

Stress–strain relationships in uniaxial extension of high *cis*-1,4-polyisoprene networks with different molecular weight precursors

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Equilibrium stress–strain relationships in uniaxial extension for high *cis*-1,4-polyisoprene (Shell IR 307) networks were obtained by extrapolation of relaxation measurements to infinite time through a BKZ constitutive equation. Three series of networks were investigated, each series being characterized by its polymer precursor molecular weight. Influence of crosslinking density was studied through varying amounts of dicumyl peroxide as crosslinking agent. These results were used to test Flory and Erman's recent molecular elasticity theory of imperfect networks with constraints on junctions. It was shown that this later theory treating entanglements as restrictions on junction fluctuations could be reasonably used to characterize network topology. A universal value of 0.50 for the interpenetration parameter I is confirmed and an interpretation of parameter ζ in terms of network inhomogeneity is tentatively given.

(Keywords: polymer networks; equilibrium stress; uniaxial extension; anionic polyisoprene; constraints on junctions)

INTRODUCTION

Stress–strain measurements in uniaxial extension are the easiest way to characterize elastic behaviour or polymeric networks¹. Therefore these experiments are routinely carried out. Rubberlike elasticity is indeed a unique property of long, flexible chains with weak interchain interactions joined together by crosslinking points to form three-dimensional nonflowing networks. Relationships between structure of these networks and their mechanical properties were investigated by making use of statistical mechanics^{2–4}. Several models of Gaussian networks, i.e. networks of sufficiently long chains between junctions, were developed⁵. The well known phantom⁶ and affine⁷ network models are extreme limits. In the former, chain crossability and large junction fluctuations are allowed. In the latter, junction fluctuations are completely suppressed and the components of the vectorial length of each chain are changed by the deformation in the same ratio as the macroscopic deformation of the sample. In both cases, the reduced force in uniaxial extension, conventionally defined as⁸:

$$[f^*] \equiv f v_2^{1/3} A_d (\alpha - \alpha^{-2})^{-1} \quad (1)$$

where α is the extension ratio defined relative to the undeformed swollen state, f the measured equilibrium force, v_2 the volume fraction of polymer in the swollen network, and A_d the cross-sectional area of the isotropic unswollen sample, is predicted to be independent of deformation. Departures from this behaviour were early reported⁹. Besides phenomenological equations like the Mooney–Rivlin expression, i.e. $[f^*] = 2C_1 + 2C_2/\alpha$, non-Gaussian analysis was proposed¹⁰. However, the chain end-to-end distance distribution keeps a Gaussian form

over a large range of deformation for the networks usually studied¹¹ and a non-Gaussian effect may exist only in the limited extensibility region of deformation. Real networks present strong chain overlapping and intermolecular steric hindrances of chain motion, commonly termed entanglements, have long been recognized as the origin of departures from phantom and affine predictions. Different formalisms were proposed to include these intermolecular effects in the rubberlike elasticity analysis at thermodynamic equilibrium^{5,12,13}. In the one due to Flory and Erman^{14,15}, entanglements are embodied as domains of constraints acting as restrictions of junction fluctuations. The Flory and Erman theory was successful in accounting for the relationships of stress to strain for all varieties of strains of typical elastomers throughout ranges accessible to experiment^{16–18}. Applied to uniaxial extension, this model effectively predicts a decrease in the reduced force with increasing deformation interpreted as a gradual transition from nearly affine behaviour (at small deformations) to phantom state.

Although model networks, i.e. networks of controllable and independently known structure, are well suited to test rubberlike elasticity models^{19,20}, the usual applications involve statistically crosslinked networks (for example, those irradiated or those reacted with dicumyl peroxide). In these latter, topological description is strenuous and may be treated with a probabilistic formalism^{21,22}. A universal quantity, the cycle rank ξ , encompassing all imperfections like loops and dangling ends, was proposed by Flory². It is defined as the number of independent circuits which have to be cut to reduce the mesh structure to an acyclic tree. The numbers of effective chains and junctions are directly related to the network cycle rank and functionality²³. Later, simple relationships between the cycle rank and the average molecular weights of

precursor and network chains were established by Queslel and Mark on the basis of reasonable assumptions²⁴. It has then become apparent that a complete characterization of network structure and behaviour may emerge with the simultaneous use of the Flory and Erman fluctuation model and the Queslel and Mark topological study²⁵. Although a uniaxial extension experiment is as simple as swelling²⁶, the restrictive condition of thermodynamic equilibrium, which is required to test models based on statistical mechanics, is respected with difficulty. Dense chain entanglements induce a large spectrum of relaxation times. Very low-frequency components may preclude final equilibrium attainment under the usual experimental conditions. One possible way to circumvent this difficulty consists of relaxation measurements at different elongations followed by extrapolation to infinite times through the establishment of a BKZ constitutive equation²⁷. This method is used in the present paper to characterize structure and elasticity of *cis*-polyisoprene polymers cured with dicumyl peroxide. Influence of precursor molecular weight and crosslinking density is investigated.

