Pulsed n.m.r. of *cis*-polyisoprene: 1

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Proton spin–spin (T_2), and spin–lattice (T_1) relaxation time measurements are reported for six monodisperse *cis*-polyisoprenes ($\bar{M}_n$ from 2000 to 200 000) over the temperature range from –50° to 170°C. At low temperatures (–30° to 10°C) T_1 and T_2 are determined by the short range segmental motions but above 10°C T_2 is sensitive to the long range motions. When $\bar{M}_n \gtrsim 30\,000$ T_2 becomes influenced by the presence of entanglements which produce a transient network structure and this confers on the spin–spin relaxation a pseudo-solid-like response. Similar behaviour is observed in crosslinked networks produced by irradiation. The results are discussed in terms of the types of motion occurring in amorphous polymers above T_g and the analogy with dynamic mechanical measurements is discussed.

Part 1: Sensitivity of T_2 to long range chain motions

INTRODUCTION

Both natural (Hevea) and synthetic rubber (*cis*-1,4-polyisoprene) have been the subject of many n.m.r. relaxation time studies[1–5]. Previous work has been concerned with the behaviour of the proton spin–lattice (T_1) and spin–spin (T_2) relaxation times in the temperature range below and around the glass transition temperature (–70°C). A large increase in T_2 occurs around –40°C which is associated with general segmental motions which are liberated at T_g. These also manifest themselves in a T_1 minimum at higher temperatures (15°C at 30 MHz). A T_1 minimum is also observed at low temperatures (≈–150°C at 30 MHz) due to methyl group rotation.

In this paper attention is focussed on the long range chain motions which only affect the n.m.r. relaxation times, particularly T_2, at temperatures well above T_g. Since it is these motions which are most influenced by intermolecular couplings such as entanglements and crosslinks, the study of T_2 at high temperature can provide a sensitive probe with which to investigate the effects of these couplings on mobility. This has been the subject of much of our earlier work on polydimethylsiloxane[6–8] and polyethylene[9] melts. *Cis*-polyisoprene, being an amorphous polymer, has an advantage over the previous two polymers in that crystallization does not intervene before the temperature is lowered to T_g. This allows for a more comprehensive investigation of the temperature range over which T_2 is sensitive to the long range motions. Furthermore, relatively monodisperse samples of this polymer are commercially available over a considerable molecular weight range. In this paper we shall use results obtained for the polymer fractions to demonstrate the sensitivity of T_2 at high temperatures to the long range motions and hence to the presence of intermolecular couplings. In the following paper the effects of radiation-induced crosslinking on T_2 are described in greater detail.

EXPERIMENTAL

Six monodisperse ($\bar{M}_w/\bar{M}_n < 1.1$) polyisoprenes (>95% *cis*) were obtained from Polymer Laboratories Ltd, Shawbury, Shrewsbury, UK having $\bar{M}_n$ = 2400, 7200, 15 000, 54 000, 84 000 and 210 000. Samples (100–200 mg) of these were degassed in n.m.r. tubes and sealed off under vacuum. The proton relaxation times were measured over the temperature range from –50° to 170°C using a Spin–Lock CPS-2 pulsed n.m.r. spectrometer operating at 40 MHz. Spin–lattice relaxation was observed using the 90°–*t*–90° pulse sequence which revealed a single exponential time dependence at all temperatures. The spin–spin relaxation decay was obtained directly from the free induction decay following a single 90° pulse for $T_2 < 100$ μs and by use of the single echo, 90°–*t*–180°, method for $T_2 > 100$ μs. As T_2 increases, the shape of the spin–spin relaxation decay becomes increasingly distorted by modulations which are attributed to scalar (*J*) couplings between protons in different chemical environments. In order to eliminate the modulations the Meiboom–Gill[11] modification of the Carr–Purcell spin-echo sequence[10] (90°–*t*–180°–*t*–180°. . .) with $t = 0.5$ ms was used when $T_2 \gtrsim 50$ ms. Two samples with $\bar{M}_n$ = 15 000 and 84 000 were γ-irradiated at 40°C in evacuated n.m.r. tubes to doses of 61 and 15 Mrad respectively. These doses are higher than the gelation doses for the two samples.

