Pulsed n.m.r. of *cis*-polyisoprene: 2

R. Folland and A. Charlesby
Department of Physics, Royal Military College of Science, Shrivenham, Swindon, Wilts, UK
(Received 24 August 1978)

Pulsed n.m.r. spin–spin relaxation time measurements are reported for a commercial whole polymer sample of *cis*-polyisoprene which has been crosslinked to varying extents by γ-irradiation. The spin–spin relaxation decays at 150°C consist of two components, T_{2S} and T_{2L}, which are attributed to protons in a network structure (entangled or crosslinked) and in non-network molecules respectively. Comparison of the n.m.r. data with solubility measurements, which only detect the presence of a crosslinked network, provides a value for the average molecular weight for entanglements which is in the region of 40 000 to 50 000.

Part 2: Effects of radiation-induced crosslinking

INTRODUCTION

In the preceding paper (part 1) we demonstrated the sensitivity of T_2 in polyisoprene at high temperatures to the long range chain motions and to the presence of intermolecular couplings. In this paper we use the same technique to investigate more fully the effects of radiation-induced crosslinking on the spin–spin relaxation in a commercial whole polymer *cis*-polyisoprene. This represents an extension of our earlier work on polydimethylsiloxanes[1,2] in which we were able to show that under certain conditions, it is possible to detect the presence of a network, whether it be of a permanent nature formed by chemical crosslinks or of a dynamic nature produced by transient entanglement couplings. In a system containing both network and non-network material the former is revealed by the presence of a shorter T_2 component. This reflects the restricted nature of the long range chain mobility in the network in comparison with the non-network molecules which possess a much longer T_2. This situation can arise in unirradiated whole polymer of sufficiently high molecular weight for longer chain species to co-exist in the form of an entanglement network with shorter chain non-network molecules. A similar situation can arise in low molecular weight systems (not entangled) which have been partially crosslinked such that both sol and gel fractions are present.

EXPERIMENTAL

The material used in this study is a whole polymer synthetic *cis*-polyisoprene (Natsyn 2200) with molecular weight of $\bar{M}_n$ = 150 000 after milling. Degassed samples in evacuated tubes were irradiated at approximately 40°C using a ^{60}Co γ source at a dose rate of 2.7 Mrad/h. After irradiation part of the sample (~200 mg) was transferred to an n.m.r. tube and sealed under vacuum. The remaining portion was extracted to constant weight with boiling benzene in order to determine the gel content. N.m.r. samples of the extracted gel fractions were also prepared.

The n.m.r. spin–spin relaxation times were measured using the single echo, 90°–t–180°, pulse sequence with the equipment described in the preceding paper. The majority of the n.m.r. data was obtained at 150°C but both the unirradiated polymer and one of the extracted gel fractions (dose 5.8 Mrad) were also investigated as a function of temperature. Subsequent osmometric measurements showed that a small amount of degradation occurred at 150°C with $\bar{M}_n$ being reduced to 136 000 after 24 h at this temperature. *Figure 1* shows typical plots of $\ln A(t)/A(0)$ versus t for various radiation doses

