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Muon Studies in Organic Conductors [and Discussion]

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Muon studies in organic conductors

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This paper contains a brief review of muon studies of organic conductors with emphasis on polymers. The species created by implanted muons in both semiconducting polymers and polymers doped to metallic values of conductivity are described. Both diamagnetic centres and paramagnetic radicals are formed in the semiconducting materials. The mechanisms of interaction of the muon with the polymers and the longitudinal relaxation of the muon species are discussed. In highly conducting polymers the muons are primarily present in diamagnetic states. Implanted muons have also been used to study both organic charge-transfer salts and Rb_3C_{60} in the superconducting state.

1. Introduction

The discovery by Shirakawa & Ikeda (1971) and Ito *et al.* (1974) that it was possible to make thin films of polyacetylene and the subsequent discovery by Chiang *et al.* (1977) that the electrical conductivity of this material could be increased to metallic values (up to 10^5 S cm^{-1}) by chemical doping led to an upsurge of interest in conducting polymers generally which still persists (Heeger *et al.* 1988; Kusmany *et al.* 1989; Tsukamoto 1992). We shall be mainly concerned in this paper with the nature of the interaction of muons with polymers (§ 2) and with the information that may be obtained about the dynamics of electronic excitations in these materials following muon implantation (§ 3). We shall concentrate on the measurement of longitudinal muon polarization at different temperatures in applied magnetic fields (for background see Chappert 1984; Schenk 1985; Cox 1987). We shall also give a brief outline of recent experiments on charge transfer salts and fullerenes (§ 4).

Before describing experimental results on polymers it is desirable that we should give an outline of the morphology and also of the electronic structure and electronic excitations of polyacetylene (see Hayes 1985). If the polymerization of polyacetylene is carried out at temperatures below *ca.* 255 K the film consists predominantly of the cis isomer (figure 1*a*). The cis isomer is converted to the trans isomer (figure 1*b*) within a few minutes if the film is held at *ca.* 150 °C. Films made in this way consist of randomly oriented fibrils with diameters of about 20 nm. The structure is open, with a density of *ca.* 0.4 g cm^{-3} compared with a limiting density of *ca.* 1.2 g cm^{-3}. The fibrils have a high crystalline content with polymer chains closely aligned along the fibril axis and with conjugation lengths of order 10 nm. Epr measurements show that isomerization from cis- to trans-polyacetylene results in a large increase in the concentration of unpaired

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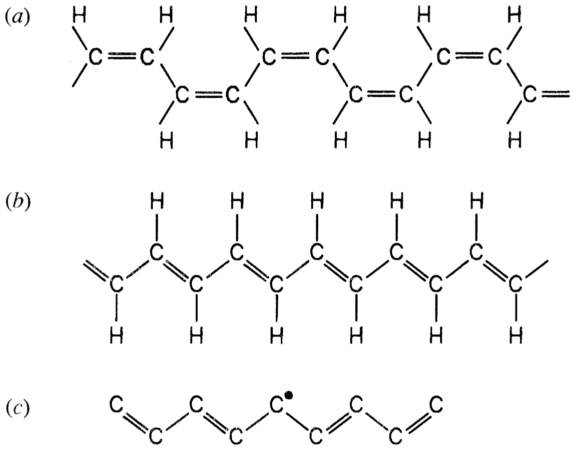

Figure 1. Schematic representation of (*a*) cis-polyacetylene, (*b*) trans-polyacetylene and (*c*) neutral bond alternation defect with unpaired electron spin (neutral soliton).

spins (to *ca.* 10^{19} cc^{-1}) some of which are localized and some mobile (see Hayes 1985 and § 3 *a*).