RESULTS

Figure 1 shows T_1 and T_2 plotted as a function of reciprocal temperature for the six molecular weight fractions. T_1 passes through a minimum in the region of 20°C and is weakly molecular weight dependent on the high temperature side of the minimum with T_1 decreasing by 25% between $\bar{M}_n$ = 2400 and 210 000. Below –30°C the spin–spin relaxation decays follow a Gaussian time dependence with $T_2 \approx 15$ μs being independent of both temperature and molecular weight. At –30°C T_2 begins to increase rapidly but remains independent of molecular weight until 10°C where $T_2 \approx 1$ ms. In the case of the lowest molecular weight (2400) this transition in T_2 begins at a temperature 4°C lower than for the five higher molecular weight samples and T_2 is also longer in the –30° to 10°C temperature range. The spin–spin relaxation decays are approximately expo-

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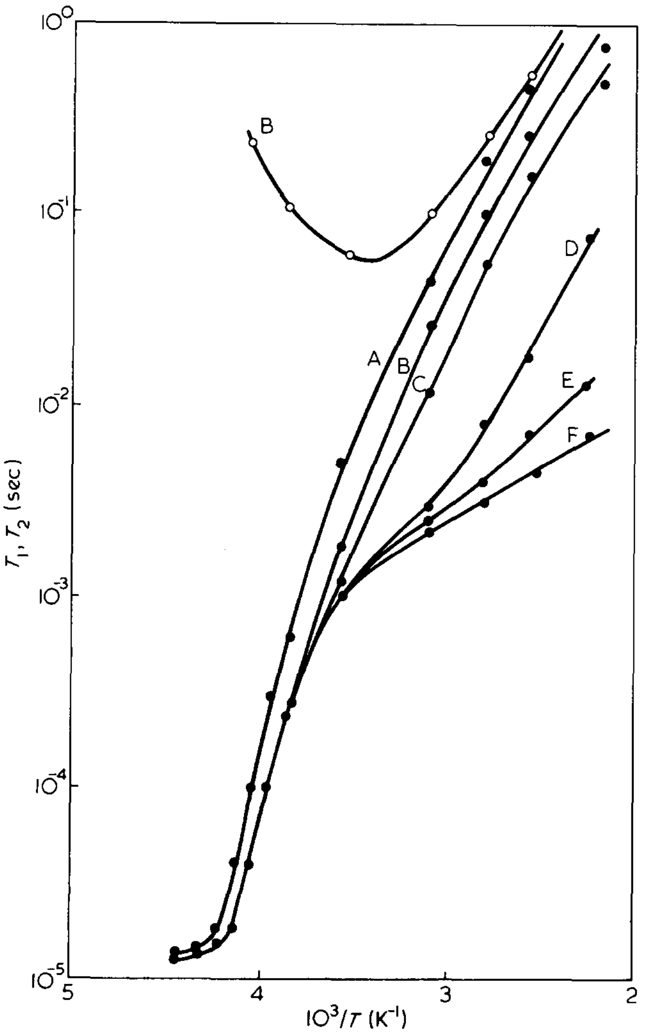

Figure 1 T_1 (○) and T_2 (●) plotted against reciprocal temperatures for the six polyisoprene samples. The molecular weights, $\bar{M}_n$, are: A, 2400; B, 7200; C, 15 000; D, 54 000; E, 84 000; F, 210 000

nential in the above temperature range. Above 10°C T_2 becomes strongly dependent on molecular weight. In the three lower molecular weight samples (2400, 7200 and 15 000) T_2 continues to increase rapidly and approaches T_1 at the highest temperature ($T_1/T_2 \approx 2$ for $\bar{M}_n = 7200$ at 172°C). The sample with $\bar{M}_n = 54\,000$ shows a weaker temperature dependence above 10°C but around 85°C the temperature dependence increases again and runs parallel with the three lower molecular weight samples. Similar behaviour is observed for the sample with $\bar{M}_n = 84\,000$ but T_2 only begins to show a stronger temperature dependence at the highest temperature (~170°C). In the case of the highest molecular weight (210 000) the weaker temperature dependence remains up to 170°C. In the region of the weaker temperature dependence, the T_2 decays no longer obey a single exponential time dependence but decay as $\exp[-(t/T_2)^X]$ where $X \approx 1.5$ over at least 90% of the decay.

Figure 2 shows the T_2 data for the two irradiated samples. Below 10°C the results are the same as for the unirradiated materials. Above 10°C the T_2 decays for the sample with initial $\bar{M}_n = 15\,000$ may be decomposed into two components, with time constants T_{2S} and T_{2L} associated with the faster and slower decays respectively. The fraction, *f*, of signal relaxing with the T_{2L} component remains approximately constant at 0.18 ± 0.02 with increasing temperature although the difference between T_{2S} and T_{2L} increases. In the case of the sample with initial $\bar{M}_n = 84\,000$ only a single T_2 component is observed over the whole temperature range. T_1 is unchanged by irradiation.

