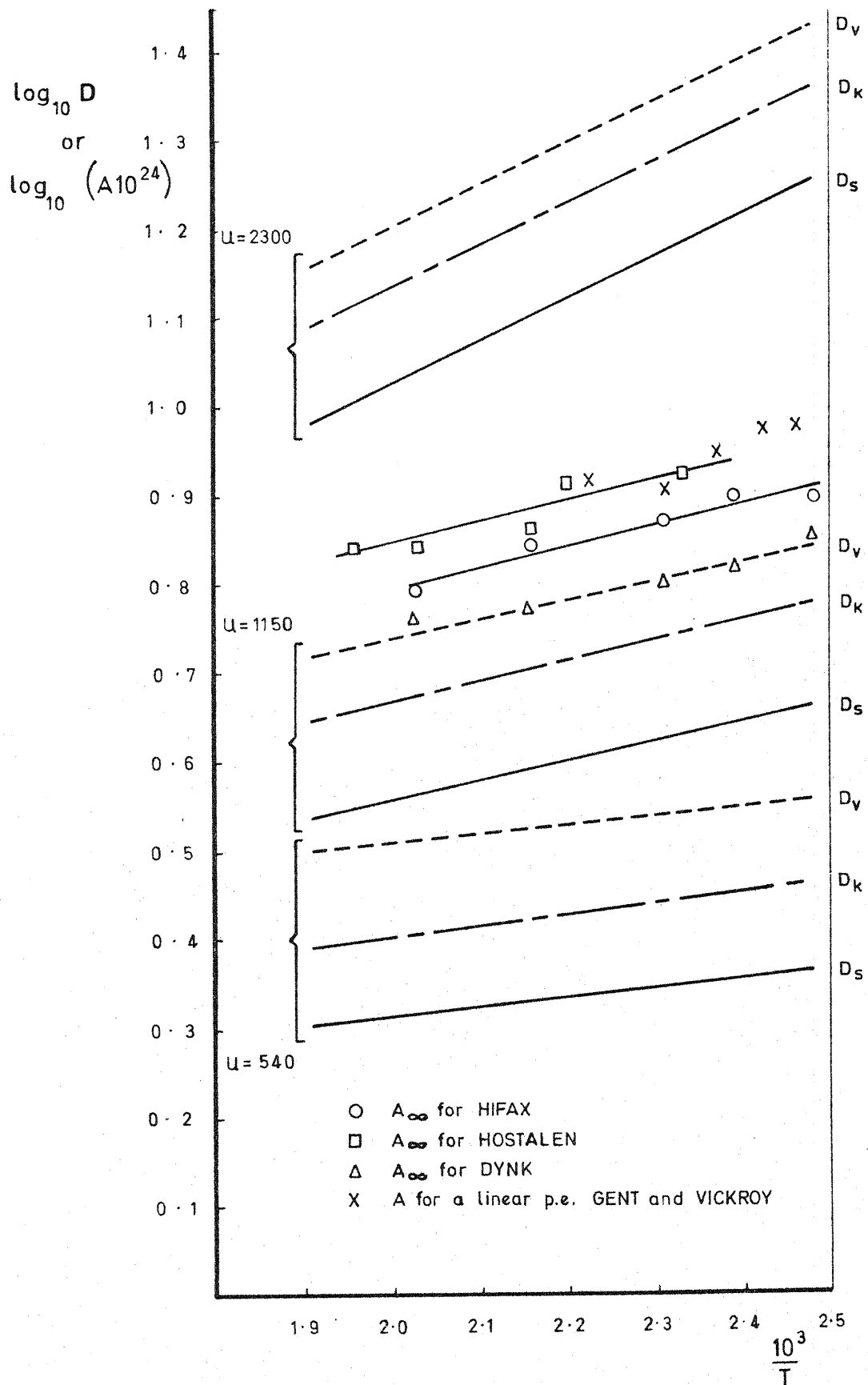


FIG. 7 EXPERIMENTAL RESULTS COMPARED WITH THE CALCULATED VALUES FOR $\log_{10} D$ ACCORDING TO THE EXPRESSIONS OF SACK, VOLKENSTEIN, KUBO.