# Analysis of the rubber elasticity of polyethylene networks based on the slip link model of S. F. Edwards *et al.**

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Force–extension data, obtained at 140°C on polyethylene monofilaments, electron-irradiated with doses from 0.7 to 6.0 Mrad, are interpreted according to a recent model of rubber elasticity proposed by Edwards and Vilgis. In this model, the free energy of single chains between the crosslinks, $N_c$, is described by the usual statistical theory, whereas the reduction of entropy due to entanglements with neighbouring chains is described by a number, $N_s$, of slip links, which are free to slide along the arc length of the chain between crosslinks. The degree of slip link freedom is measured by a parameter $\eta$. Finally, the extra constraints introduced by the entanglements limit the extensibility of the chains long before the single chain limit is reached. In the Edwards' model this introduces a further parameter $\alpha$. Using these four parameters ($N_c$, $N_s$, $\eta$, $\alpha$), good fits are obtained to all sets of data. The parameter $\alpha$ is shown to describe particularly well the increase in the reduced stress at high deformation, observed for the more highly crosslinked samples. Both $N_c$ and $N_s$ increase monotonically with dose, indicating that each crosslink renders effective a certain number of topological entanglements. The parameter $\eta$ is essentially constant at about 1.1, a higher value than that found by other workers. The theoretical value of 0.2343 is shown to be not applicable for these samples. The effect of strain rate and orientation history on the samples is also described. Our data suggest that slip links are dynamic, and can behave as crosslinks, at higher strain rate. The effect of solid state drawing on an irradiated polymer is to alter permanently the structure of the network; increasing the number of effective crosslinks, at higher dose, and removing a fraction of non-permanent entanglements, at lower dose.

**(Keywords: polyethylene; radiation crosslinking; rubber elasticity; slip links)**

## INTRODUCTION

The general features of the rubber-like elastic behaviour of electron beam crosslinked polyethylene, apparent above the melt, have been described in a previous publication[1]. An attempt was made to relate the force–extension data to the network chain density using the well-known Mooney–Rivlin approach. Although this interpretation assisted a qualitative description of the chain entanglement contribution, and the effect of strain rate, it is known to be suspect, being entirely phenomenological. A far more satisfactory approach is supplied by the recently developed theory of Edwards and coworkers[2,3], which attacks directly the problem of chain entanglements by the slip link model, derived from the theoretical concept of reptation. In this paper, we examine the applicability of this theory to the elasticity of radiation crosslinked polyethylene.

## THEORY

The classical statistical theory of rubber elasticity[4] predicts the free energy, $F$, of single chains between crosslinks, $N_c$, to be proportional to the sum of squares of the principal extension ratios (equation (1)).

$$\frac{F}{kT} = \tfrac{1}{2}N_c \sum_{i=1}^{3} \lambda_i^2 \qquad (1)$$

Chain entanglements, not accounted for in the classical theory, provide topological constraints which are modelled by considering a number $N_s$ of slip links[2], which make a sliding contact between polymer chains, producing additional elastic free energy. The degree of slip link freedom, compared with that of a crosslink, is given by a parameter $\eta$, and the expression for the free energy is modified to equation (2).

$$\frac{F}{kT} = \tfrac{1}{2}N_c \Sigma \lambda_i^2 + \tfrac{1}{2}N_s \sum \left[ \frac{(1+\eta)\lambda_i^2}{1+\eta\lambda_i^2} + \ln(1+\eta\lambda_i^2) \right] \qquad (2)$$

Ball *et al.*[2] have suggested a theoretical value of 0.2343 for $\eta$, consistent with minimizing $F$. Thirion and Weil[5], in their study of chemically crosslinked rubbers, determined $\eta$ experimentally, and found a best fit for $\eta$ equal to 0.40. Furthermore, their work showed $\eta$ to be independent of $N_c$ and molecular structure.