DISCUSSION

In previous studies of polyisoprene the rapid increase in T_2 which occurs at −30°C has been attributed to segmental motions which are liberated at T_g. These motions are capable of producing motional narrowing of the resonance line and hence an increase in T_2 when the average correlation time, $\bar{\tau}$, is of the same order of magnitude as T_2 (inverse line width), $\bar{\tau} \approx T_2 \approx 10^{-5}$ sec. Below −30°C these motions are too slow ($\bar{\tau} > T_2$) and we observe rigid-lattice T_2 behaviour which is typified by Gaussian decays and T_2 being independent of temperature. The fact that the sample with $\bar{M}_n = 2400$ shows a T_2 transition at a lower temperature may be taken as an indication of a lower T_g for this low molecular weight material. Between −30° and 10°C T_2 increases by two orders of magnitude but remains independent of molecular weight (except for $\bar{M}_n = 2400$). This implies that the motions determining T_2 in this region are short range in nature, probably involving monomer rotations, which are not appreciably affected by changes in overall chain length. The T_1 minimum which occurs at 20°C is a high frequency

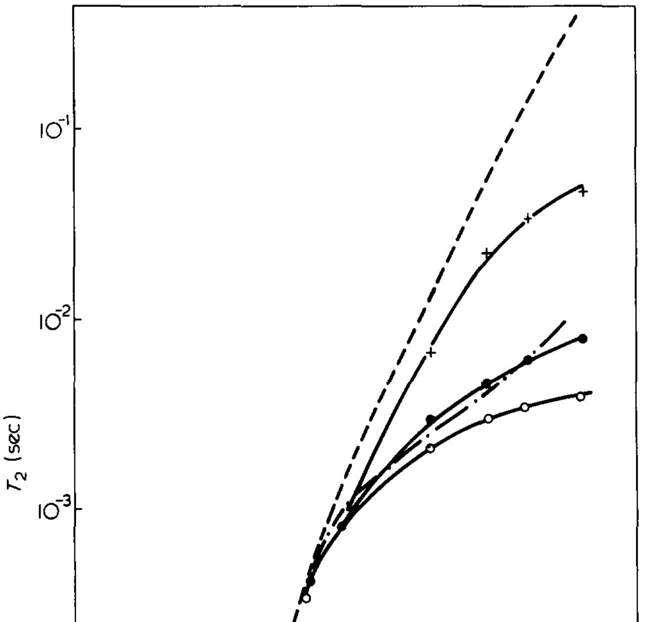

Figure 2 T_2 for the crosslinked samples plotted against reciprocal temperature, (○)T_2 for 84 000, dose = 15 Mrad, (●) T_{2S} and (+) T_{2L} for 15 000, dose = 15 Mrad (— — — —) and (— · — ·) T_2 for unirradiated 15 000 and 84 000 respectively

manifestation ($\bar{\tau} \approx 1/\omega_0 \approx 10^{-8}$ sec) of these motions. This is consistent with absence of any appreciable molecular weight dependence of T_1.

Before discussing the behaviour of T_2 above 10°C, where a strong molecular weight dependence appears, it is instructive to draw an analogy with the dynamic mechanical behaviour observed in amorphous polymers. It is well established[12] in systems of sufficiently high molecular weight for entanglements to play a role that the real part of the modulus when plotted against the time scale of measurement shows three distinct regions. At short times there is the transition zone where the modulus decreases from that of a glassy polymer to that of a rubbery material. The modulus in the transition zone is largely independent of molecular weight and is determined by short range segmental motions. The rubbery modulus forms a plateau extending to longer times the extent, but not magnitude, of which is strongly molecular weight dependent. This plateau represents the range of measurement time scales over which the polymer responds as a rubber due to the presence of a transient network formed by chain entanglements. The plateau modulus itself is determined by the average entanglement spacing. At long times the terminal zone is reached where the modulus decreases to zero as the system responds as a viscous liquid. In the terminal zone the time scale of measurement is sufficiently slow to enable long range configurational rearrangements of the entangled polymer chains to occur. The position (on the time scale axis) of the terminal zone is strongly molecular weight dependent because the time scale of the long range configurational changes is controlled by the number of entanglements per molecule. In low molecular weight polymers where entanglement effects are absent there is only a single transition from glassy to liquid behaviour, there being no intermediate rubbery plateau. The above behaviour of the modulus in entangled polymer systems has been largely accounted for by the Rouse model[13] modified in an empirical manner[12] to incorporate entanglement effects. The chain motions are represented by a set of normal modes each with an appropriate relaxation time. The distribution of relaxation times consists of a block of modes at shorter times associated with short chain lengths and a block shifted to longer times for modes which transcend the average entanglement spacing and which will therefore experience greatly increased frictional resistance to motion.