MATERIALS AND METHODS

Samples were generously provided by Manufacture Française des Pneumatiques Michelin. Precursor polymer was an anionic commercial polyisoprene (Shell IR 307) with a high *cis*-1,4 configuration (92% *cis*, 5% *trans*) and T_g (d.s.c.) = -60°C. Three batches of varying number-average molecular weight, namely $M_n = 3.60 \times 10^5$, 2.45×10^5 and 1.25×10^5 g mol⁻¹, were prepared by degradative work on a two-roll mill. Each precursor was mixed in bulk with several amounts of pure dicumyl peroxide, moulded and cured. Curing conditions (30 min at 170°C) were chosen to ensure full decomposition of the peroxide with negligible chain scission during curing. Designation of vulcanizates, number-average molecular weight of precursor polymer and quantity of peroxide are reported in Table 1.

A complete description of the test method and the relaxation curve analysis has been reported in a preceding paper²⁷. A brief summary is given here.

The same sample (70 × 4 × 2 mm), stored at -15°C except for a recovery period of about two days at room temperature, is stretched by a pneumatic device which imposes positive or negative change of elongations in a maximum time lapse of 0.2 s. The force on the sample is recorded from this instant at 30°C and at constant

extensions measured by a cathetometer. A reproducibility of the order of ±0.1% is obtained in these conditions for transient modulus determinations, free of sample cross-section error. Equilibrium stress-strain relationships have been deduced from stress measurements following either a single step extension or a fast retraction in succession to a previous relaxation, the duration of which controls the stress maxima observed in this condition²⁷. These data have been analysed through a BKZ constitutive equation with a memory function derived from the Helfand and Pearson theory of random walk statistics for a chain in an obstacle net²⁸ in the case of the randomly distributed networks already considered by Curro and Pincus²⁹. Good agreement has been found by this method by extrapolating to infinite time each kind of data for one or two steps of extension. Since these limiting stresses result from different strain histories leading to the same ultimate states, they should closely correspond to the virtual equilibrium behaviour of the strained vulcanizates²⁷.

RESULTS AND DISCUSSION

The equilibrium reduced forces obtained by the relaxation and extrapolation method described in the preceding section are reported *versus* the inverse of deformation ratio in Figures 1 and 2 for the nine vulcanizates listed in Table 1. As mentioned in the Introduction, the usual decrease of reduced force with increasing deformation was observed for all the samples. Deformation was kept low enough to avoid limited extensibility upturn.

The Flory and Erman model of a real network and the Queslel and Mark topological study were chosen to characterize the networks. The network elastic behaviour is taken to depend on two parameters, the most important being κ which measures the severity of entanglement constraints relative to those imposed by the phantom network. Another parameter ζ takes into account the non-affine transformation of the domains of constraints with strain, but is expected to be small. The Flory and Erman treatment leads to the following expression for a tetrafunctional network:

$$[f^*] = (\xi/V_0)RT \{ 1 + [\alpha K(\alpha^2 v_2^{-2/3}) - \alpha^{-2} K(\alpha^{-1} v_2^{-2/3})] \times (\alpha - \alpha^{-2})^{-1} \} \quad (2)$$

where the function K depending on κ and ζ is defined in ref. 14 (equation (37)). R is the gas constant and T the