The additional problem of finite network extensibility due to the constraints imposed by the topological entanglements has recently been considered by Edwards and Vilgis[3]. The number of entanglements determine the step length of the reptation tube primitive path. The length of a polymer chain within the tube is far greater than the length of the primitive path, and so a large proportion of the chain is 'slack'. The chain is considered to be terminated by a crosslink at each end, therefore no reptation is possible. As the network is deformed, the main consideration is the amount of slack chain between entanglements, which is gradually reduced until,

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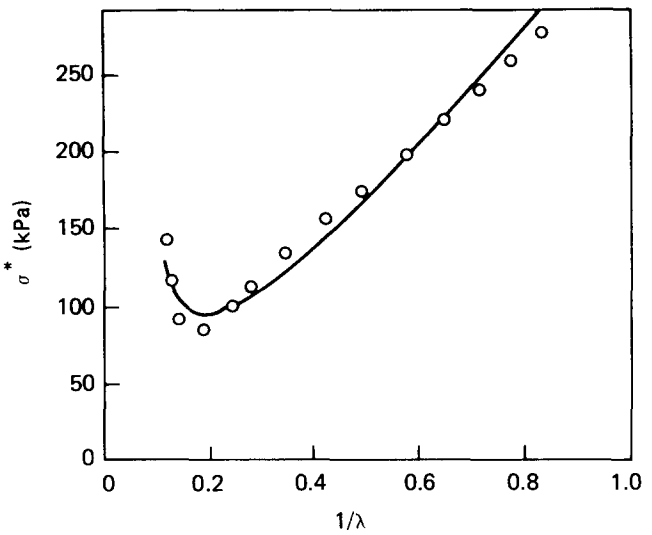


**Figure 1** Reduced stress $\sigma^*$ ($\sigma/\lambda-\lambda^{-2}$) *versus* $1/\lambda$ for 6.0 Mrad sample, drawn, at low strain rate (DL). The solid line is the theoretical fit with parameters $N_c kT = 42.3$ kPa, $N_s kT = 1.24$ MPa, $\eta = 1.08$, $\alpha = 0.07$

eventually, the chain is taut. This process limits the extensibility of the chains long before the single chain limit is reached. These concepts introduce an additional parameter $\alpha$, equal to $l/a$, where $l$ is the Kuhn step length, and $a$ the step length of the primitive path. The full expression for the free energy is now given[3] by equation (3).

$$\frac{F}{kT} = \tfrac{1}{2}N_c\left[\frac{\Sigma(1-\alpha^2)\lambda_i^2}{1-\alpha^2\Sigma\lambda_i^2} + \ln(1-\alpha^2\Sigma\lambda_i^2)\right] + \tfrac{1}{2}N_s\left[\sum\left\{\frac{\lambda_i^2(1+\eta)(1-\alpha^2)}{(1+\eta\lambda_i^2)(1-\alpha^2\Sigma\lambda_i^2)} + \ln(1+\eta\lambda_i^2)\right\} + \ln(1-\alpha^2\Sigma\lambda_i^2)\right] \quad (3)$$

It is readily seen that by putting $\alpha$ equal to zero (no inextensibility), equation (3) reduces to equation (2). Furthermore, with $\eta$ also equal to zero, implying slip links as rigid as crosslinks, we obtain the classical result (equation (1)) for a phantom network.

## EXPERIMENTAL

The sample preparation and the techniques involved in the elasticity measurements have been described previously[1,6]. The essential details are that isotropic polyethylene monofilaments were crosslinked with electron beam irradiation, and the elasticity behaviour examined above the melt, at two different nominal strain rates. This procedure was also performed with samples oriented by tensile drawing, after crosslinking, to a draw ratio of 12:1. In this case, the samples were carefully heated and allowed to revert to the isotropic state before the stress–strain experiments were performed. In the following discussion, the two sets of samples are designated spun (S) and drawn (D). The two nominal strain rates of $9\times10^{-3}$ and $9\times10^{-2}$ $s^{-1}$ are referred to as low (L) and high (H).

For uniaxial extension, we apply the usual incompressibility condition, $\lambda_1 = \lambda$, $\lambda_2 = \lambda_3 = \lambda^{1/2}$, and for each sample, the $\sigma-\lambda$ data were initially fitted to equation (2), using the expression given by Thirion and Weil[5]:

$$\frac{\sigma}{\lambda-\lambda^{-2}} = kT[N_c + N_s H(\eta,\lambda)] \quad (4)$$

where $\sigma$ is the force per unit unstrained area, equal to $dF/d\lambda$, and $H(\lambda,\eta)$ is given by[5]

$$H(\eta,\lambda) = \frac{\lambda^2}{\lambda^2+\lambda+1}\left[\frac{1}{(\lambda+\eta)^2} + \frac{\lambda+1}{\lambda(1+\eta\lambda^2)^2}\right] \quad (5)$$