In polyacetylene three of the four valence electrons of carbon form sp^2 hybrid bonds pointing towards the nearest carbons and the nearest hydrogen in the chain (figure 1.) These σ bonds are strong and determine the elastic constants of the chain. The fourth valence electron is in a $\text{p}_z(\pi)$ orbital perpendicular to the plane of the chain. Overlap of the π electrons gives rise to the highest occupied electronic band, of width *ca.* 10 eV (interchain overlap also occurs but is about two orders of magnitude smaller). At first glance one would expect polyacetylene to be a metal since the π band is only half full. However, linear systems are unstable against a distortion that opens up a gap at the Fermi energy (Peierls 1955). It was pointed out by Longuet-Higgins and Salem (1959) that bond alternation along the chain, represented by single and double bonds in figure 1 (and referred to as dimerization), was an appropriate distortion and X-ray scattering (Fincher *et al.* 1982) showed that the double bonds were shorter than the single bonds by *ca.* 0.03 Å. The resulting bandgap in cis-polyacetylene is *ca.* 2.0 eV and in trans-polyacetylene is *ca.* 1.4 eV.

Trans-polyacetylene is unusual among long-chain polymers because the infinite chain has a two-fold structural degeneracy, giving rise to the possibility of a bond-alternation defect (Pople & Walmsley 1962) across which the dimerization changes sign (figure 1*c*). Su *et al.* (1980), in a theoretical investigation, concluded that this paramagnetic defect extends over *ca.* 14 CH units and that it is pinned intrinsically with a small activation energy. This mobile defect is now generally referred to as a soliton and it can also exist in charged (non-magnetic) states, the carriers in highly conducting doped material (Kivelson 1986). In structurally non-degenerate polymers such as cis-polyacetylene (figure 1) the symmetry between positive and negative dimerization is broken and defects across which dimerization changes sign are less stable. However, charged polarons, analogous to polarons found in ionic solids (Hayes & Stoneham 1985), are stable on such chains and contribute to electrical conductivity (Heeger *et al.* 1988; see also Conwell & Mizes (1993) for a discussion of interchain interaction on polaron stability). In addition,

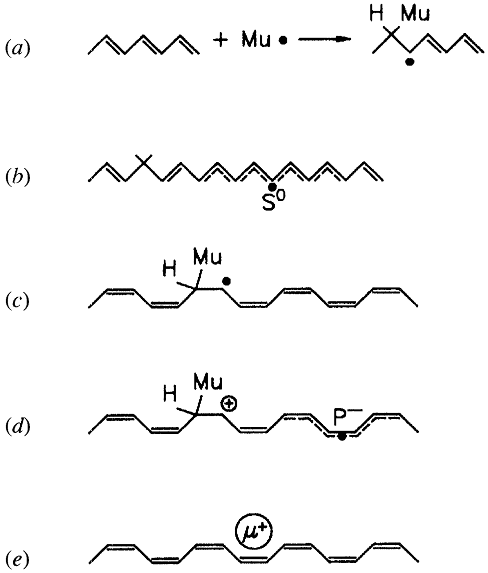

Figure 2. Schematic representation of (*a*), (*b*) muonium interaction with trans-polyacetylene to produce a diamagnetic radical and a mobile neutral soliton. A similar reaction in the non-degenerate cis-polyacetylene produces a paramagnetic radical (*c*) but the unpaired spin may also move away as a negatively charged polaron (*d*). In polymers doped to metallic conductivities the muon may also exist in a diamagnetic state (*e*) (see the text for a discussion of interaction with the chain) (after Pratt *et al.* 1993).

polarons may interact to form spinless bipolarons despite the coulomb repulsion (see Heeger *et al.* 1988)

