

Figure 5 Meridional scan after poling

(001) reflection from form I in this scan and hence estimate the amount of phase I prior to poling. After poling, however, as shown in Figure 5, there is a drastic reduction in the form II (002) intensity without a corresponding increase in the form I (001) reflection. We therefore conclude that the reduction in the form II (002) intensity is due to a structure factor change and not due to a substantial degree of form II to form I conversion. A low structure factor for the (002) reflection of form IIp can be obtained either by raising the chain by $0.22c$ as it rotates or by lowering it by $0.28c$. Rotation without translation, or with a translation of $0.5c$, would leave the structure factor unchanged. We therefore conclude that the reduction in intensity of the (002) reflection on poling implies a translation of about $c/4$ on rotation.

If one assumes that the unit cell and the chain conformations do not change on rotation, then a shift of $0.22c$ on rotation to form the structure shown in Figure 1 leads to closest interchain atomic contacts of 2.76 \AA for fluorine—

fluorine contacts, 2.78 \AA for fluorine—hydrogen contacts and 2.73 \AA for hydrogen—hydrogen contacts. These are all reasonable values; hence the proposed rotation and translation can be accommodated without a major change in the lattice parameters.

CONCLUSIONS

We have confirmed that a new polar modification of PVDF exists and that it is present in conventionally poled samples of uniaxially oriented PVDF initially in crystal form II. It is possible, therefore, that the piezoelectric and pyroelectric activity of our initially form II samples arises as an intrinsic response of the non-centrosymmetric form IIp.

Alternatively, the crystal phase may act as an inert but polar 'filler' which produces internal fields in the amorphous phase. Piezoelectric and pyroelectric activity may then arise from the changes in dimension and permittivity of the amorphous phase with stress or temperature. The lower activity of form II samples compared with form I is then a natural consequence of the lower dipole moment of the polar form II and a general similarity of the behaviour of form I and form II samples is to be expected since the major effects are due to changes in the common amorphous phase.

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REFERENCES

- 1 Rushworth, A. *PhD Thesis*, University of Leeds, UK (1977)
- 2 Hasegawa, R., Takahashi, Y., Chatani, Y. and Tadokoro, H. *Polym. J.* 1972, 3, 5, 660–610
- 3 Davis, G. T., McKinney, J. E., Broadhurst, M. G. and Roth, S. C. *J. Appl. Phys.* 1978, 49, 10, 4998–5002

Some kinetic aspects of the radiation grafting of acrylic acid to nylon-6

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INTRODUCTION

γ -irradiation of nylon-6 (NY) immersed in aqueous acrylic acid (AA) induces grafting and homopolymerization¹. The influence of reaction variables on both processes has been described previously^{2–5} and the kinetics of the homopolymerization of AA discussed in detail⁶. We now attempt to provide a more quantitative description of the heterogeneous grafting reaction.

Previous kinetic analyses of other radiation grafting systems⁷ have been basically similar to those applied to conventional, free radical, homogeneous homopolymerization. Recent theoretical treatments^{8,9} have dealt with the influence of monomer diffusion on the rate of grafting and the molecular weight of the graft. Earlier results³ for the present system indicated that monomer diffusion apparently plays no dominant role in the kinetics of grafting, but it should be emphasised that NY/AA is not a typical grafting system, since cupric chloride is always included as a retarder and the overall kinetics are consequently much affected by its presence.

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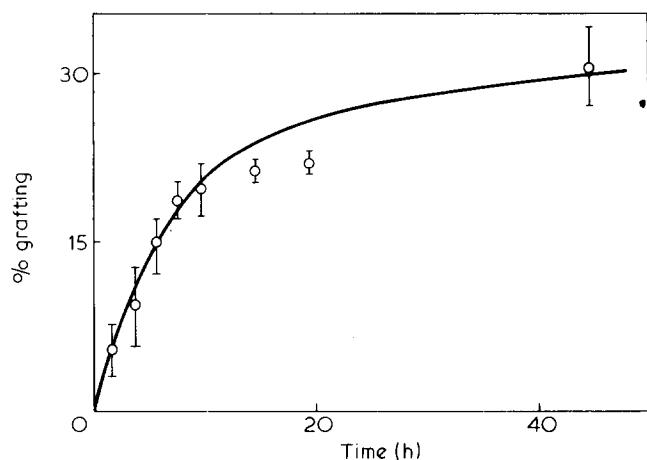