Thus the reduced stress $\sigma/(\lambda-\lambda^{-2})$ was plotted against H, and $\eta$ iterated so as to produce the best linear fit, $N_s$ and $N_c$ being determined from the slope and intercept, respectively. For the samples showing an upturn in the reduced stress, the points in this high $\lambda$ region were temporarily ignored, consistent with $\alpha$ equal to zero. The calculated values for $N_c$, $N_s$ and $\eta$ were then used as initial guesses to fit all the data to equation (3), using a least squares criterion to obtain the best values of $N_c$, $N_s$, $\eta$ and $\alpha$.

## RESULTS AND DISCUSSION

*Figure 1* shows a typical fit to the theory for a sample irradiated to a dose of 6.0 Mrad. We have chosen to present the data in the form of a Mooney–Rivlin plot, as this illustrates a sharp upturn in the reduced stress at high deformation for the more highly crosslinked samples. This is the feature that is accounted for in the theory by the parameter $\alpha$. Although a dose of 6.0 Mrad is known to produce a substantial gel fraction[1] (55%), it is evident that the slip links make by far the bigger contribution to the modulus. The inextensibility parameter, $\alpha$, of 0.07 corresponds to a theoretical maximum draw ratio ($1/\alpha$) of about 14. This agrees well with the experimental $\lambda_{max}$ of 12 obtainable for this sample by solid-state drawing[6]. *Figure 2* shows the fit for a sample irradiated to a dose of 3.5 Mrad. This quite excellent agreement between theory

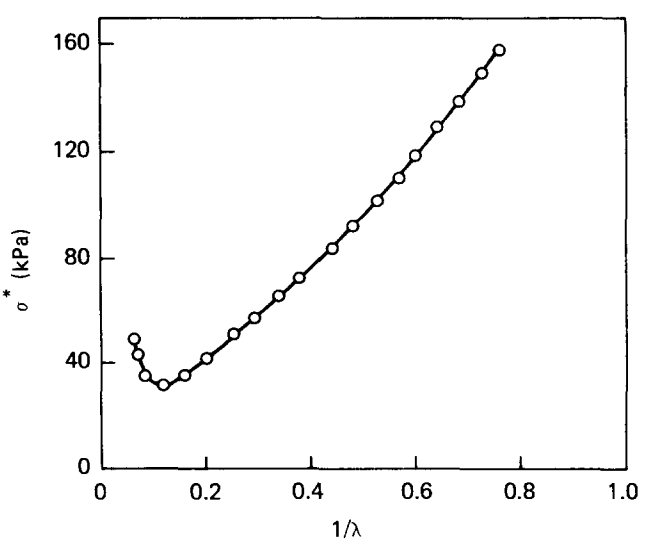


**Figure 2** Reduced stress *versus* $1/\lambda$ for 3.5 Mrad, DL sample. Symbols as for *Figure 1*, with theoretical parameters $N_c kT = 12.9$ kPa, $N_s kT = 1.18$ MPa, $\eta = 1.46$, $\alpha = 0.04$

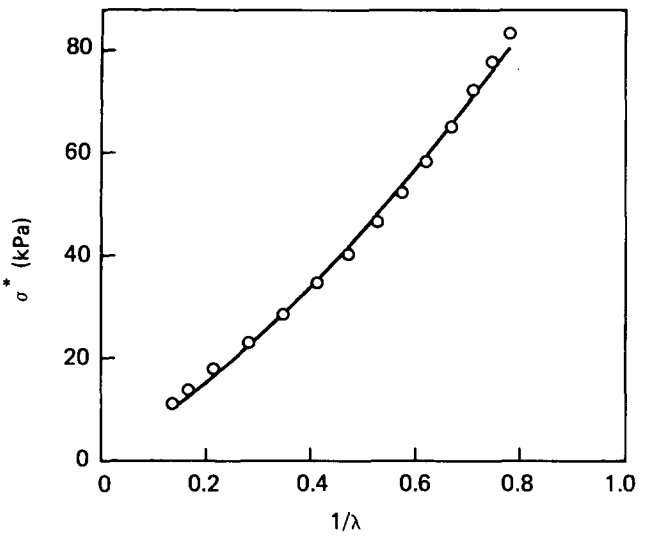


**Figure 3** Reduced stress *versus* $1/\lambda$ for 2.4 Mrad, DL sample. Symbols as for *Figure 1*, with theoretical parameters $N_c kT = 3.10$ kPa, $N_s kT = 0.54$ MPa, $\eta = 1.29$, $\alpha = 0$