Table 1 Characterization of the *cis*-polyisoprene vulcanizates

Sample	$10^{-5} \times M_n$ (g mol ⁻¹)	Dicup ^a x	$[f^*]_{ph}^b$ (N mm ⁻²)	κ	ζ	$10^{-3} \times M_c$ (g mol ⁻¹)	$10^5 \times \mu/V_0$ (mol cm ⁻³)	$10^2 \times Q^c$	$10^5 \times \mu_t/V_0$ (mol cm ⁻³)	μ/μ_t
1 IR 360	3.60	1.0	0.2350	4.6	0	4.69	9.58	5.28	3.34	2.9
2 IR 360	3.60	0.8	0.2113	4.9	0.011	5.19	8.63	5.86	2.67	3.2
1 IR 245	2.45	0.8	0.1967	4.9	0.017	5.44	8.17	9.09	2.67	3.1
2 IR 245	2.45	0.6	0.1592	5.4	0.011	6.62	6.68	11.12	2.02	3.3
3 IR 245	2.45	0.35	0.0930	6.8	0	10.72	4.06	18.30	1.18	3.4
1 IR 125	1.25	1.2	0.2452	4.3	0	4.21	10.46	13.92	4.00	2.6
2 IR 125	1.25	0.6	0.1445	5.3	0.035	6.67	6.46	22.54	2.01	3.2
3 IR 125	1.25	0.45	0.0989	6.0	0.010	9.08	4.65	31.31	1.51	3.1
4 IR 125	1.25	0.3	0.0747	6.6	0.016	11.22	3.69	39.46	1.01	3.7

^a Weight per cent in bulk

^b At $T = 303$ K

^c $Q = (2\rho/M_n)/(\mu/V_0)$

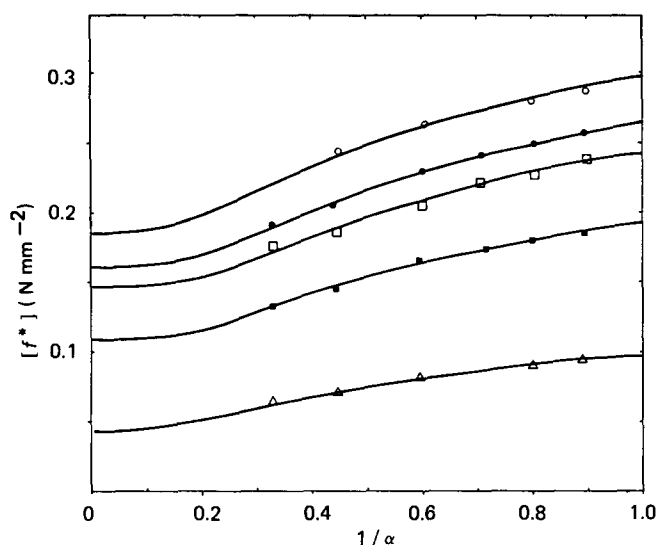


Figure 1 Plot of equilibrium reduced force versus reciprocal of extension ratio. Experimental points were obtained by extrapolation of relaxation measurements to infinite time. Continuous curves are theoretical predictions calculated with parameters listed in Table 1: (○) 1IR 360; (●) 2IR 360; (□) 1IR 245; (■) 2IR 145; (△) 3IR 245

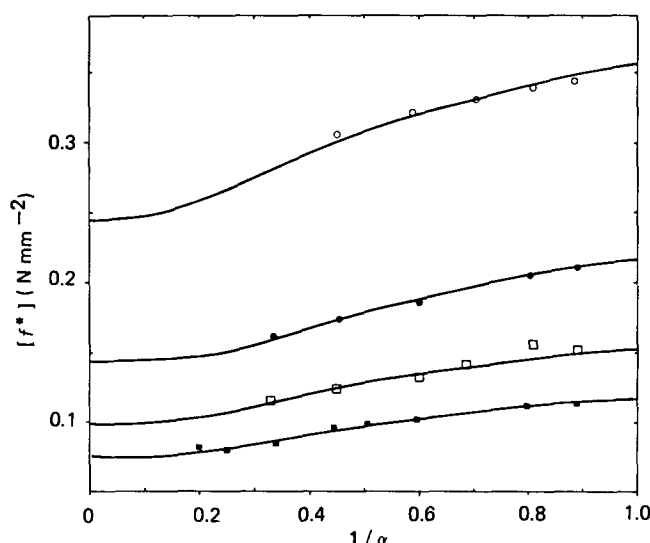


Figure 2 Plot of equilibrium reduced force versus reciprocal of extension ratio. Same extrapolations as in Figure 1: (○) 1IR 125; (●) 2IR 125; (□) 3IR 125; (■) 4IR 125

absolute temperature. On the plausible grounds that the constraints on junctions are determined by the degree of interpenetration of the chain about the junctions in the network^{16,23}, the parameter κ and the number of junctions μ in the volume V_0 of the state of reference should be related^{23,30} according to:

$$\kappa = I \langle r^2 \rangle_0^{3/2} (\mu/V_0) \quad (3)$$

I is an interpenetration parameter which was originally thought^{16,24} to be ~ 0.5 but may differ from this value³¹. The quantity $\langle r^2 \rangle_0$ is the mean-square end-to-end length of the (unperturbed) network chain. For *cis*-polyisoprene, the relationship between $\langle r^2 \rangle_0$ and the number-average molecular weight between crosslinks M_c is:

$$\langle r^2 \rangle_0 = 3.8 \times 10^7 M_c / N_A \quad (4)$$

where N_A is Avogadro's number. The quantities M_c and $\langle r^2 \rangle_0$ are expressed in g mol^{-1} and cm^2 , respectively.

