

The dielectric properties of poly(hexylisocyanate) solutions in electric fields

H. Block, J. J. Gosling and S. M. Walker

Donnan Laboratories, University of Liverpool, PO Box 147, Liverpool L69 3BX

(Received 1 February 1984; revised 24 April 1984)

The effect of large electric fields ($\leq 0.8 \text{ MV m}^{-1}$) on solutions of poly(*n*-hexylisocyanates) of differing molecular weights is described. Non-linear dielectric effects are observed and their magnitudes are in fair agreement with those predicted theoretically for inflexible dipolar molecules of low polarizability. Small enhancements of relaxation frequencies are also caused by the application of large electric fields.

(Keywords: poly(hexylisocyanate); dielectric saturation; dipole)

INTRODUCTION

The response of a material to a static external electric field is normally such that a polarization is set up with a magnitude that is proportional to the strength of the field (E). However, under conditions of sufficiently high field strengths the susceptibility, or the parameter more usually considered the relative permittivity (ϵ'), becomes field dependent. This non-linear dielectric response, or dielectric saturation as it is sometimes termed, can occur when dipolar orientation is the polarization mechanism, but does so in a significant way only when the orientation energy is sufficiently large. In terms of dipole strength (μ) and temperature T the parameter of significance is $\chi = \mu E/kT$ in which k is Boltzmann's constant. For small molecules, even if very polar, the maximum sustainable field strengths without breakdown of $\approx 10^7 \text{ V m}^{-1}$ only result in rather minor changes of between 10^{-3} and 10^{-6} in $[\epsilon'(E) - \epsilon'(0)]/\epsilon'(0)$. This is because $\chi \ll 1$ even at these fields (for nitrobenzene at ambient temperature $\chi \sim 0.03$ at $E = 10^7 \text{ V m}^{-1}$ and for $\chi = 1$, $E \approx 3 \times 10^8 \text{ V m}^{-1}$). With such materials non-linear dielectric effects show up as small perturbations in the permittivity and consequently their measurement are difficult. It is therefore desirable to obtain data under conditions when E approaches kT so as to test the models for the dependence of ϵ' on E more fully. Macromolecular substrates with macro-dipole moments such as the poly(isocyanates) are suitable in this respect as this paper demonstrates.

Poly(alkyl isocyanates) have a helical conformation which results from a slightly non-planar *cis-trans* amide alternation¹. The chains have a high rigidity and the structure confers a tendency for the total dipole per macromolecule to be the sum of resolved residue contributions, at least for chains whose degree of polymerization $p \lesssim 800$. Even above this value the chain still retains high rigidity with a total dipole increasing with p but with an exponent in p below one, a 'worm-like' chain generally being considered as descriptive of those polymers. Thus it is that poly(isocyanates) have a large dipole rendering them useful as model compounds in a study of non-linear dielectric phenomena. The hexyl derivative was chosen

for this study because of its solubility in toluene, a solvent of low polarity able to sustain high fields. Further, the condition for fractionation to obtain essentially monodisperse samples has been established^{2,3}.

The poly(α -amino acid), poly(γ -benzyl-L-glutamate) has a conformation of higher rigidity and an accessible molecular weight range giving macromolecules of even greater dipole moment and indeed its non-linear dielectric behaviour has been studied⁴, but it has a number of disadvantages for high field studies. The solvents are generally more polar, or more prone to polar impurities. The polymer is more difficult to fractionate and has a tendency to aggregation in solution which persists even on dilution unless polar de-aggregants are added^{4,5}. Although there is evidence for dipole-dipole association in poly(isocyanates)⁶, dilution to sufficiently low concentration removes such association. For these reasons poly(hexylisocyanate) in toluene presents an advantageous system for studying non-linear dielectric effects. Below, we report on such a study using fractionated poly(hexylisocyanate) samples.

EXPERIMENTAL

Poly(*n*-hexylisocyanate) was prepared by the method of Sashoua⁷. The polydisperse and trimer-containing product was fractionated from a 0.12% (w/v) solution in tetrachloromethane using methanol as precipitant and a well-controlled coacervation temperature ($30.7^\circ \pm 0.05^\circ \text{C}$). Since to obtain significant non-linear field effects only material of large dipole and hence high molecular weight is suitable, the fractionation was terminated after a 25% recovery. Six fractions of high molecular weight were isolated. Their molecular weights were obtained using high pressure g.p.c. with tetrahydrofuran as solvent and poly(styrene) calibration. Molecular weights were established using the Benoit universal calibration method⁸, the Mark-Houwink K and α being known for poly(*n*-hexylisocyanate)⁹ and poly(styrene)⁸ in tetrahydrofuran. The results obtained are given in Table 1.