Figure 1 Percentage grafting versus irradiation time for $[\text{CuCl}_2] = 1.0 \text{ mol m}^{-3}$ in bulk monomer solution. Data bars indicate overall uncertainty based on (i) data for several films in the same ampoule, (ii) similarly irradiated films in different ampoules and (iii) repetition of whole grafting experiment

Table 1 Influence of cupric chloride on the grafting of AA to NY

$[\text{CuCl}_2]$ in bulk solution (mol m^{-3})	$[\text{Cu}^{2+}]$ in grafted film (ppm)	Percentage grafting	\bar{M}_n (kg mol^{-1})	\bar{M}_w (kg mol^{-1})
1.0	1.9 ± 0.21	5.2 ± 2.5	37.2	48.0
0.1	0.72 ± 0.14	5.4 ± 2.5	105	176
0.05	0.38 ± 0.14	7.4 ± 3.5	128	490

EXPERIMENTAL

Materials

Cupric chloride (AnalaR $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was used as received and AA was purified as described previously⁶. Film of NY was Soxhlet extracted with methanol for 24 h, vacuum dried at 313K for five days and then stored in a desiccator.

Irradiation

Glass ampoules, containing strips of NY film ($0.01 \text{ m} \times 0.05 \text{ m} \times 220 \mu\text{m}$) immersed in aq. AA (always at a fixed concentration of 10% vol $\equiv 1.46 \text{ mol dm}^{-3}$) and cupric chloride at different desired concentrations, were outgassed by freeze thaw cycles and sealed off at a nominal pressure of $6.6 \times 10^{-3} \text{ Nm}^{-2}$. The ampoules were then exposed to γ -radiation from a ^{60}Co source located at the University of Salford at a constant temperature of 303K and a dose rate of 3.1 mW kg^{-1} , as determined by Fricke dosimetry.

Post irradiation

After irradiation the grafted films were washed in warm water, Soxhlet extracted with de-ionized water to remove occluded homopolymer and dried at 313K *in vacuo* to constant weight (W). The percentage grafting was obtained as $100(W - W_0)/W_0$, where W_0 is the initial weight of film prior to irradiation.

The poly-AA grafts were isolated from the NY backbone by the following procedure, which has been shown¹⁰ to have no deleterious effect on the grafts: glass ampoules, containing grafted film immersed in an excess of conc. HCl, were outgassed and sealed off. They were maintained at 313K for 24 h to hydrolyse the NY to low molecular weight products, which were removed by dialysis against de-ionized water for

48 h. The residual grafts were methylated with diazomethane as described previously⁶.

Molecular weights

Molecular weights \bar{M}_n and \bar{M}_w of the grafts in their methylated form, i.e. poly(methyl acrylate), were measured by procedures reported earlier⁶. The degree of polymerization was obtained by dividing the molecular weight expressed in kg mol^{-1} by that of the segment, $0.086 \text{ kg mol}^{-1}$.

PROCEDURE AND RESULTS

The influence of total dose (equivalent to irradiation time) on the percentage grafting is illustrated in Figure 1 for the concentration of AA in the bulk solution already quoted and for that of CuCl_2 in the bulk solution equal for 1.0 mol m^{-3} . The plot is typical of many heterogeneous grafting systems, viz. grafting proceeds at a steady rate initially and thereafter slows down to an almost zero rate at large doses. The general form is similar for different concentrations of CuCl_2 in the solution. The initial rate R_g is calculated from the initial slope.

Variation of $[\text{CuCl}_2]$ was selected as the means of effecting changes in the kinetic chain lengths of the grafts and hence in the actual chain lengths obtained by molecular weight measurements. For this purpose, values of $[\text{CuCl}_2] = 1.0, 0.1$ and 0.05 mol m^{-3} were used, maintaining the dose and all other potential variables constant. In principle, a large dose would have been convenient for obtaining a high yield of the grafts. However, for $[\text{CuCl}_2] = 0.05 \text{ mol m}^{-3}$, irradiation times longer than *ca.* 3 h yielded a crosslinked gel of poly-AA in the monomer solution, which vitiated removal of the grafted film. Hence a constant irradiation time of 2 h was adopted for all three samples.