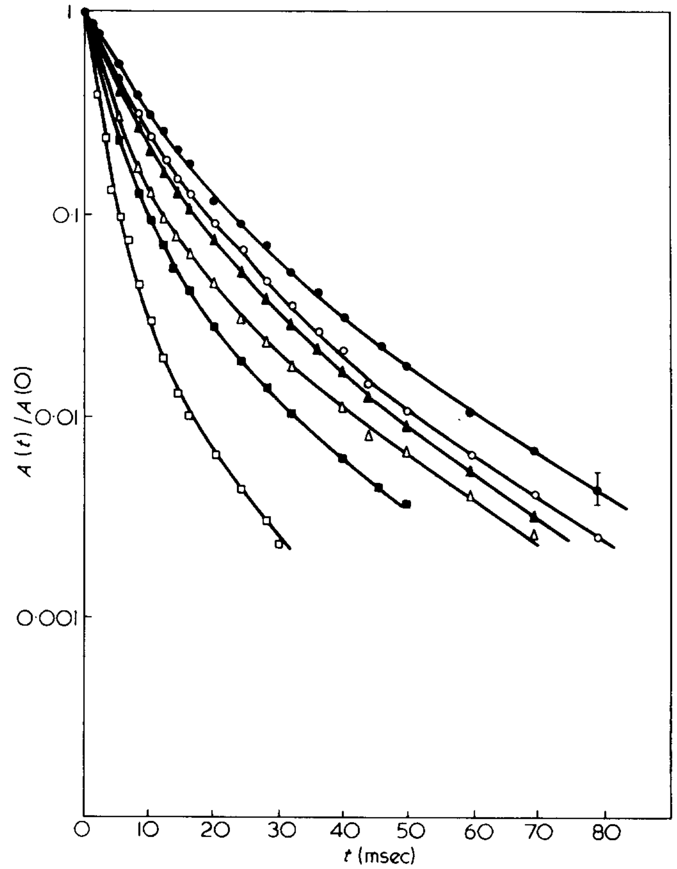

Figure 1 Proton spin–spin relaxation decays for polyisoprene at 150°C at various doses: (●) 0; (○) 3.0; (▲) 5.8; (△) 15.0; (■) 22.5 and (□) 52 Mrad respectively

0032–3861/79/020211–04$02.00

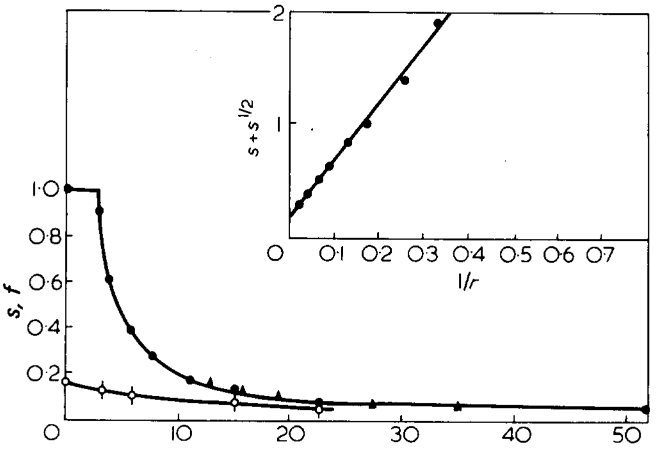

Figure 2 Sol fraction, *s*, from solubility data and n.m.r. *f* values as a function of radiation dose. (●) *s*, (○) *f* and (▲) *f* with virtual dose, r_e = 13 Mrad added. Inset: Charlesby–Pinner plot, $s + s^{1/2}$ vs. $1/r$, of the solubility data

where $A(O)$ and $A(t)$ are the signal amplitudes at times 0 and t, respectively.

RESULTS

Solubility data

Figure 2 shows the sol fraction, s, as a function of radiation dose, r. These data are seen to fit very well to the Charlesby–Pinner[3] relationship appropriate to a random molecular weight distribution.

$$s + s^{1/2} = 2r_g/r + \lambda \qquad (1)$$

where r_g is the gelation dose and $\lambda = 2G(S)/G(X)$ where $G(X)$ and $G(S)$ are the G values for crosslinks and main chain scission respectively. The G value for crosslinks is given by

$$G(X) = 4.8 \times 10^5/\bar{M}_w r_g \qquad (2)$$

We do not have a value for $\bar{M}_w$ of this sample but, since the data fit so well to equation 1, we shall assume a random molecular weight distribution where $\bar{M}_w = 2\bar{M}_n \sim$ 300 000. From the slope of the Charlesby–Pinner plot we obtain r_g = 2.4 Mrad giving $G(X) = 0.7$. We also obtain $\lambda = 0.15$ and assuming that this is due entirely to main chain scission $G(S) \sim 0.05$. A rough check on the above $G(X)$ value is provided by the solubility data for the two molecular weight fractions studied in the preceding paper with $\bar{M}_n$ = 15 000 and 84 000. For doses of 61 and 15 Mrad respectively these gave $s = 0.31$ and 0.11. For a monodisperse system we have[4,5]

$$-\frac{\ln s}{1 - s} = \frac{r}{r_g} + \lambda \qquad (3)$$

and assuming $\lambda = 0.15$ we calculate r_g = 39 Mrad for $\bar{M}_n$ = 15 000 and r_g = 6.6 Mrad for $\bar{M}_n$ = 84 000 giving $G(X)$ = 0.81 and 0.88 respectively. These values are in reasonable agreement with the above value for the whole polymer and with a value of 0.8 reported[6] for natural (Hevea) rubber.

