Notes to the Editor

Raman scattering from the longitudinal acoustic modes of crystalline poly(ethylene oxide) swollen by oligomers of various molecular weights

Joyce M. Edward, R. D. Mulley*, G. A. Pape, C. Booth and I. W. Shepherd†
Departments of Chemistry and Physics, University of Manchester, Manchester M13 9PL, UK
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Low molecular weight poly(ethylene oxide) (PEO) crystallizes into well defined stacked lamella structures: several orders of Bragg scattering can be observed by small-angle X-ray scattering (SAXS)[1–4] and there is strong Raman scattering from the longitudinal acoustic modes (*LAM*) of the helices in the crystalline lamellae[5,6]. The evidence[1–6] 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[6–8], and we have examined[6] the Raman scattering from crystals of poly(ethylene oxide) of molecular weight $\bar{M}_n$ = 2000 swollen with oligomers of molecular weight $\bar{M}_n$ = 200. The *LAM* frequencies were found to vary systematically with the thickness of the non-crystalline layer. The experimental results for a given polymer swollen to different extents could be adequately described[6] in terms of the vibration of a composite rod[9] comprising a crystalline core (length l_c, density ρ_c, elastic modulus E_c) and non-crystalline ends (length $l_a/2$, density ρ_a, elastic modulus E_a) with l_a the only variable dependent on swelling. We have experimental evidence[6] for the constancy of l_c and the constancy of ρ_c and E_c seems self-evident. Possible variation in ρ_a with swelling would be unimportant in our experiments but variation in E_a might be significant. The assumption that E_a is constant, independent of swelling by an oligomer, seems reasonable in view of the high frequencies (10^{11}–10^{12} Hz) involved. Nevertheless we have thought it prudent to subject our assumptions to an experimental test and have therefore studied the Raman scattering from crystals of PEO 2000 which have been swollen to various extents by oligomers of various molecular weights.

Samples of α,ω-hydroxy-poly(ethylene oxide) were gifts from Hoechst Chemicals ($\bar{M}_n$ ~ 2000) and Shell Chemical Co. Ltd ($\bar{M}_n$ ~ 400, 600). Diethylene glycol (Shell Chemical Co. Ltd, commercial grade, *MW* = 106) and the samples 400 and 600 were used without purification; sample 2000 was purified as previously reported[6]. The mixtures were prepared as before[6]; the experimental details of the Raman and SAXS techniques have also been described[6].

The experimental results are summarized in *Table 1*. These are the Raman frequencies of the *LAM* fundamentals (υ_1) and third overtone (υ_3) and the lamellar spacing (l_x) measured by SAXS. Heats of fusion were determined from endotherm peak areas by differential scanning calorimetry (Perkin–Elmer DSC-2 or DSC-1B) and found to be constant, to ± 10 J/(g of PEO 2000), when corrected to 54°C: the near constancy of these values is consistent with a constant extent of crystallinity of the 2000 within the mixtures.

Table 1 Raman frequencies of the *LAM* fundamental υ_1 and third overtone υ_3 for PEO 2000 swollen by different weight fractions *W* of various low molecular weight oligomers. The SAXS spacing l_x is also shown

Weight fraction, *W*	υ_1 (cm^{-1})	υ_3 (cm^{-1})	l_x(nm)
W_{106}			
0.00	9.2	19.0	12.3
0.05	8.3	17.5	13.3
0.10	8.2	17.5	14.1
0.14	7.6	17.5	14.3
0.20	7.6	17.5	14.5
W_{400}			
0.10	8.5	18.8	13.5
0.21	7.8	18.5	14.3
0.31	7.5	18.5	14.3
W_{600}			
0.10	8.4	18.1	13.4
0.20	8.0	18.3	13.6
0.29	7.3	18.7	14.1

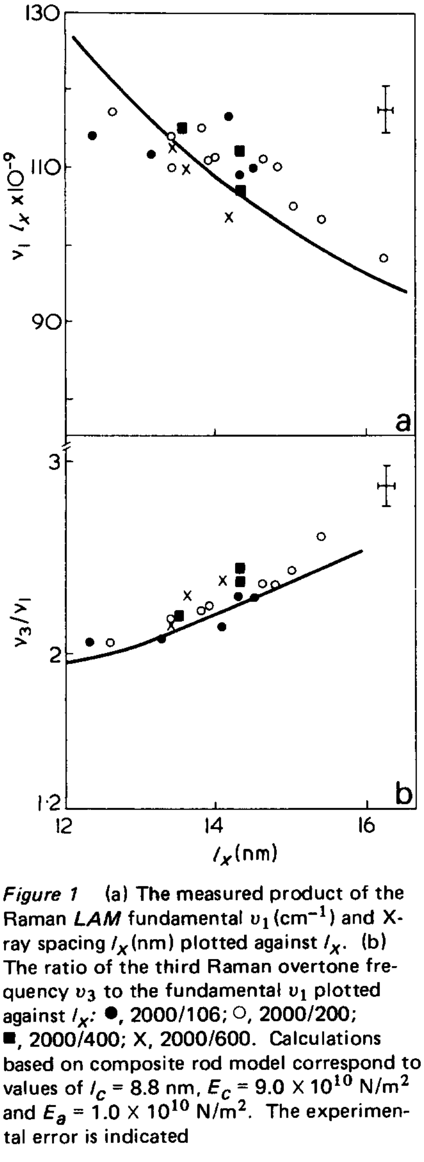

Figure 1 (a) The measured product of the Raman *LAM* fundamental υ_1(cm^{-1}) and X-ray spacing l_x(nm) plotted against l_x. (b) The ratio of the third Raman overtone frequency υ_3 to the fundamental υ_1 plotted against l_x: ●, 2000/106; ○, 2000/200; ■, 2000/400; X, 2000/600. Calculations based on composite rod model correspond to values of l_c = 8.8 nm, E_c = 9.0 × 10^{10} N/m^2 and E_a = 1.0 × 10^{10} N/m^2. The experimental error is indicated

The variations in the frequencies υ_1 and υ_3 with swelling are shown in *Figures 1a* and *1b* where $\upsilon_1 l_x$ and υ_3/υ_1 are plotted against l_x. The results previously obtained[6] for the 2000/200 system are also plotted. It can also be seen that, within the experimental error of about ±4%, the changes in frequency are independent of the molecular weight of the oligomer used in swelling.