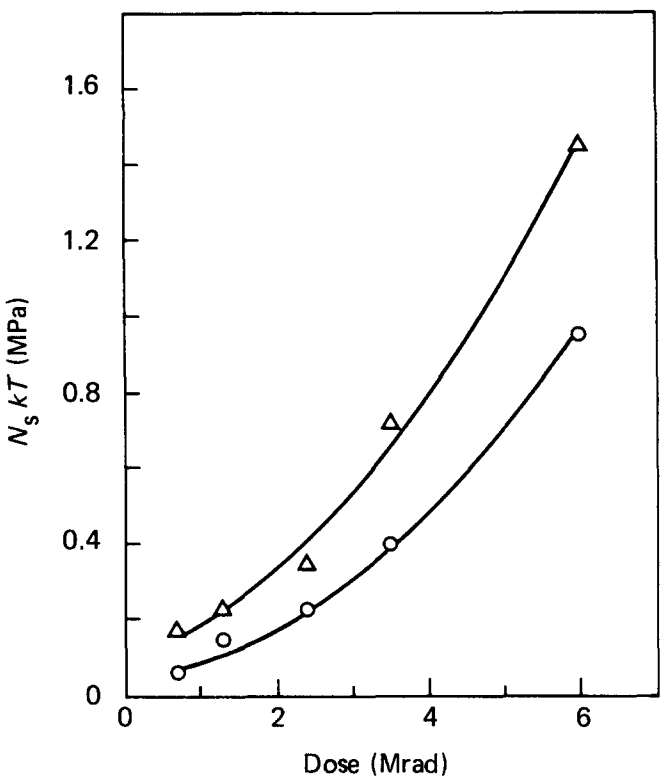


**Figure 4** $N_s kT$ *versus* dose for spun samples. (○) Low strain rate, (△) high strain rate

and experiment results in a lower $N_c$ than for 6.0 Mrad, consistent with the expected effect of lower dose; $\alpha$ is also lower, at 0.04, corresponding to a $\lambda_{max}$ of about 25, again a value close to that obtained experimentally[6]. For a 2.4 Mrad sample (*Figure 3*), we obtain an $\alpha$ of 0, indicating the absence of any chemical network chain connectivity capable of imposing a restriction on the finite extensibility of the sample. This is in accordance with the gel content determination[1], which indicates virtually no insoluble fraction.

*Figure 4* shows how the slip-link contribution varies with dose for the spun samples, at the two extension rates. It is apparent that $N_s$ increases monotonically with dose. According to Edwards and Vilgis[3], $N_s$ might be expected to be a constant, independent of $N_c$ (and therefore dose), and obtainable from the plateau modulus of the uncrosslinked melt. However, the present results suggest that the formation of each crosslink renders a certain number of topological entanglements elastically effective. There is also a clear dependence of $N_s$ on the strain rate. This result gives some insight into the dynamics, and suggests that, by shortening the time scale of the experiment, we can access an additional number of entanglements, which are then capable of contributing to the modulus. We can extrapolate back to zero dose, and at the higher strain rate we arrive at a finite intercept of about 100 kPa on the vertical axis. This corresponds to a molecular weight between entanglements of about 27 kg mol$^{-1}$ for the unirradiated polymer, a figure that could be confirmed from plateau shear modulus measurement.

*Figure 5* shows the equivalent plot for the drawn samples, and reveals some significant differences resulting from the influence of solid phase orientation on a crosslinked polymer. It would appear that $N_s$ is no longer strain-rate dependent. Also, the plot extrapolates to the origin. This indicates that drawing has permanently altered the network topology, to the extent of entirely removing the entanglements at low dose.