Copper contents of grafted films were determined via neutron activation analysis at the Universities Research Reactor, Risley, Lancashire England (courtesy of Dr G. R. Gilmore). For this purpose an attempt was made to simulate closely the actual grafting environment. Hence grafted films were not subjected to the extraction procedure but were merely vacuum dried prior to analysis. Characteristics of the grafts are assembled in Table 1.

KINETIC ANALYSIS

Previous work on this system²⁻⁴ has afforded the following relationship in which $[M]$ denotes the concentration of AA and I is the radiation intensity:

$$R_g \propto [M]^{1.2} [\text{CuCl}_2]^{-0.3} I^{0.7} \quad (1)$$

For purely bimolecular termination (rate constant k_t) between growing radicals the exponents of $[\text{CuCl}_2]$ and I in equation (1) would be 0 and 0.5 respectively. If termination were exclusively via reaction of radicals with cupric ions (rate constant $k_{t\text{Cu}}$), these exponents would have values of -1.0 and 1.0 respectively, as found for homopolymerization^{2,3}. The observed exponents in equation (1) provide evidence that termination in this grafting system occurs by both processes, and we assume that these are the sole modes of termination.

On this assumption, coupled with the further ones that (a) grafting emanates from radical sites on the NY generated

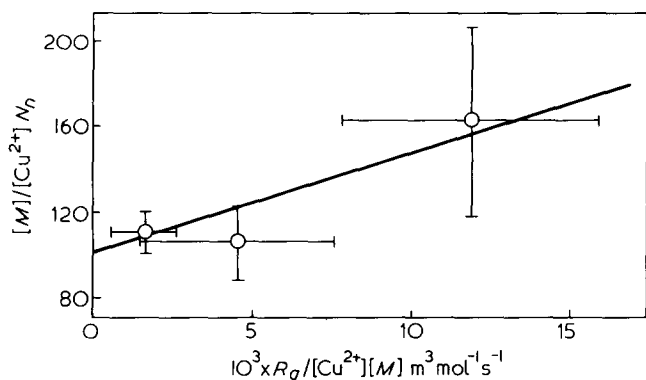


Figure 2 Estimation of rate constant ratios according to equation (4)

by direct action of γ -radiation, (b) there are no chain transfer processes and (c) the volumes of the components of the swollen film are additive, a simplified rate expression (equation 2) can be derived on the basis of a stationary state hypothesis. In it the rate of propagation (rate constant k_p) is identified with R_g and the rate of initiation is denoted by R_i :

$$R_i = (2k_t/k_p^2)R_g^2/[M]^2 + (k_{tCu}/k_p)[Cu^{2+}]R_g/[M] \quad (2)$$

It was not possible to obtain consistent solutions from equation (2) for the desired ratios k_{tCu}/k_p and $2k_t/k_p^2$ on account of the uncertainties in the experimental quantities and in R_i . The latter arises from the form of R_i (equation 3) in which ρ is the density of NY, N_A is the Avogadro number and G denotes the G (radical) value of NY. Unfortunately, there is no definitive value available for G , the reported range¹⁰⁻¹⁵ lying between 0.7 and 7.0.

$$R_i = G\rho/1.6 \times 10^{-17}N_A \quad (3)$$

Fortunately, the required ratios can be derived by using the relation between R_g and the number-average degree of polymerization of the grafts, \bar{M}_n . The simple statistical treatment of Bamford *et al.*¹⁶ has been invoked in deriving this expression[†] which we have then recast in the following equivalent forms for convenience of graphical manipulation:

$$[M]/[Cu^{2+}]\bar{M}_n = (2k_t/k_p^2)R_g/[Cu^{2+}][M] + (k_{tCu}/k_p) \quad (4)$$

$$[M]^2/R_g\bar{M}_n = (k_{tCu}/k_p)[M][Cu^{2+}]/R_g + (2k_t/k_p^2) \quad (5)$$

With regard to equations (4) and (5) it is important to emphasise that grafting occurs heterogeneously, i.e. in a swollen film comprising several species. The weight of the film, the dry weight after extraction and analysis of the composition of the film are used in conjunction with the densities

[†] With regard to the radical (R \cdot)–radical (R \cdot) part of chain termination, the contributions due to combination and disproportionation are not known definitely for AA. Consequently, in the expression

$$\text{Rate of termination} = 2k_t[R\cdot]^2,$$

the rate constant k_t is defined as

$$k_t = k_{tc}/2 + k_{td}$$

where k_{tc} and k_{td} are the rate constants for termination by combination and disproportionation respectively.