Permittivity measurements of the poly(*n*-hexyl-

Table 1 Data for the poly(n-hexylisocyanate) fractions

Fraction	10 ⁻³ molecular weight* (±7%)	Dielectric data at E = 0			High field $\mu/10^{-27}$ Cm**
		$\mu/10^{-27}$ Cm†	log(f_c /Hz)	α	
1	187	4.28	3.08	0.205	4.8
2	151	3.57	3.36	0.136	4.3
3	134	3.42	3.48	0.098	5.3
4	115	3.18	3.63	0.074	4.7
5	87	2.68	3.77	0.028	4.3
6	77	2.48	3.82	0.017	4.7

*Mark-Houwink constants used for poly(styrene)⁸ $K = 9.63 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$, $\alpha = 0.728$ and for poly(n-hexylisocyanate)⁹ $K = 2.2 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$, $a = 1.06$

**Best fit value for equation (1)

† Based on Guggenheim's equation¹⁰

isocyanates) dissolved in Analar toluene were made as a function of both frequency (2×10^2 – 2×10^4 Hz) and field strength (0 – 0.8 MV m^{-1}) using the three terminal cell previously described⁴. The d.c. field was provided by a Wareham source having $< 20 \text{ mV}$ peak-to-peak ripple at the maximum voltage of 800 V used. It was delivered to the measuring electrode via a current limiting resistor of $1 \text{ M } \Omega$. The d.c. was supplemented at the electrode by a variable frequency a.c. sensing voltage of 20 V generated by an Advance J2E oscillator. The capacitances and resistances of the cell were determined using a Wayne-Kerr B221A bridge isolated from any d.c. voltage by incorporating an isolation capacitor ($0.15 \mu\text{F}$) between the bridge and the measuring electrode. This capacitor introduced a 0.1% difference between the total system and cell capacities, a negligible difference in terms of the overall accuracy of measurement. A switch whose contacts were strapped with an in-series capacitance ($0.1 \mu\text{F}$) resistance (330Ω) train was used for trimming. These capacitance-resistance trains effectively limited surges which, if present, could damage the bridge-detector system. For null detection the out-of-balance signal from the bridge was, after amplification via a Brookdeal LA 350 low noise amplifier, connected to the X-plates of an oscilloscope and the balance point detected by Lissajou's Figures obtained from the source acting on the Y-plates. All measurements were made at a thermostatically controlled temperature of $31.5^\circ \pm 0.5^\circ \text{C}$.

RESULTS AND DISCUSSION

Dielectric measurements in the frequency (f) range 10^2 – 2×10^4 Hz were made on the fractions dissolved in toluene both in the absence and presence of imposed d.c. fields. The increments of relative permittivity, $\Delta\epsilon'(f) = \epsilon'(f) - \epsilon'$ (solvent) and dielectric loss $\epsilon''(f)$ were found within random error to be proportional to the substrate concentration (c) when this was within the range 0.2 – 1.0 kg m^{-3} . This proportionality was upheld for all levels of d.c. field investigated. In the absence of a d.c. field the data were processed to provide the dipole moments (μ), critical frequency (f_c) and Cole-Cole parameters (α) shown in Table 1. The first was calculated using the Guggenheim equation¹⁰ with averaged $\Delta\epsilon'_0/c$ for a number of concentrations and using $\Delta\epsilon'_0$ values obtained as the difference between low and high frequency ϵ' intercepts of Cole-Cole plots¹¹. The quoted critical frequencies and α parameters refer to a common concentration of 0.4 kg m^{-3} . These results are consistent with published

data^{2,6,12} and show that the macromolecules within the molecular weight range used have little flexibility and are rod-like or possibly for the higher molecular weights, tend towards 'worm-like' chains.