The relationship between $N_c$ and dose for the spun samples is summarized in *Figure 6*. The result that there is apparently permanent network formation only above 2.4Mrad is in excellent agreement with the previously reported[1] gel fraction results. Also, the $N_c$ values show a significant strain rate dependence, $N_c$ appearing to increase at higher rate. This suggests that a fraction of entanglements can be made to contribute in the same manner as permanent crosslinks, on the shorter experimental time scale. A recent paper by Edwards[7]

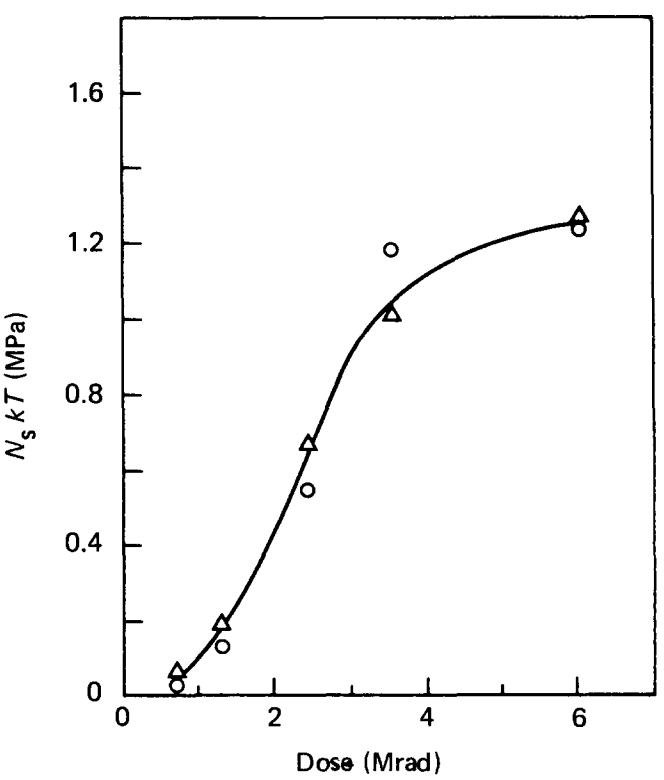


**Figure 5** $N_s kT$ *versus* dose for drawn samples. Symbols as for *Figure 4*

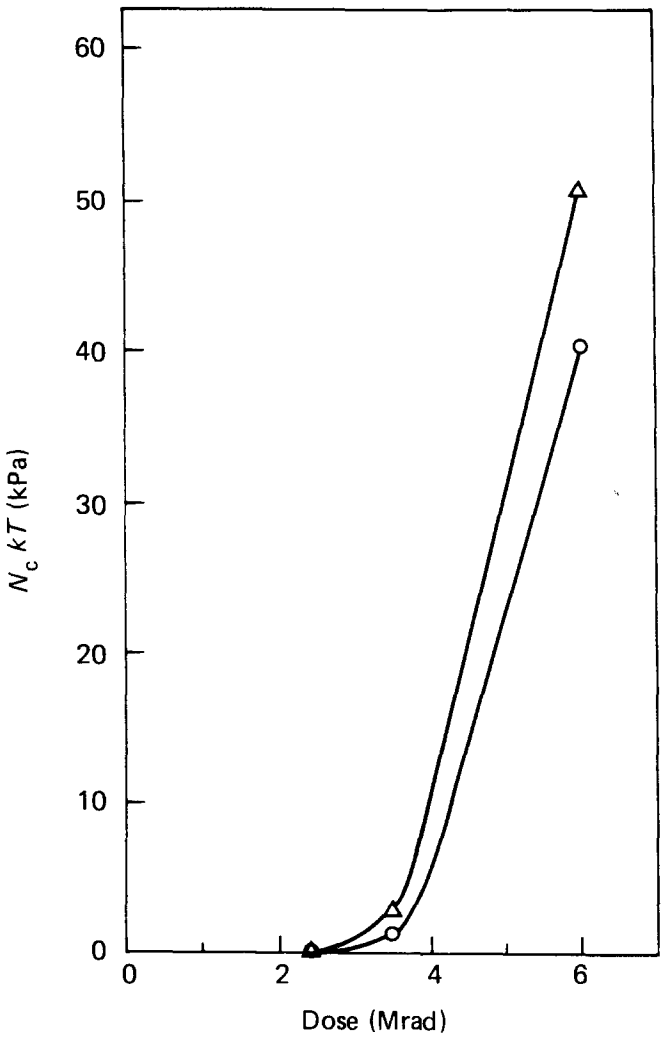


**Figure 6** $N_c kT$ *versus* dose for spun samples. Symbols as for *Figure 4*

points towards a similar interpretation of the plateau modulus in uncrosslinked polymers. The present result would indicate that there is a distribution of $\eta$ values, and increasing the effective strain rate requires an extra fraction of sliplinks to have $\eta = 0$, i.e. they are crosslinks.