Equation (4) was obtained by choosing a characteristic ratio C_∞ equal to 5.0, a mean-square bond length of 2.18 \AA^2 and an average number of bonds per monomer of 3.94, which are typical values for IR 307 polymer^{32,33}.

Extrapolation of the Flory and Erman function (equation (2)) to infinite deformation ($\alpha^{-1} = 0$) gives the phantom modulus depending only on the cycle rank²:

$$[f^*]_{\text{ph}} = (\xi/V_0)RT \quad (5)$$

Queslel and Mark^{24,26} have used topological arguments to obtain the following relationships between the total number of junctions μ , the cycle rank ξ , the average molecular weight M_c of the randomly crosslinked network chains and the number-average molecular weight M_n of polymer precursor:

$$\mu/V_0 = (\rho/2M_c)(1 - M_c/M_n) \quad (6)$$

$$\xi/V_0 = (\rho/2M_c)(1 - 3M_c/M_n) \quad (7)$$

where ρ is the polymer density.

Equations (6) and (7) are of particular interest in the present study for the number density of dangling chains, i.e. $2\rho/M_n$, varies in the different samples tested and a dangling chain-end correction is then necessary. Furthermore, with equations (3) and (5) they provide a connection between M_c , M_n , κ , ξ , $[f^*]_{\text{ph}}$, μ and I . Experimental reduced forces were fitted by least-squares analysis with theoretical curves calculated through equation (2). The interpenetration parameter I was kept constant for all the vulcanizates and set equal to 0.50. Two independent parameters ζ and M_c were chosen for the least-squares fitting. The other quantities κ , $[f^*]_{\text{ph}}$ and μ/V_0 were then calculated from M_c through equations (3) to (7) with the knowledge of independently determined values of M_n . As shown in Figures 1 and 2, excellent agreement was reached between theory and experiment. The values of ζ and M_c determined by the fitting and the calculated values of $[f^*]_{\text{ph}}$, κ and μ/V_0 are reported in Table 1 for each sample. It can already be concluded that the Flory and Erman model of real networks with constraints on junctions is consistent with all the data presented in this study. Moreover, the interpenetration concept providing a physical meaning for the mean parameter κ of the theory is successfully tested with the usual $I = 0.50$ value. The range of κ is in agreement with values previously reported^{12,16}. Model networks are often used to test rubber elasticity theories, for their crosslinking densities may be independently known by controlling the chemical crosslinking process. In randomly crosslinked networks, initial dicumyl peroxide amount x may be considered as approximately proportional to the crosslinking density, which may be otherwise evaluated by chemical analysis. According to the interpenetration concept, κ should be a decreasing function of the crosslinking density. This trend is effectively observed in Figure 3 where κ is shown as a function of the amount of dicumyl peroxide. Moreover the regularity of the evolution of κ enables us to conclude that all the stress-strain data and theoretical fitting are consistent. According to the theory outlined above, the affine network model corresponds to the limits $\kappa \rightarrow \infty$ and $\zeta \rightarrow 0$ whereas the phantom state is reached when $\kappa \rightarrow 0$ and $\kappa\zeta \rightarrow 0$. Parameter ζ has been plotted with respect to κ in Figure 4. It seems effectively that ζ decreases to zero in the

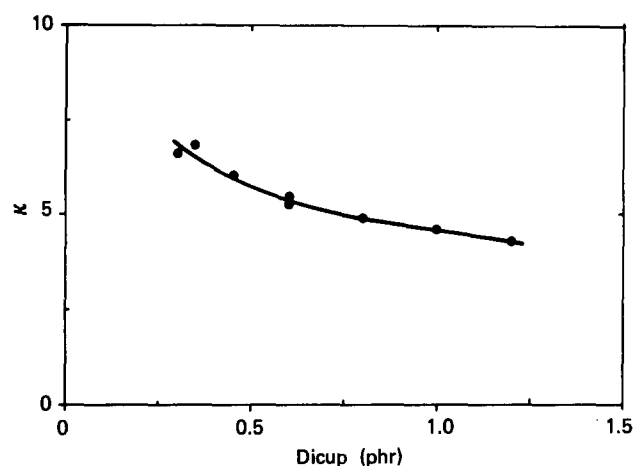


Figure 3 Dependence of physically determined parameter κ on initial amount of dicumyl peroxide crosslinking agent