Under d.c. fields both $\Delta\epsilon'(f)$ and $\epsilon''(f)$ are reduced as illustrated in Figure 1 for fraction (1) at a concentration of 0.4 kg m^{-3} in toluene. There is also a slight increase in critical frequency with field. Both these observations are similar to previous results obtained with the rigid macro-dipole: poly(γ -benzyl-L-glutamate)⁴, although the effects here are less marked because the dipoles per macromolecule are smaller in the poly(hexylisocyanates).

The extent of saturation observed under combined d.c. and a.c. sensing fields has been discussed by Kielich¹³. If, as we believe is the case here, the saturation is dominated by dipolar orientation and polarizability plays an entirely insignificant role in macromolecular alignment, then changes in the zero-to-high-frequency increment of relative permittivity with the d.c. field E [$\Delta\epsilon'_0(E)$] is given by¹³

$$\Delta\epsilon'_0(E)/\Delta\epsilon'_0(0) = 3\{1 - \coth^2\chi + \chi^{-2}\} \quad (1)$$

To obtain $\Delta\epsilon'_0(E)$, Cole-Cole plots¹¹ were constructed, an

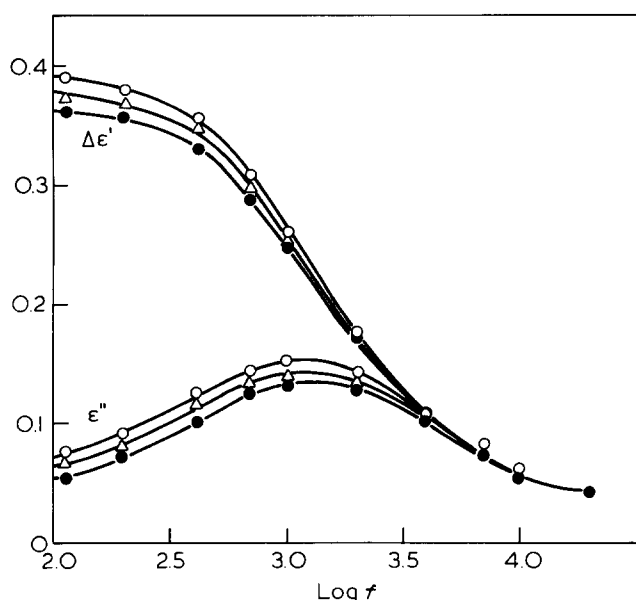


Figure 1 The changes in relative permittivity ($\Delta\epsilon'(f)$) and loss [$\epsilon''(f)$] as a function of frequency (f) for various applied d.c. fields (E). Fraction (1) in toluene at 0.4 kg m^{-3} and 31.5° . (○) $E=0$; (△) $E=0.4 \text{ MV m}^{-1}$; (●) $E=0.8 \text{ MV m}^{-1}$

example being shown in Figure 2 for fraction (1). The Cole-Cole parameters α appear to be insensitive to the d.c. field, the centres for the arcs lying on a common radius for all the polymers. Data in the form of Cole-Cole plots such as that shown in Figure 2 also demonstrated that the d.c. fields employed influenced only the low frequency relative permittivity, the high frequency component being invariant under field. This supports our contention that induced dipole effects due to polarizability are not involved in the non-linear dielectric behaviour of these systems. Figures 3 and 4 show the experimental data for

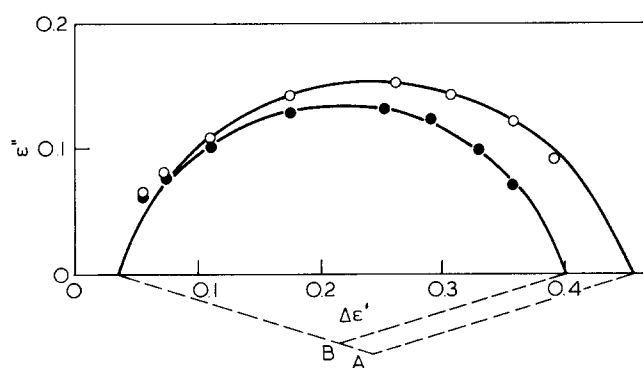


Figure 2 Cole-Cole plots for fraction (1) in toluene at 0.4 kg m^{-3} , (○) $E=0$ and (●) $E=0.8 \text{ MV m}^{-1}$ with positions A and B as respective arc-centres