of the constituents to yield parameters in the appropriate units, viz. $[Cu^{2+}]$ and $[M]$ in mol/(m³ of swollen film) and R_g in mol/m³ of swollen film/s. The resultant plots corresponding to equations (4) and (5) are given in Figures 2 and 3 respectively. Using the slopes and intercepts, the average rate constant ratios are:

$$k_{tCu}/k_p = 100 \pm 10$$

$$2k_t/k_p^2 = 4000 \pm 2000 \text{ mol m}^{-3}\text{s}$$

The uncertainties in derived and experimental quantities comprise (a) accuracy of measuring \bar{M}_n by membrane osmometry, (b) accuracy quoted for determination of copper by neutron activation analysis, (c) reproducibility of grafting experiments under identical conditions to obtain the slope and thence R_g . (Determination of $[M]$ is considered to be subject to negligible error.)

DISCUSSION

Although the principal interest here lies in grafting, it will be useful to compare the results with those obtained for the simultaneous homopolymerization (see Table 2).

Value of k_{tCu}/k_p

For the radiation induced homopolymerization of AA we have noted that k_{tCu}/k_p is ca. 50 times smaller than the value reported here for grafting. In homopolymerization, termination proceeds solely by a one electron transfer mechanism with cupric ions. It will be necessary to examine if the mixed modes of termination and/or other factors are responsible for the increased value of k_{tCu}/k_p in grafting.

In view of the fluid and viscous natures of the homopolymerization and grafting media respectively, the role of the terminator, Cu^{2+} , would seem important, *a priori*. The force opposing the diffusion of an ion is dependent on the ionic radius and the viscosity of the medium. If one postulates that the chemical nature, and hence the size, of the solvated cupric ion is the same in both media (and there is evidence that this is so, except at values of $[M]$ much higher than used here⁴), then the diffusion coefficient of the cupric ion should be smaller in the film than in the aqueous bulk medium; hence k_{tCu} (graft) will be smaller than k_{tCu} (homo). Rather surprisingly, Meares¹⁷ has shown that the activation energies for diffusion of counterions in solution and in a swollen, ionized, carboxylic resin are very similar in magnitude. However, irrespective of whether k_{tCu} (graft) is equal to or less than k_{tCu} (homo), the experimental finding that (k_{tCu}/k_p) (graft) $>$ (k_{tCu}/k_p) (homo), indicates that k_p (graft) must be much smaller than k_p (homo) and we shall make a semi-quantitative estimate of this effect.

Schulz¹⁸ has derived the following interrelation among k_p and the diffusion coefficients D_M and D_R of the monomer and the reacting chain radical respectively:

$$k_p = 3.4 \times 10^{15} (D_M + D_R) \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

In grafting, the poly-AA radicals have a restriction imposed on their motion, since they are localized on the NY backbone; hence $(D_M + D_R) \approx D_M$. For the vapour phase grafting of the same system, Kachan and Mertvichenko¹⁹ obtained a value of $D_M \approx 10^{-16} \text{ m}^2 \text{ s}^{-1}$. Consequently, in the present

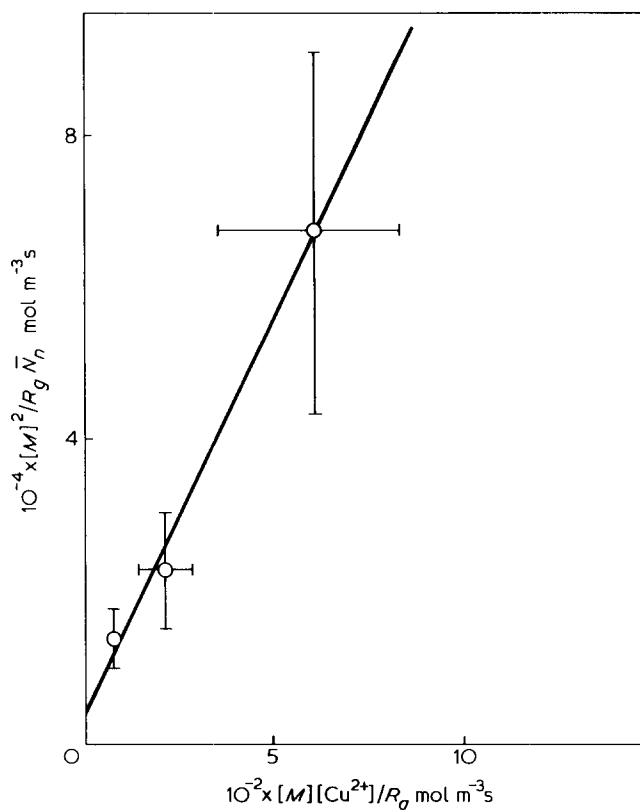


Figure 3 Estimation of rate constant ratios according to equation (5)