Essentially the same trend is shown for the drawn sample (*Figure 7*). Comparison with *Figure 6* shows that, for the drawn samples, the curves are shifted to lower dose, so that, for a fixed dose, $N_c$ (drawn) $> N_c$ (spun). This shows again the dynamic nature of the slip links. Furthermore, this result reveals some further interesting consequences of solid phase orientation. In addition to removing some entanglements, drawing can apparently make other entanglements more permanent and effectively trapped structures, which retain their conformation even after reversion of the entire sample to the isotropic state.

*Table 1* gives the value of $\eta$ obtained for each sample under the different experimental conditions; $\eta$ is remarkably constant at about 1.1, indicating that in this system the slip links are relatively loose. We find $\eta$ to be independent of dose ($N_c$), in agreement with Thirion and Weil[5], and also of strain rate and orientation history. Viewing $\eta$ to be the average of a distribution, it would appear that altering either of these variables may alter the shape of this distribution function, but not the mean value. Ball *et al.*[2] have suggested a theoretical value of 0.2343 for $\eta$, consistent with minimizing the free energy. *Figure 8* shows the best fit to $N_c$, $N_s$ and $\alpha$ that can be obtained using this value of $\eta$ for the 3.5 Mrad (drawn, low) sample. The fit in this case is not good, especially when compared with the free fit shown in *Figure 2*. Thus, it would appear that for these samples the theoretical value is not appropriate. The difference between our value for $\eta$ (1.1) and that of Thirion and Weil[5] (0.4) may well be due to the differences in material and in the method of