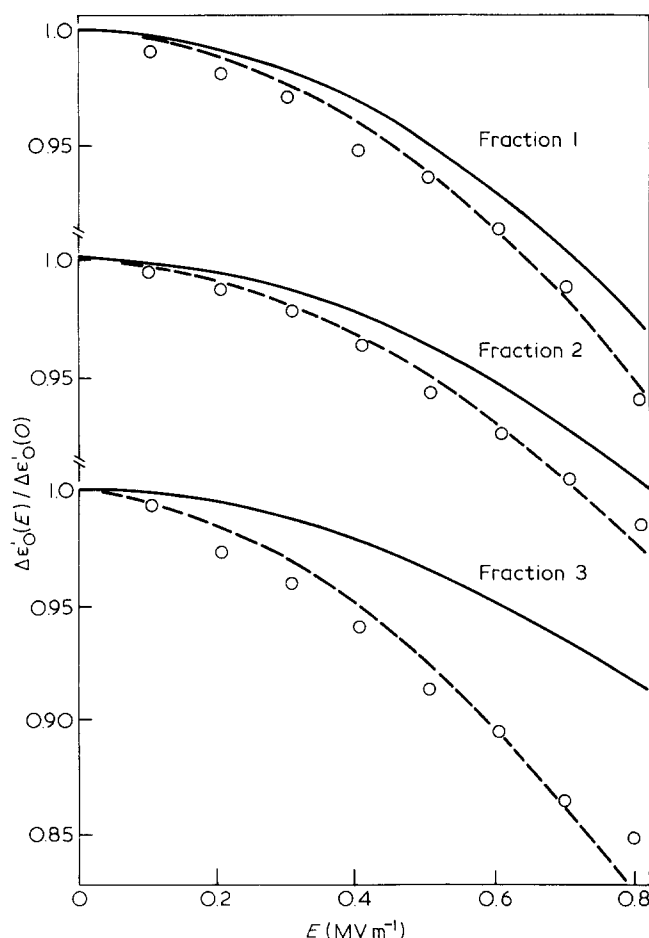


Figure 3 The dependence of $\Delta\epsilon'_0(E)/\Delta\epsilon'_0(0)$ on E for fractions 1, 2 and 3 in toluene at 0.4 kg m^{-3} and 31.5° . Solid lines calculated with low-field dipole values and broken lines for 'best-fit' dipole values, these values being specified in the Table. To avoid overlap, curves for fractions 1 and 2 are displaced vertically as indicated by the ordinate scale