Table 2 Comparison of results for grafting and homopolymerization at different concentrations of CuCl_2 in the bulk monomer solution

Process	$[\text{Cu}^{2+}]^a$	$[M]^a$	R^b	\bar{M}_n (kg mol^{-1})
Homopolymerization	1.0	1460	27.7	51.4
Grafting	$(3.34 \pm 0.37) \times 10^{-2}$	1610	323 ± 160	37.2
Homopolymerization	0.1	1460	45.2	560
Grafting	$(1.27 \pm 0.25) \times 10^{-2}$	1610	335 ± 172	105
Homopolymerization	0.05	1460	124	1350
Grafting	$(0.67 \pm 0.25) \times 10^{-2}$	1610	461 ± 240	128

^a Units of mol. m^{-3} for homopolymerization and $\text{mol}/(\text{m}^3$ of swollen film) for grafting

^b Rate expressed in $\text{mol m}^{-3} \text{h}^{-1}$ for homopolymerization, and R_g expressed in $\text{mol}/(\text{m}^3$ of swollen film)/h for grafting

grafting system, $k_p = (3.4 \times 10^{15}) (10^{-16}) \approx 0.3 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is *ca.* 10–100 times smaller than the corresponding one for the homopolymerization of similar acrylic monomers²⁰. This reduction in propagation constant can thus account, at least partially, for the large increase in $k_t \text{Cu}/k_p$ and for the prevalence of termination over propagation.

Value of $2k_t/k_p^2$

Bimolecular termination contributes here to grafting but not to homopolymerization. Comparison with homopolymerizations wherein such termination does occur²⁰ shows that the values of $2k_t/k_p^2$ for the latter are *ca.* 100 times greater than the present value of $4 \times 10^3 \text{ mol m}^{-3} \text{ s}$ for grafting. Similarly, in systems where both grafting and homopolymerization are terminated bimolecularly^{21,22}, it is generally found that $(2k_t/k_p^2)(\text{graft}) < (2k_t/k_p^2)(\text{homo})$. Since we have seen that k_p (graft) is smaller than k_p (homo), it follows that $2k_t$ (graft) $\ll 2k_t$ (homo), where k_t (homo) is the bimolecular

termination constant, which would obtain in the bulk solution, if cupric chloride were totally absent. This conclusion is consistent with the immobilization of one end of the graft as well as the high viscosity^{9,23} of the medium containing the reactive end.

Molecular weights

The molecular weights listed in *Tables 1* and *2* show a discernible trend for the distribution of the grafts (as given by the ratio \bar{M}_w/\bar{M}_n) to broaden with decreasing concentration of cupric chloride. This suggests that possible transfer reactions, assumed to be absent, are indeed of minor importance provided that Cu^{2+} ions are present at a high enough concentration for transfer to them (i.e. termination) to be a more important competing process.

The observation that \bar{M}_n (graft) $< \bar{M}_n$ (homo) is the opposite of what is usually found^{16,24} in heterogeneous grafting accompanied by homopolymerization. Since the rate of homopolymerization is more strongly influenced by $[\text{CuCl}_2]$ than is R_g , the intuitive explanation based on more efficient termination in homopolymerization cannot be tenable, and here again the main factor would seem to be the decreased value of k_p in grafting. Although k_p in bulk polymerization of liquid monomers is not expected to be diffusion controlled except at high conversion²⁵ (*ca.* 40%), Zimmerman has demonstrated²⁶ that it is possible for the activation energy of diffusion of a monomer to exceed that of propagation in a semicrystalline matrix such as NY.

Magat *et al.*¹⁰ have discussed the nature of possible chain transfer reactions in the radiation grafting of styrene to NY in the presence of an added swelling agent but in the absence of CuCl_2 (since styrene is much less radiation sensitive than AA). However, as here, it was not possible to assess them quantitatively due to the lack of relevant transfer constants.