Spin–spin relaxation decays

Figure 1 shows the effect of radiation on the T_2 decays of the whole polymer sample at 150°C. These decays were decomposed into two components of the form

$$A(t)/A(0) = (1 - f)\epsilon(t) + f\exp(-t/T_{2L}) \qquad (4)$$

where $\epsilon(t)$ represents the initial part of the decay, which does not conform to a single exponential time dependence, and the second term is the slower exponential decay with which a fraction, f, of the total signal relaxes. Since $\epsilon(t)$ is non-exponential we define its time constant, T_{2S}, as the time for its signal decrease to $1/e$ of its initial amplitude. Since the differences between the two rates of decay are rather small in comparison with those observed in polydimethylsiloxane, the extrapolation to $t = 0$ of the data at long times is susceptible to rather large uncertainty. In order to assess the reliability of our decomposition into two components the separated decay $\epsilon(t)$ was compared with the T_2 decay for the extracted gel fraction obtained at the same dose. From our experience with polydimethylsiloxane we found that small amounts of non-network material ($s < 0.1$) did not appreciably affect the network T_2 decays. Although this comparison could only be made for $r > r_g$, the good agreement between $\epsilon(t)$ and the gel fraction T_2 decay illustrated in *Figure 3* provides confidence in

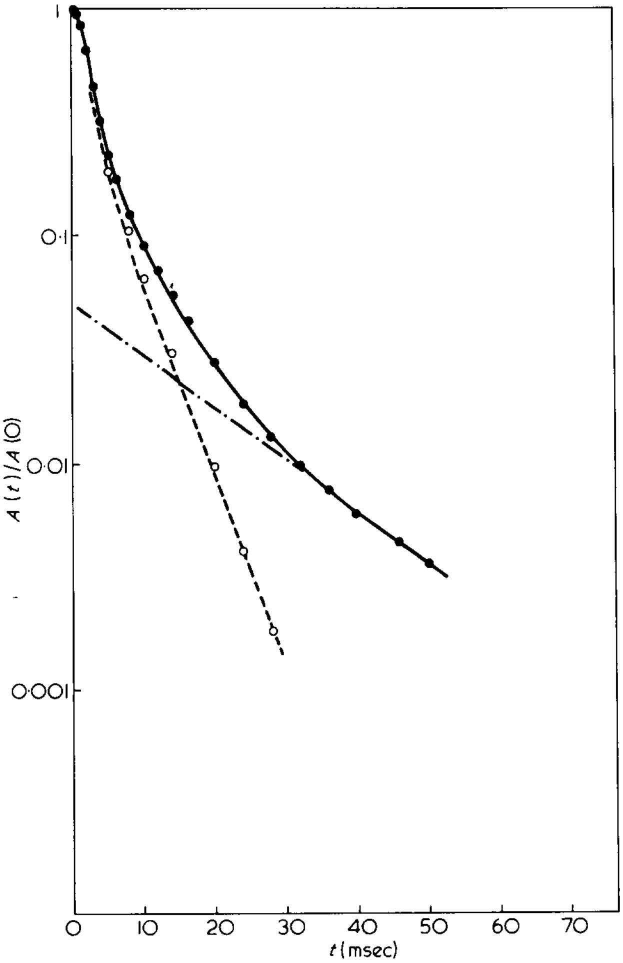

Figure 3 An example of the decomposition of the total spin–spin relaxation into two components for polyisoprene with r = 22.5 Mrad. (●) T_2 decay for unextracted material, (— · — · —) T_{2L} component (— — — —) T_2 decay for gel fraction alone (○) T_{2S} decay obtained by subtraction of T_{2L} component from total decay