region of high κ , but also in the region of low κ . This consistent set of equilibrium data gives the first opportunity to interpret tentatively the second parameter ζ of the theory. Parameter ζ is the result of a convolution between κ and network inhomogeneities. A high value of κ improves deformation affinity of constraint domains ($\kappa \rightarrow \infty, \zeta \rightarrow 0$). However, this state of affinity is perturbed by network inhomogeneities. These network inhomogeneities can be considered to consist of dangling chains, in a first approximation. Indeed, if difunctionally active junctions are neglected, the number of dangling chains is equal to the number of trifunctionally active junctions^{24,26}. The degree of inhomogeneity Q can then be defined as the number density of trifunctionally active junctions, each connected to a dangling chain, normalized with the total number density of junctions:

$$Q = (2\rho/M_n)/(\mu/V_0) \quad (8)$$

This quantity is reported in Table 1 for the nine vulcanizates. The comparison of ζ values with Q at constant κ is a way to suppress the effect of the convolution of κ with Q . This is done in Table 2. It is effectively confirmed that the parameter ζ is an increasing function of degree of inhomogeneity Q at constant κ .

The characterization of network structure by analysis of mechanical properties with an elasticity model gives some insight into the chemical crosslinking process. Indeed the number density of junctions μ/V_0 determined above may be compared with the number density of junctions μ_t/V_0 calculated with the knowledge of the initial amount x (weight per cent) of peroxide assuming full decomposition of peroxide and a 1:1 crosslinking efficiency. The quantity μ_t/V_0 is related to x through the following equation:

$$\mu_t/V_0 = \rho x / [270(100 + x)] \quad (9)$$

The quantity μ_t/V_0 and the ratio μ/μ_t are reported in Table 1 for the nine vulcanizates. The real density of junctions is about three times higher than the calculated density μ_t/V_0 . Furthermore crosslinking efficiency increases slightly with decreasing initial amount of peroxide. The issue concerning peroxide crosslinking efficiency is not yet entirely clarified in the literature³⁴⁻³⁹. However, use of an inadequate elasticity model may have led to uncertain conclusions. In a recent analysis by the alkaline fusion

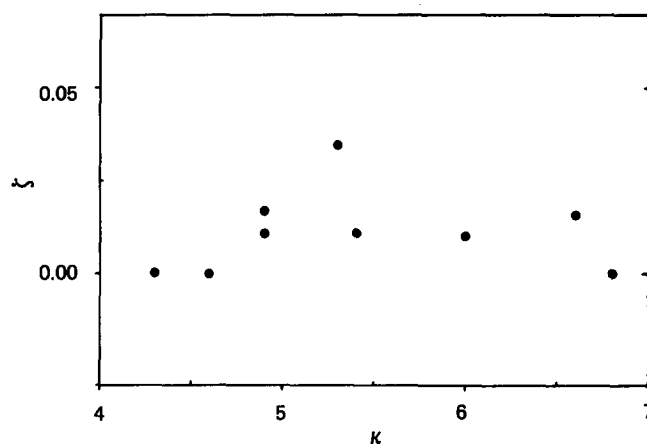


Figure 4 Plot of parameter ζ versus parameter κ corresponding to the nine studied networks

Table 2 Influence of degree of network inhomogeneity Q on parameter ζ at constant κ . Increase of ζ corresponds to loss of deformation affinity of constraint domains

κ	ζ	$10^2 \times Q$
4.9	0.011	5.86
4.9	0.017	9.09
5.4	0.011	11.12
5.3	0.035	22.54
6.8	0	18.30
6.6	0.016	39.46

method of dicumyl peroxide ultraviolet-cured poly(dimethylsiloxane) containing pendant vinyl groups, Barral *et al.*⁴⁰ have found that the total number of crosslinks formed by chemical bonds in this type of siloxane can exceed the number predicted on the basis of vinyl chemistry by a significant amount. Our results seem to show that one mole of dicumyl peroxide creates about three moles of C-C crosslinks. However, this conclusion is only qualitative, for our precursor polymers were not carefully extracted before the study.