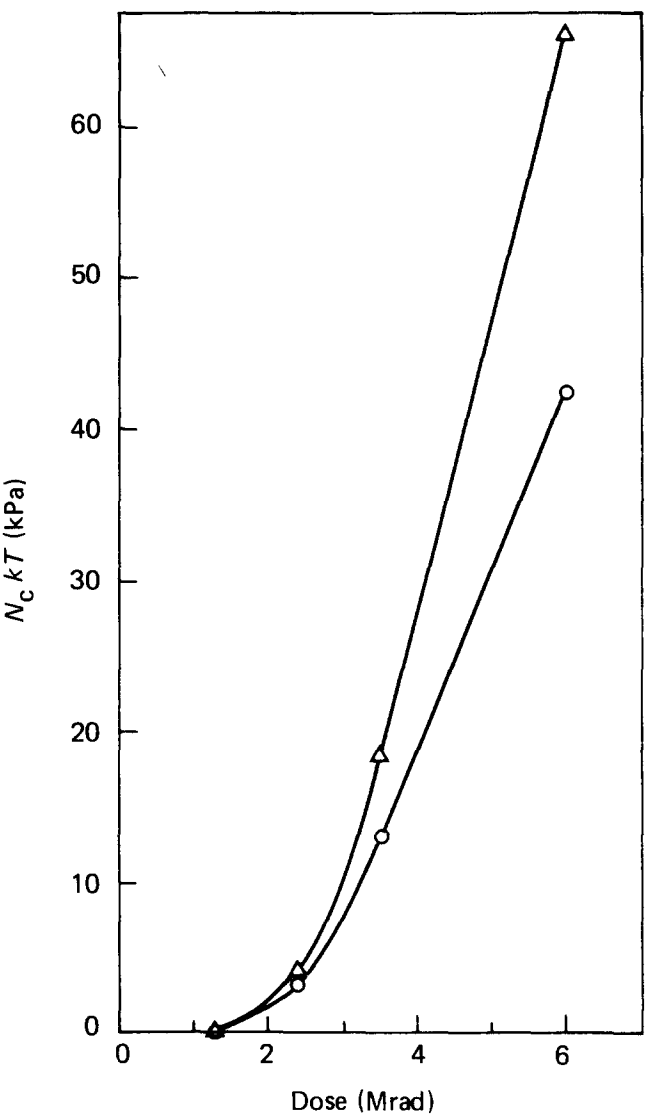


**Figure 7** $N_c kT$ *versus* dose for drawn samples. Symbols as for *Figure 4*

**Table 1** The parameter $\eta$; effect of radiation dose and experimental conditions

| | Experimental conditions[a] | | | |
|---|---|---|---|---|
| Dose (Mrad) | SL | SH | DL | DH |
| 6.0 | 1.07 | 1.05 | 1.08 | 1.03 |
| 3.5 | 1.12 | 1.19 | 1.46 | 1.38 |
| 2.4 | 1.09 | 0.90 | 1.29 | 1.27 |
| 1.3 | 1.18 | 0.97 | 0.94 | 0.86 |
| 0.7 | 1.20 | 1.05 | 0.92 | 1.05 |
| $\bar{\eta}$ | 1.13±0.05 | 1.03±0.10 | 1.14±0.21 | 1.12±0.18 |

[a] See text for details

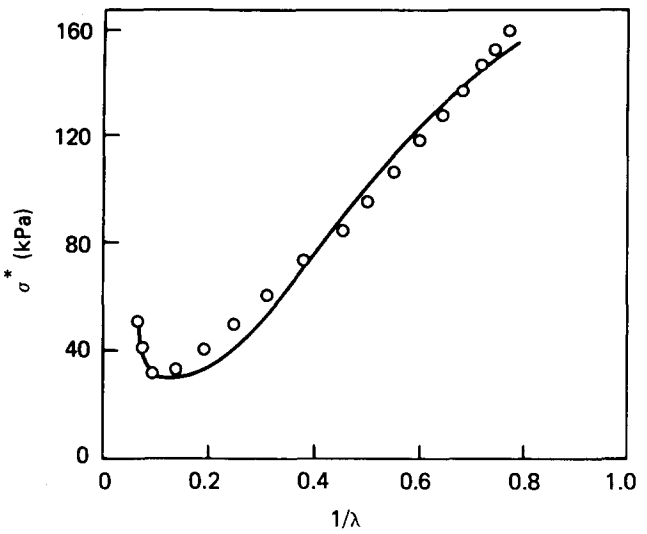


**Figure 8** Reduced stress *versus* $1/\lambda$ for 3.5 Mrad, DL sample. Symbols as for *Figure 1*, with parameters $N_c kT = 17.6$ kPa, $N_s kT = 0.23$ MPa, $\eta = 0.2343$, $\alpha = 0.04$

network formation. Our samples were prepared from polyethylene irradiated in the solid state, comprising about 60% crystallinity. Since crosslinking may only occur in the amorphous phase, or at the crystal fold surfaces, the result will be a non-homogeneous network in the melt, which may well respond differently to a chemically crosslinked, non-crystalline elastomer.

## CONCLUSION

The recent model of rubber elasticity proposed by Edwards and Vilgis[3] has been shown to provide a good description of the behaviour of irradiated polyethylene, above the melt. $N_s$ increases with dose, indicating that the formation of each crosslink 'ties in' a certain number of entanglements, thereby rendering them elastically effective. Both $N_c$ and $N_s$ show a dependence on the effective strain rate, suggesting that slip links are dynamic. The effect of solid state tensile drawing on a crosslinked network is to remove entirely some entanglements, and to render others more effective and permanent. The parameter $\eta$, reflecting the degree of freedom of the slip links, is equal to 1.1, independent of $N_c$, rate and orientation history. The theoretical value of 0.2343 appears to be inappropriate for these samples.

## ACKNOWLEDGEMENT

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## REFERENCES

1 Klein, P. G., Ladizesky, N. H. and Ward, I. M. *Polymer* 1987, **28**, 393
2 Ball, R. C., Doi, M., Edwards, S. F. and Warner, M. *Polymer* 1981, **22**, 1010
3 Edwards, S. F. and Vilgis, Th. *Polymer* 1986, **27**, 483
4 Sperling, L. H. 'Introduction to Physical Polymer Science', Wiley Interscience, 1986, Ch. 7
5 Thirion, P. and Weil, T. *Polymer* 1984, **25**, 609
6 Ladizesky, N. H., Chaoting, Y. and Ward, I. M. *J. Macromol. Sci. (B) Phys.* 1986, **25**, 185
7 Edwards, S. F. *Br. Pol. J.* 1985, **17**, 122