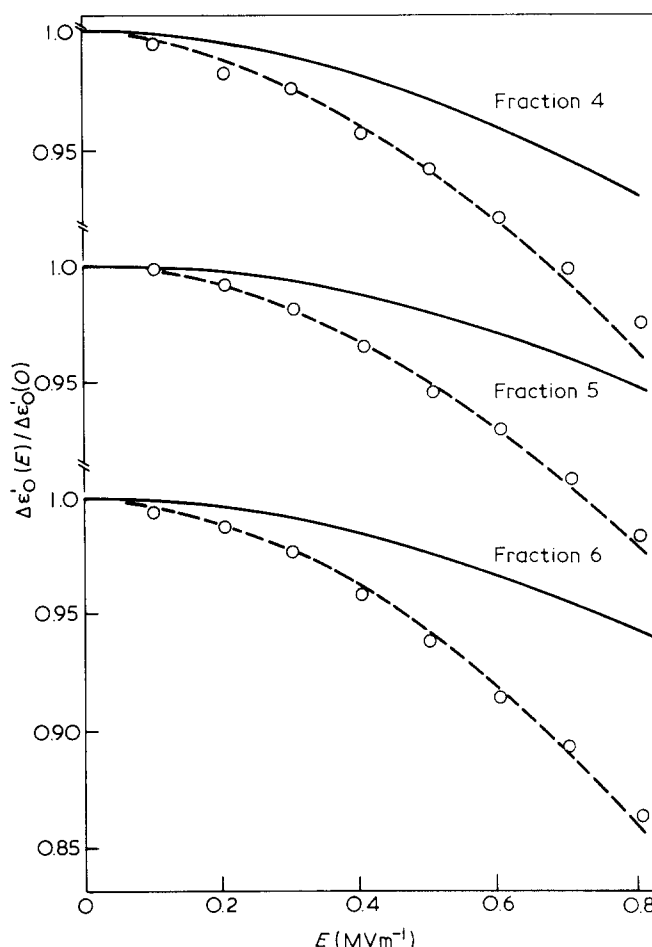


Figure 4 The dependence of $\Delta\epsilon'_0(E)/\Delta\epsilon'_0(0)$ on E for fractions 4, 5 and 6 in toluene at 0.4 kg m^{-3} and 31.5° . Solid lines calculated with low field dipole values and broken lines for 'best-fit' dipole values, these values being specified in Table 1. To avoid overlap, curves for fractions 4 and 5 are displaced vertically as indicated by the ordinate scale

$\Delta\epsilon'_0(E)/\Delta\epsilon'_0(0)$ as a function of E and the theoretical curves (solid lines) for the various fractions in terms of equation (1) and the low field dipole moments quoted in Table 1. In all cases the saturation is more marked than would be predicted on the basis of these low field dipole moments. Better agreement can be obtained with equation (1) if the effective dipole moment involved in χ is larger than given by the Guggenheim equation. The required dipole moments for best fit behaviour according to equation (1) are also given in Table 1 as high field values and the loci of the curves based on these values are shown in Figures 3 and 4 by broken lines. Although not very marked there is some trend in that the discrepancy appears to be largest for the smallest macromolecule (fraction 6), and for the largest macromolecule (fraction 1) it is barely outside experimental error. The discrepancies are less pronounced than would result from application of our previous model⁴ which does not properly take into account the situation of a d.c. field plus sensing field as does Kielich's theory¹³. It may well be that a failure to take account of an internal field correction in terms of an ellipsoidal cavity in the Kielich model is the cause for the present, remaining imperfections. Alternatively, it is possible that the magnitude of the dipole is itself field dependent. Such a situation is quite possible since there are indications that the poly(isocyanates) have some flexibility¹². However, if a field enhancement of dipole were operative one would

expect the high molecular weight samples, which have the highest flexibility, to show the most discrepancy. Also, the form of field dependence given by equation (1) would be incorrect and there is no indication of such a failure of functional form. More definitive answers as to the remaining differences between theory and observation require the development of appropriate models to take these effects into account.

As well as dielectric saturation, shifts in the critical frequencies to higher values were observed on the application of d.c. fields. The largest observed change occurs with fraction (1) under the maximum field. Figure 5 shows this in terms of a plot of $\log(v/u)$ against $\log f$ in which v and u are the arc lengths from the high frequency and low frequency limits of ϵ' to the datum point in the Cole-Cole semi-circles¹¹. In such a plot, $\log f_c$ is given by the condition $v = u$ and in the case illustrated results in a shift of f_c from 1150 to 1320 Hz on the application of 0.8 MV m^{-1} . Such an increase in critical frequency has been predicted¹⁴⁻¹⁶ and observed previously with poly(γ -benzyl-L-glutamate)^{4,14}. If we neglect the influence of polarizability in field induced alignment then according to the theories of Benoit¹⁵ and Beevers *et al.*¹⁶ the ratio of critical frequency under the influence of a field E to the field free value is given by

$$f_c(E)/f_c(0) \approx [1 + 0.1\chi^2] \quad (2)$$

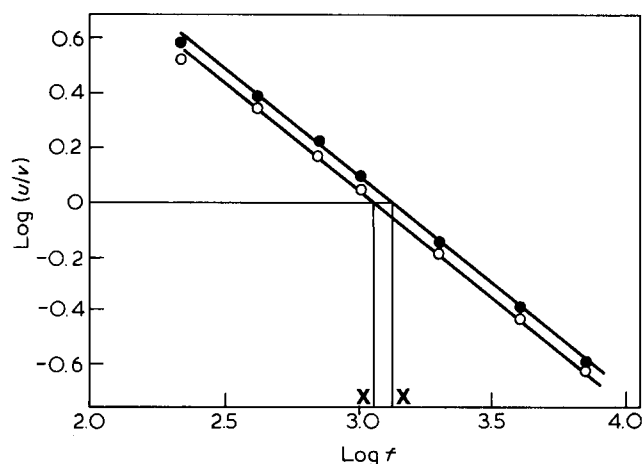


Figure 5 Plots derived from Cole-Cole arcs for locating the critical frequencies. v and u are the arc lengths from data points on the Cole-Cole semicircle to the high and low frequency axial intercepts respectively¹¹. Results are for fraction (1) at 0.4 kg m^{-3} in toluene at 31.5° and (○) zero or (●) 0.8 MV m^{-1} fields. Points (x) define the critical frequencies