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REFERENCES

- Huglin, M. B. and Johnson, B. L. *J. Polym. Sci. (A-1)*, 1969, 7, 1379
- Huglin, M. B. and Johnson, B. L. *J. Appl. Polym. Sci.* 1972, 16, 921
- Huglin, M. B. and Johnson, B. L. *Kolloid Z. Z. Polym.* 1971, 249, 1080
- Huglin, M. B. and Johnson, B. L. *Eur. Polym. J.* 1972, 8, 911
- Huglin, M. B., Johnson, B. L. and Richards, R. W. *Eur. Polym. J.* 1973, 9, 579
- Huglin, M. B., Johnson, B. L. and Richards, R. W. *J. Polym. Sci. - Polym. Chem. Edn.* 1976, 14, 1363
- Odian, G., Sobel, M., Rossi, A., Klein, R. and Acker, T. *J. Polym. Sci. (A)* 1963, 1, 639
- Odian, G., Henry, R., Koenig, R., Mangaraj, D., Trung, I. D., Chao, B. and Derman, A. *J. Polym. Sci. Polym. Chem. Ed.*, 1975, 13, 623
- Imre, K., Odian, G. and Rabie, A. *J. Polym. Sci. Polym. Chem. Edn.* 1976, 14, 3045
- Magat, E. E., Miller, I. K., Tanner, D. and Zimmerman, J. *J. Polym. Sci. C*, 1964, 4, 615
- Kurilenko, A. I., Smetanina, L. B. and Aleksandrova, L. B., Karpov, V. L. *Polym. Sci. USSR* 1965, 7(11), 2123
- Graves, C. T. and Ormerod, M. G. *Polymer* 1963, 4, 81

- 13 Brodskii, A. I., Fumenko, A. S., Abramova, T. M., Dar'Yeva, E.P. Galina, A. A., Furman, Y. G., Kotorlenko, L. A. and Gardenina, A. P. *Polym. Sci. USSR* 1965, 7, 124
- 14 Kurilenko, A. I., Glukhor, V. I. *Dokl. Acad. Nauk. SSR* 1966, 166, No. 4, 901
- 15 Whiffen D. H. and Abraham, R. J. *Trans. Faraday Soc.* 1958, 54, 1291
- 16 Bamford, C. H., Barb, W. G., Jenkins, A. D., Onyon, P. F. 'The Kinetics of Vinyl Polymerization by Radical Mechanisms', Butterworths, London, 1958
- 17 Meares, P. 'Diffusion in Polymers' (Ed. J. Crank and G. S. Park) Academic, London, Ch 10 (1968)
- 18 Schulz, G. V. *Z. Phys. Chem.* 1956, 8, 284
- 19 Kachan, A. A., Mertvichenko, Y. F. *Vysokomol Soedin* 1967, A9 1424
- 20 Korus, R. and O'Driscoll, K. F. *The Polymer Handbook* (Eds J. Brandrup, E. H. Immergut), 2nd Edition, Wiley, New York, Section II-45 (1975)
- 21 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *J. Polym. Sci. (C)* 1972, 37, 205
- 22 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *J. Appl. Polym. Sci.* 1972, 16, 1017
- 23 North, A. M. *Progress in High Polymers* (Ed. J. C. Robb and F. W. Peaker) Vol 2, Heywood, London, (1968)
- 24 Guthrie, J. T., Huglin, M. B. and Phillips, G. O. *Polymer* 1977, 18, 521
- 25 Hayden, P. and Melville, H. W. *J. Polym. Sci.* 1960, 63, 201
- 26 Zimmerman, J. *J. Polym. Sci.* 1960, 44, 107

The effect of swelling on the longitudinal acoustic mode in crystalline α,ω -methoxy-poly(ethylene oxide)