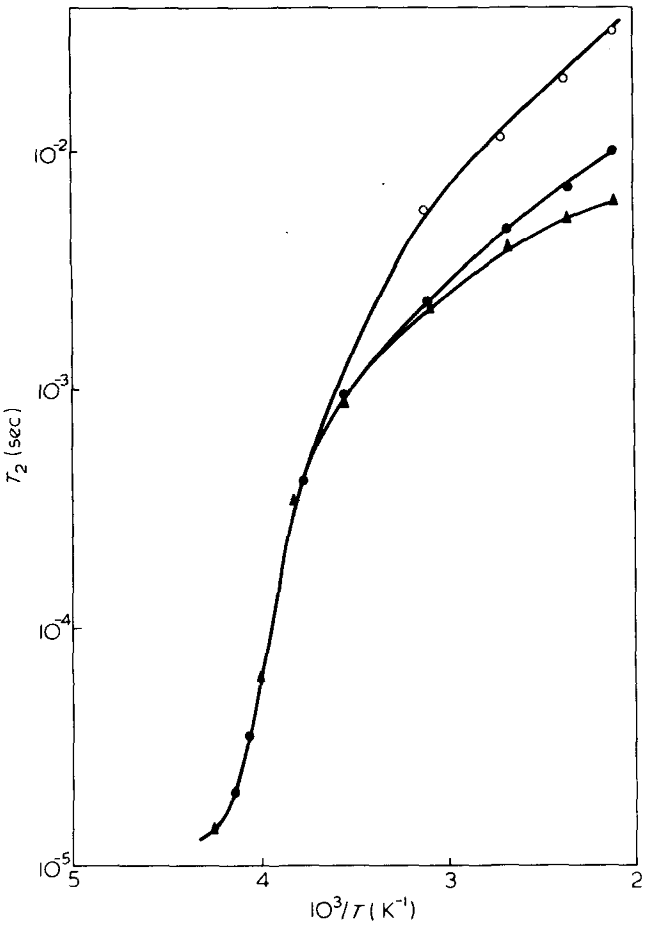

Figure 4 T_2 for unirradiated whole polymer and gel fraction at r = 5.8 Mrad plotted against reciprocal temperature. (○) T_{2L} and (●) T_{2S} for unirradiated material and (▲) T_2 for gel fraction

our separation procedure. The f values are considered to be accurate to ±10% and are shown as a function of dose together with the solubility data in *Figure 2.*

Temperature dependence

Figure 4 shows the temperature dependence of T_{2S} and T_{2L} for the unirradiated polymer and T_2 for the 5.8 Mrad gel fraction. Below about 10°C the T_2 values follow the same molecular weight independent curve obtained for the monodisperse samples in the preceding paper. Above 10°C they follow a similar temperature dependence to that for the high molecular fractions (84 000 and 210 000). In the unirradiated polymer the two components T_{2S} and T_{2L} are only observable above about 10°C and the f value remains constant up to 200°C.

DISCUSSION

It can be seen from *Figure 2* that the f values fall consistently below the s values and from the n.m.r. point of view the unirradiated material behaves as though it is in a post-gel state. In the case of high molecular weight polydimethylsiloxane we were able to obtain a consistent interpretation of the dose dependence of f if we assumed that the two components T_{2S} and T_{2L} at $r = 0$ arise from network (entangled) and non-network material respectively. Since the present sample of polyisoprene has an average molecular weight well above the molecular weight for entanglement effects, it seems likely that a similar analysis should be applicable. In contrast to the solubility method, which can only detect a permanent crosslinked network, the n.m.r. technique is sensitive to the presence of a network formed from both crosslinks and/or entanglements. If this view is correct then the n.m.r. f value for the unirradiated polymer represents a non-network fraction which comprises low molecular weight species which do not participate in an entanglement network. On irradiation this non-network fraction f, decreases as more molecules are incorporated in a network containing both crosslinks and entanglements. If we assume that the entanglements seen by n.m.r. may be treated as equivalent crosslinks then we may consider the unirradiated sample to have received a virtual radiation dose, r_e. This represents the dose necessary to produce a density of crosslinks equivalent to that of the intrinsic entanglement density. In *Figure 2* this corresponds to a horizontal shift of the f vs r curve until it coincides with the s vs r curve. Such coincidence is obtained when a virtual dose of $r_e = 13$ Mrad is added to the f data. This corresponds to an equivalent density per weight average molecule for entanglements, $\delta_e = r_e/r_g = 5.4$ or an average molecular weight per entanglement, M_{ent}, of 50 000. A similar analysis may also be applied to the irradiated monodisperse sample with $\bar{M}_n$ = 15 000. The solubility data gave $s = 0.31$ for $r = 61$ Mrad whereas the n.m.r. data gave $f = 0.18$ at the same dose. In order for the solubility data to give $s = 0.18$ a calculated dose of 75 Mrad is required. Thus this sample may be considered to have received a virtual dose for entanglements of 75–61 = 14 Mrad. Since the calculated gelation dose for this sample is 36 Mrad, $\delta_e = 14/36 = 0.4$ and M_{ent} = 15 000/0.4 ~ 40 000. This is in reasonable agreement with the value obtained for the whole polymer sample and with $M_c \sim 30\,000$ derived from the molecular weight dependence of T_2 in the previous paper.