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* Present address: ICI Limited, Plastics Division, Welwyn Garden City, Hertfordshire, UK.

† Present address: Department of Physics, Michigan Technological University, Houghton, Michigan 49931, USA.

The best fit to the data for the 2000/200 samples has been calculated previously[6] for the composite rod model[9] using the parameter values $l_c \sim 9$ nm, $E_c \sim 9 \times 10^{10} \mathrm{N/m^2}$ and $E_a \sim 10^{10} \mathrm{N/m^2}$. These theoretical lines are shown on *Figure 1* and can be seen to adequately represent the data for all the mixtures.

In summary, the data show that within the approximation of the composite rod model, the modulus of the amorphous layer, E_a, can be assumed constant and equal to 10^{10} $\mathrm{N/m^2}$.

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Effect of γ-irradiation on chemically crosslinked poly(dimethyl siloxane)

C. G. Delides and I. W. Shepherd*
Physics Department, Manchester University, Manchester M13 9PL, UK
(Received 9 June 1977)

INTRODUCTION

The processes of radiation or chemical crosslinking in poly(dimethyl siloxane) (PDMS) have been extensively studied by many workers[1–4]. The crosslink formation efficiency in PDMS introduced by a chemical agent (e.g. benzoyl peroxide) was found to decrease markedly as the peroxide concentration increased, apparently tending to zero at high values. Therefore it is not possible to obtain high crosslink densities by chemical means. On the other hand the crosslink density of networks formed by radiation can reach very high values. The effect of γ-radiation on rubbers that have already been chemically crosslinked has not been extensively studied. Bopp and Sisman[5] studied the effect of radiation on natural rubber chemically vulcanized by sulphur. No data have been published for PDMS. In this Note we report the effect of γ-radiation on a series of PDMS samples that have been crosslinked using different amounts of benzoyl peroxide. The effect of temperature on the rate of formation and quality of the networks during the chemical curing has also been studied.

EXPERIMENTAL

The material used in this study was a linear PDMS 5273-11-1 provided by ICI Ltd with molecular weight 7.7×10^4 as determined by g.p.c. techniques. Benzoyl peroxide was used for the chemical vulcanization. Accurately determined weights of peroxide dissolved in dichloromethane were added to PDMS gum. After thorough mixing the solvent (CH_2Cl_2) and dissolved gases were removed by putting the mixture under vacuum and heating to 44°C (boiling point of solvent ~41°C). Square moulds containing the samples were placed in a circulating air oven at 80°C for a few hours. Then the temperature was increased to 150°C and held constant for 24 h.

When the sheets were removed from the moulds they were exposed to γ-radiation in the ^{60}Co facility at Salford University. Doses ranged from 3.5 up to 500 Mrad at rates of 3.5 or 0.01 Mrad/h. The samples were annealed at 50°C for 12 h in order to remove any undesirable crystallinity[6]. The crosslink density was estimated from ball-bearing indentation[7,8], extension and swelling measurements[2,3]. The samples were characterized by the crosslink density $\langle n \rangle^{-1}$, where $\langle n \rangle$ represents the average number of monomer units between crosslinks, because this gives a clear picture of the network at the molecular level. It also has the advantage of providing a common base for comparison of the three types of experimental measurement.

RESULTS AND DISCUSSION

The variation in crosslink density with benzoyl peroxide concentration is shown in *Figure 1*. It is worth pointing out here that the two stage heating (80° and thereafter 150°C) plays an important role especially in the sample quality. Previous curing methods[2–4] in which samples are first held at ~120°C for a few minutes before increasing to ~150°C for 24 h, with or without pressure are not always successful. Bubbles of gas evolved during the crosslinking process are trapped in the network, especially when the sample is thick and the crosslink density high. This can be partly avoided by pressure control but the samples are then not uniform in thickness and their surfaces not smooth. Using the two stage curing the crosslink density seems to be independent of the sample thickness. no bubbles are present for any thickness or any peroxide concentration and the surfaces are extremely smooth with a very high degree of reflectivity.

Following an analysis described elsewhere[9] the crosslink density $\langle n \rangle^{-1}$ can be expressed as a function of the peroxide concentration C:

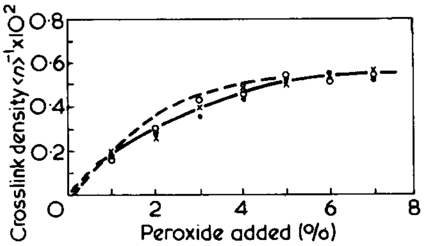

Figure 1 Crosslink density as a function of benzoyl peroxide concentration. ———, corresponds to experimental data; – – – –, to equation (1). ●, Swelling; ○, ball-bearing indentation; X, extension

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[*] Present address: Department of Physics, Michigan Technological University, Houghton, Michigan 49931, USA.