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Low molecular weight poly(ethylene oxide) crystallizes into well defined layer structures. Raman scattering from the longitudinal acoustic mode (LAM) of vibration of the lamellae is readily detected¹⁻³. The experimental evidence¹⁻⁶ favours a structure in which crystalline and non-crystalline layers alternate. It is possible to swell the non-crystalline layers with low molecular weight liquids, and oligomers of ethylene oxide have been used for this purpose^{2,3,7}. For α,ω -hydroxy-poly(ethylene oxide) of molecular weight 2000 g mol⁻¹ swollen with α,ω -hydroxy-oligomers of various molecular weights less than $\bar{M}_n = 600$ g mol⁻¹, it is found^{2,3} that the LAM frequencies vary systematically with the lamella spacing ($l_x =$ thickness of crystalline plus non-crystalline layer) determined by small-angle X-ray scattering (SAXS). These results are given in *Figures 1(a)* and *2(a)*, where the hydroxy ended samples are denoted by molecular weight and suffix H. We plot $\nu_1 l_x$ and ν_3/ν_1 against l_x (ν_1 is the frequency of the LAM fundamental and ν_3 that of the third overtone). For the ideal case of crystalline lamellae vibrating independently of the non-crystalline layer, $\nu_1 l_x$ would increase with l_x and ν_3/ν_1 would be constant and equal to 3. Our results show a considerable effect of the non-crystalline layer on the LAM.

For the α,ω -hydroxy systems the effect of swelling is independent of the molecular weights of the oligomers studied ($\bar{M} = 106$ to $\bar{M}_n = 600$: see *Figures 1* and *2*). However the liquid properties of α,ω -hydroxy-poly(ethylene oxide) may be insensitive to molecular weight. For example^{8,9} the liquid density of α,ω -hydroxy-oligomers of ethylene oxide is constant at 1.12 g cm⁻³ (20°C). This is in contrast to the liquid densities of α,ω -methoxy-oligomers which increase from 0.94 g cm⁻³ ($\bar{M} = 134$ g mol⁻¹) to 1.08 g cm⁻³ ($\bar{M}_n = 600$ g mol⁻¹) and to 1.12 g cm⁻³ only in the high molecular weight limit of extrapolation. Hydrogen bonding, principally of hydroxy to ether oxygen, provides a rationalization of this effect. Consideration of this point prompted us to reinvestigate the effect of molecular weight of the swelling agent on the LAM under conditions where hydrogen bonding is absent.

Samples of α,ω -hydroxy-poly(ethylene oxide) of molecular weights $\bar{M}_n = 2000, 600$ and 200 g mol⁻¹, obtained from various commercial sources, were methoxylated by the procedure described elsewhere⁹. Methoxylated samples are denoted by the original molecular weight with suffix M. Conversion of hydroxy to methoxy was better than 98%. Molecular weight distributions were checked by gel permeation chromatography and were essentially unchanged by the methoxylation process. The crystallizable α,ω -methoxy-poly(ethylene oxide) 2000M had a narrow molecular weight distribution, $\bar{M}_w/\bar{M}_n = 1.03$. Dimethyldigol ($\bar{M} = 134$ g mol⁻¹) was Synchemica grade (Hopkins and Williams) used without further purification. Mixtures were prepared by melting at 70°C and shaking several times over a period of 30 min. Crystallization was at 25°C. LAM frequencies and lamella spacings were determined by laser Raman spec-

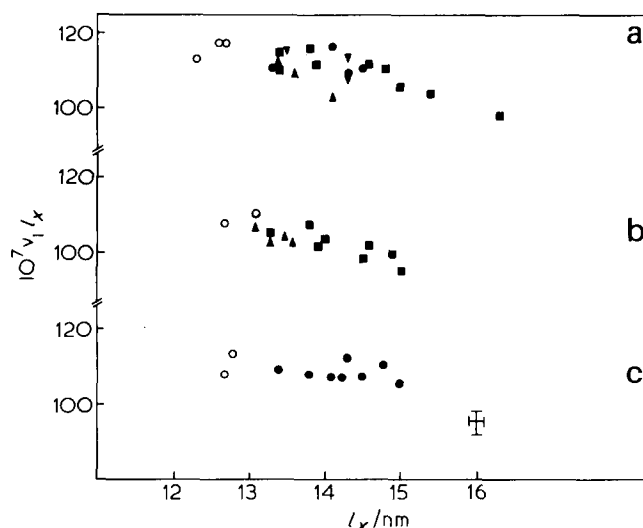


Figure 1 The variation of $\nu_1 l_x$ with l_x for mixtures of: (a) 2000H (○) with 106H (●), 200H (■), 400H (▼) and 600H (▲); (b) 2000M (○) with 200M (■) and 600M (▲); (c) 2000M (○) with 134M (●). The experimental error is indicated