The temperature dependences of the spin–spin relaxation for the unirradiated whole polymer and for the gel fraction (r = 5.8 Mrad) are consistent with the interpretation given in the previous paper. At low temperatures (<10°C) the presence of a network structure is not revealed by T_2 because the short range motions which control the relaxation behaviour are not significantly affected by the crosslink densities attained here. It is only at higher temperatures where the long range motions influence T_2 that there is a distinction between network and non-network molecules. The T_{2S} component for the unirradiated polymer and T_2 for the gel fraction both exhibit typical network (pseudo-solid-like) behaviour with non-exponential decays and a weak temperature dependence of T_2 itself above 10°C.

In our previous work with siloxanes we observed an empirical relationship between the network T_2 and dose of the form $1/T_{2S} \propto r$. This implies that the network T_2 is largely determined by the crosslink or entanglement density. *Figure 5* shows such a plot for polyisoprene at 150°C. The data conform reasonably well to the above relationship and there is an intercept on the dose axis of 17 Mrad which is fairly close to the virtual dose for entanglements obtained from the f values.

CONCLUSIONS

We have shown that the study of n.m.r. spin–spin relaxation times at high temperatures provides a technique for investigating the effects of intermolecular couplings on the molecular mobility. In contrast to the conventional solubility method. N.m.r. represents a rapid and non-destructive

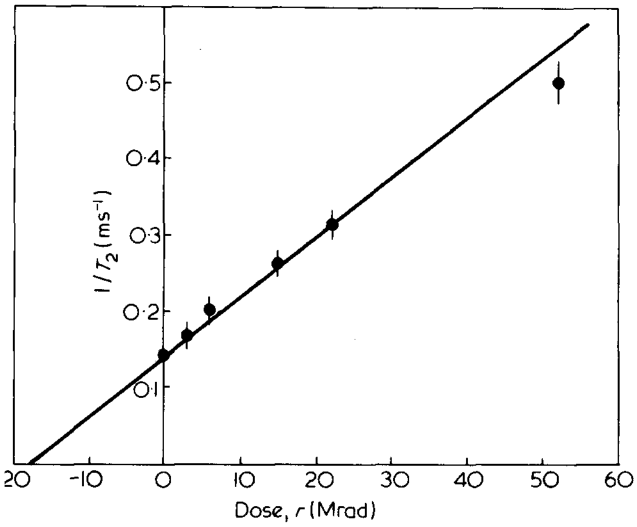

Figure 5 Network T_2 component as a function of ratiation dose. The two points at low doses are T_{2S} components and the four at higher dose are T_2 for gel fractions alone

method which is sensitive to the presence of networks formed not only from crosslinks but also from entanglements and is also capable of assessing the extent of such couplings.

ACKNOWLEDGEMENTS

We are grateful to Dr B. K. Tidd, Malaysian Rubber Producers' Research Association, Brickendonbury, Herts. for providing the characterized sample of polyisoprene.

REFERENCES

1 Folland, R. and Charlesby, A., *Int. J. Radiat. Phys. Chem.* 1976, **8**, 855
2 Folland, R. and Charlesby, A., *Int. J. Radiat. Phys. Chem.* 1977, **10**, 61
3 Charlesby, A. and Pinner, H., *Proc. Roy. Soc.* 1959, **A249**, 367
4 Flory, P. J., *J. Am. Chem. Soc.* 1941, **63**, 3097
5 Stockmeyer, W. H., *J. Chem. Phys.* 1944, **12**, 125
6 Hayden, P., *Nature* 1959, **184**, 1865