In n.m.r. the spin–spin relaxation time is providing information concerning the way in which the magnetic interactions between nuclear dipoles are being averaged out by the aforementioned type of motions as the temperature and hence motional frequencies increase. The two extremes of behaviour for the spin–spin relaxation are the solid-like (rigid–lattice, $\tau \gg T_2$) regime in a glassy polymer where $T_2 \sim 10\ \mu s$ and liquid-like behaviour at high temperature when $\omega_0\tau \ll 1$ and $T_2 \approx T_1 \approx 1$ sec for many polymers. The transition in T_2 which occurs in the temperature range −30° to 10°C has its origin in the short range segmental motions in the same way as the transition zone for the modulus. Although these motions are responsible for averaging out most of the rigid-lattice dipolar interactions, they do not lead to complete averaging of the dipolar interactions because they are anisotropic. In order for final averaging out of the dipolar interactions to occur and liquid-like T_2 to prevail it is necessary for the participation of the long range motions volving the translational or rotational diffusion of the whole macromolecule. In the case of polydimethylsiloxane[8] we were able to show that liquid-like behaviour of T_2 is only observed when $\tau_1 \ll T_2$, where τ_1 is the longest (terminal) relaxation in the Rouse model ($\tau_1 = 6\pi\eta M/\rho RT$). Values for τ_1 have not been measured for polyisoprene nor are data such as the temperature dependence of the viscosity available which would enable us to calculate τ_1. However it is apparent from *Figure 1* that final averaging of the dipolar interactions by long range chain motions occurs for the three low molecular samples where T_2 continues to increase rapidly above 10°C and approaches T_1 in magnitude. With the three high molecular weight samples we observe behaviour which is somewhat analogous to the plateau and terminal zones in the modulus. There is a temperature interval before the long range (entangled) chain modes reach sufficiently high frequency ($\tau_1 \approx T_2 \approx 1$ to 10 ms) for final averaging of the dipolar interactions to occur. This stage is reached at 85°C for the sample with $\bar{M}_n$ = 54 000 where T_2 increases rapidly again and tends towards T_1 (liquid-like behaviour). Evidence for the presence of residual unaveraged dipolar interactions is provided by the pseudo-solid-like nature of the T_2 decays ($\propto \exp[-(t/T_2)^{1.5}]$) in the weakly temperature dependent region. Similar types of T_2 decay have been observed[8] in polydimethylsiloxane under the same conditions. The extent of the pseudo-solid-like region in T_2, as with the rubbery plateau modulus, increases with increasing molecular weight. For the highest molecular weight sample (200 000) a transition to liquid-like behaviour does not occur over the temperature range covered.

An alternative representation of the effect of entanglements on T_2 is shown in *Figure 3* where T_2 is plotted against molecular weight at various temperatures. The high temperature (>80°C) plots show that initially T_2 decreases slowly with $\bar{M}_n$, then the dependence increases before T_2 levels off

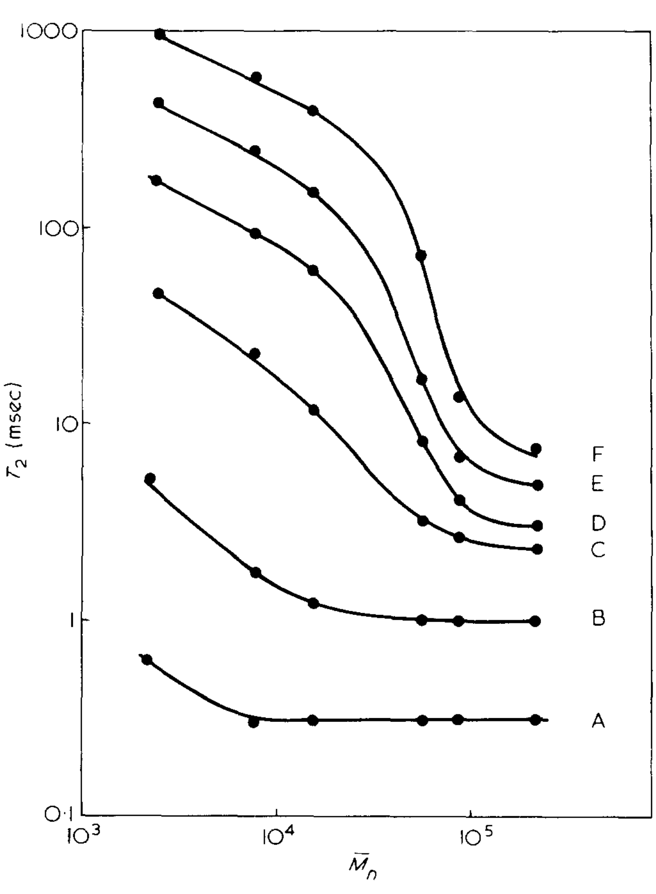

Figure 3 T_2 as a function of molecular weight, $\bar{M}_n$, at six different temperatures. The temperatures are A, −12°; B, 9°; C, 51°; D, 85°; E, 118°; F, 170°C