CONCLUSIONS

The condition of measuring, at thermodynamic equilibrium, force response to a uniaxial network deformation required to test the elasticity model based on statistical mechanics analysis can be fulfilled by extrapolating relaxation curves to infinite time through a BKZ constitutive equation in agreement with the Helfand and Pearson treatment of chain disentanglement in a mesh. The Flory and Erman model with restrictions of junction fluctuations and the Queslel and Mark topological study of imperfect networks may be reasonably applied to characterize fully statistically crosslinked network structure. Results confirm the Flory and Erman interpenetration concept with a universal constant I of 0.50. Physical characterization of a vulcanizate may furthermore help the understanding of the chemical crosslinking process.

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REFERENCES

- 1 Brown, R. P. 'Physical Testing of Rubbers', Applied Science, London, 1979
- 2 Flory, P. J. *Proc. R. Soc. Lond.* 1976, **A351**, 351
- 3 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1969
- 4 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley-Interscience, New York, 1969
- 5 Eichinger, B. E. *Ann. Rev. Phys. Chem.* 1983, **34**, 359
- 6 James, H. M. and Guth, E. J. *Chem. Phys.* 1947, **15**, 669
- 7 Wall, F. T. *J. Chem. Phys.* 1943, **11**, 527
- 8 Mooney, M. J. *J. Appl. Phys.* 1940, **11**, 582
- 9 Gee, G. *Trans. Faraday Soc.* 1946, **42**, 585
- 10 Treloar, L. R. G. *Trans. Faraday Soc.* 1954, **50**, 881
- 11 Yoon, D. Y. and Flory, P. J. *J. Chem. Phys.* 1974, **61**, 5366
- 12 Queslel, J. P. and Mark, J. E. *Adv. Polym. Sci.* 1984, **65**, 135
- 13 Queslel, J. P. *Rubber Chem. Technol.* 1984, **57**, 145
- 14 Flory, P. J. and Erman, B. *Macromolecules* 1982, **15**, 800
- 15 Flory, P. J. *Rubber Chem. Technol.* 1975, **A8**, 513
- 16 Erman, B. and Flory, P. J. *Macromolecules* 1982, **15**, 806
- 17 Erman, B. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 829
- 18 Treloar, L. R. G. *Br. Polym. J.* 1982, **14**, 121
- 19 Mark, J. E. *Adv. Polym. Sci.* 1982, **44**, 1
- 20 Queslel, J. P. and Mark, J. E. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1201
- 21 Charlesby, A. and Pinner, S. H. *Proc. R. Soc. Lond.* 1959, **A249**, 367
- 22 Pearson, D. S. and Graessley, W. W. *Macromolecules* 1978, **11**, 528
- 23 Flory, P. J. *Br. Polym. J.* 1985, **17**, 1
- 24 Queslel, J. P. and Mark, J. E. *J. Chem. Phys.* 1985, **82**, 3449
- 25 Queslel, J. P. and Mark, J. E. *Eur. Polym. J.* in press
- 26 Queslel, J. P. and Mark, J. E. *Adv. Polym. Sci.* 1985, **71**, 229
- 27 Thirion, P. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn.* submitted
- 28 Helfand, E. and Pearson, D. S. *J. Chem. Phys.* 1983, **79**, 2054
- 29 Curro, J. G. and Pincus, P. *Macromolecules* 1983, **16**, 559
- 30 Erman, B. and Flory, P. J. *Macromolecules* 1983, **16**, 1607
- 31 Brotzman, R. W. and Mark, J. E. *Macromolecules* submitted
- 32 Mays, J. W., Ph.D. Thesis, University of Akron, 1984
- 33 Mays, J. W., Hadjichristidis, N. and Fetters, L. J. *Macromolecules* 1984, **17**, 2723
- 34 Moore, C. G. and Watson, W. F. *J. Polym. Sci.* 1956, **19**, 237
- 35 Loan, L. D. *J. Appl. Polym. Sci.* 1963, **7**, 2259
- 36 Van der Hoff, B. M. E. *Rubber Chem. Technol.* 1965, **38**, 560
- 37 Hummel, K. and Kaiser, G. *Rubber Chem. Technol.* 1965, **38**, 581
- 38 Scheele, W. and Rohde, E. *Rubber Chem. Technol.* 1966, **39**, 768
- 39 Loan, L. D. *Rubber Chem. Technol.* 1967, **40**, 149
- 40 Barral, E. M., Hawkins, R., Fukushima, A. A. and Johnson, J. F. *J. Polym. Sci., Polym. Symp.* 1984, **71**, 189