This relation predicts a shift of critical frequency from 1150 to 1250 Hz for fraction (1) ($\mu = 4.8 \times 10^{-27} \text{ C.m.}$) under the experimental conditions of $E = 0.8 \text{ MV m}^{-1}$ and $T = 304.5 \text{ K}$. Any field induced dipole, whether due to polarizability or field induced alterations in chain conformation would increase the shift and could be the reason for its somewhat larger experimental magnitude: alternatively internal field corrections could also account for these differences. Similar but smaller shifts were observed at lower fields and for the lower molecular weight fractions. Their magnitudes, however, were too low for accurate quantitative assessment.

REFERENCES

- Bur, A. J. and Fetters, L. J. *Chem. Revs.* 1976, **76**, 727
- Block, H., Gregson, E. M., Ritchie, A. and Walker, S. M. *Polymer* 1983, **24**, 859
- Rubingh, D. N. and Yu, H. *Macromolecules* 1974, **7**, 930
- Block, H. and Hayes, E. F. *Trans. Faraday Soc.* 1970, **66**, 2512
- Block, H. in 'Poly(γ -benzyl-L-glutamate) and other glutamic acid, γ -ester containing polymers', Gordon and Breach Science Publishers Ltd., (London), 1983, in press
- Coles, H. J., Gupta, A. K. and Marchal, E. *Macromolecules* 1977, **10**, 182
- Sashoua, V. E., Sweeney, W. and Tietz, R. F. *J. Am. Chem. Soc.* 1960, **82**, 866
- Grubisic, Z., Remp, P. and Benoit, H. *J. Polym. Sci. B.* 1976, **5**, 753
- Berger, M. N. and Tidswell, B. M. *J. Polym. Sci. Polym. Symp.* 1973, **42**, 1063
- Guggenheim, E. A. *Trans. Faraday Soc.* 1949, **45**, 714
- Cole, K. S. and Cole, R. M. *J. Chem. Phys.* 1941, **9**, 341; Hill, N. E., Vaughan, W. E., Price, A. H. and Davies, M. 'Dielectric Properties and Molecular Behaviour' 1969, Van Nostrand Reinhold Co.
- Bur, A. J. and Roberts, D. E. *J. Chem. Phys.* 1969, **51**, 406; Tsvetkov, V. N., Ryumtsev, Ye. I., Aliyev, F. M. and Shtennikova, I. N. *Eur. Polym. J.* 1974, **10**, 55; Tsvetkov, V. N., Ryumtsev, Ye., Aliyev, F. M., Shtennikova, I. N. and Savvon, S. M. *Polym. Sci. USSR* 1974, **16**, 1627; Yu. H., Bur, A. J. and Fetters, L. J. *J. Chem. Phys.* 1966, **44**, 2468; Bur, A. J. *J. Chem. Phys.* 1970, **52**, 3813; Lochhead, R. Y. and North, A. M. *J. Chem. Soc. Faraday Trans. II* 1972, **68**, 1089; Ryumtsev, Ye. I., Aliyev, F. M. and Tsvetkov, V. N. *Polym. Sci. USSR. A* 1975, **17**, 1967; Tsvetkov, V. N., Ryumtsev, Ye. I., Pogodina, N. V. and Shtennikova, I. N. *Eur. Polym. J.* 1975, **11**, 37; Anderson, J. S. and Vaughan, W. E. *Macromolecules* 1975, **8**, 454; Beevers, M. S., Garrington, D. C. and Williams, G. *Polymer* 1977, **18**, 540
- Kielich, S. 'Dielectric and related molecular processes' Vol. 1, Chem. Soc., Specialist Periodical Reports, 1972, p. 192
- Ullman, R. *J. Chem. Phys.* 1972, **56**, 1869
- Benoit, H. *Ann. Phys. (Paris)* 1951, **6**, 561
- Beevers, M. S., Crossley, J., Garrington, D. C. and Williams, G. *J. Chem. Soc. Faraday II* 1976, **72**, 1482