in the pseudo-solid-like regime ($\tau_1 \gg T_2$). The increased molecular weight dependence of T_2 reflects, through the frequencies of the long range motions, the changes in dependence of the viscosity on molecular weight at the critical molecular weight for entanglements, M_c ($\eta \propto M$ for $M < M_c$ and $\eta \propto M^{3.4}$ for $M > M_c$). A similar break in the T_2 vs M plots has been observed before for polyethylene[14], polyisobutylene[3] and polydimethylsiloxane[14]. For *cis*-polyisoprene we estimate that $M_c \sim 30\,000$ over the temperature range 80° to 170°C.

The sensitivity of T_2 to the long range motions at high temperature (>10°C) is further confirmed by the results obtained for the two samples crosslinked by γ-irradiation. These two samples were chosen such that their initial molecular weights fell either side of M_c as determined above. On this basis the high molecular weight sample (84 000) is expected to exist as a dynamic entanglement network whereas in the low molecular weight sample (15 000) entanglements may be present but their concentration (per molecule) is insufficiently high for a network to exist. Irradiation of the former adds crosslinks to the entanglement network already present. This leads to a reduction of T_2 as the long range chain mobility is further reduced by the additional intermolecular constraints. Irradiation of the $\bar{M}_n = 15\,000$ sample to dose of 61 Mrad produces a partially crosslinked system containing a network with estimated average of two crosslinks per molecule. Above 10°C, this network is revealed by the presence of a shorter T_2 component (T_{2S}) in addition to the initial longer T_2 component arising from 'free' non-network molecules of the sol fraction. This network T_2 component behaves in a similar manner to that already observed for high molecular weight entangled polymers by exhibiting pseudo-solid-like behaviour ($\tau_1 \gg T_2$) up to the highest temperature. Below 10°C, T_2 is not sensitive to the long range motions and network and non-network species cannot be distinguished by this method. The non-network component (T_{2L}) follows a similar temperature dependence to T_2 of the unirradiated polymer except that at higher temperatures T_{2L} levels off due presumably, to the restrictions imposed on the mobility by the surrounding network material. The fraction of signal relaxing with T_{2L} ($f = 0.18$) is lower than the sol fraction ($s = 0.31$) determined by extraction. We attribute this difference to a contribution from entanglements which appear to act in the same way as crosslinks as far as n.m.r. is concerned. This will be discussed more fully in the following paper.

CONCLUSIONS

In this n.m.r. study of polyisoprene we have followed the transition of T_2 from solid-like (rigid-lattice) behaviour in the glassy polymer at low temperatures to that typical of a viscous liquid at high temperatures. In low molecular weight samples ($\bar{M}_n \lesssim 30\,000$) there is a single, continuous transition from one type of behaviour to the other with change in temperature but at higher molecular weight ($\bar{M}_n \gtrsim 30\,000$) this transition occurs in two stages. For all molecular weights the majority of the rigid-lattice dipolar interactions are motionally averaged out by the short range segmental motions with an accompanying increase in T_2 of two orders of magnitude from −30° to 10°C. For $\bar{M}_n \leqslant 30\,000$ T_2 approaches T_1 on further increase in temperature and becomes molecular weight dependent as final averaging of the dipolar interactions occurs *via* the long range motions. When $\bar{M}_n \geqslant 30\,000$ entanglements influence the T_2 behaviour and there is a range of temperature over which T_2 exhibits pseudo-solid-like behaviour and the system behaves as a network on the timescale of T_2 (1–10 ms). It is only at a higher temperature, which is molecular weight dependent, that the long range chain motions reach sufficiently high frequency for final averaging of the dipolar interactions to occur prior to the onset of liquid-like T_2 behaviour. Measurements on crosslinked networks appear to confirm this interpretation. It is noted that there is a close correspondence between the n.m.r. behaviour (i.e. T_2 vs. temperature) and mechanical properties (e.g. modulus vs. time scale of measurement). This reflects the fact that both properties are sensitive to the same motional processes.

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