2. Interaction of muons with polymer chains

The first muon studies of polymers were carried out on polyacetylene (Nagamine *et al.* 1984; Nagamine & Ishida 1986) and were interpreted on the reasonable assumption that muons form muonium as they slow down and that muonium then interacts with a double bond on the polymer chain (see also Cox 1987). A theoretical minimum-energy study of this interaction by Fisher *et al.* (1991) showed that for a perfect single chain of trans-polyacetylene the paramagnetic radical formed by this interaction (figure 2*a*) dissociates into a diamagnetic muon defect and a mobile paramagnetic soliton (figure 2*b* and figure 3*a*); the muon is a barrier to motion of the soliton. With the corresponding reaction for the non-degenerate cis-polyacetylene the paramagnetic radical is predicted to remain intact (figures 2*c* and 3*b*). However, we should also consider the possibility that the reaction between muonium and the chain is sufficiently energetic that the unpaired spin may move away as a negatively charged polaron, possibly to another chain, leaving a diamagnetic muon complex behind (figure 2*d*). There is in addition the possibility that in doped (highly conducting) systems the muon may not thermalize as muonium and may interact directly with a polymer chain to form a bound configuration (figure 2*e*) although the nature of the binding in this situation is not yet clear (see §§ 3 *b*, *c*).

In distinguishing between paramagnetic and diamagnetic systems we note that in the former case the positron emission asymmetry in longitudinal repolariza-

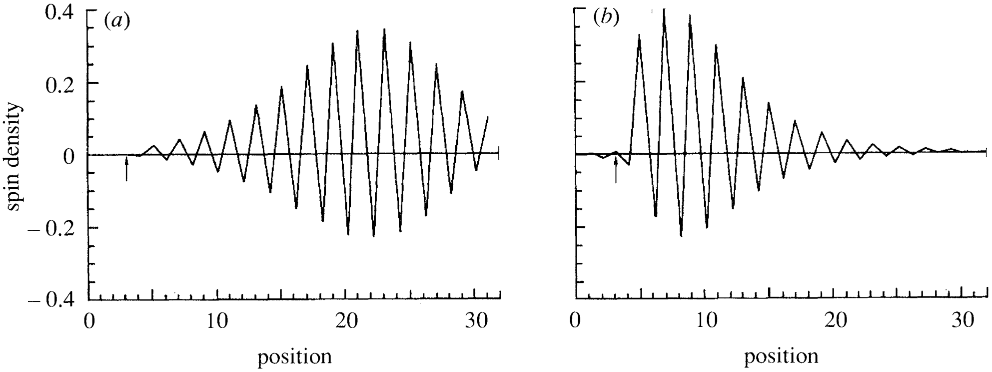

Figure 3. Calculated spin density following reaction of muonium with a chain of (*a*) trans-polyacetylene and (*b*) cis-polyacetylene consisting of 32 carbon atoms. The arrow indicates the muon site (after Fisher *et al.* 1991).

tion experiments is quenched to some extent by hyperfine interaction (see Beck *et al.* 1975). In the case of muonium, with an isotropic hyperfine interaction, this reduction is 50% in zero applied field. As the applied field is increased the polarization is gradually restored to its full value as the electron and muon spins are decoupled. This restoration has the form $P = \frac{1}{2}[1 + (x^2/(1 + x^2))]$ with $x = H/H_0$, where H is the applied field and $H_0 = 1580$ G is the characteristic hyperfine field for muonium. The quenching may be enhanced in systems with anisotropic hyperfine interaction (Pratt 1994). The positron emission asymmetry of diamagnetic muons in a small transverse applied magnetic field shows the characteristic muon precession frequency (with a possible Knight shift). Use of the term 'diamagnetic' in the present context is associated with the observation of such a frequency or with the absence of observable repolarization.

3. Experimental results

(*a*) *Polyacetylene*

We briefly describe in this section some results of longitudinal muon repolarization experiments for polyacetylene obtained by Nagamine and co-workers (Nagamine *et al.* 1984; Nagamine & Ishida 1986). There is a fairly clear distinction between the behaviour of the two isomers (figure 4). In the case of the cis isomer the muon is mostly present as a paramagnetic radical (see figure 2*c*); the longitudinal positron asymmetry is strongly quenched in zero applied field but is restored by application of a field (figure 4*a*). Muon spin rotation experiments in a transverse field give a hyperfine coupling constant of 91MHz (Nishiyama *et al.* 1986), characteristic of a radical state. This may be compared with the value of $A \approx 170$ MHz calculated by Fisher *et al.* (1991) for the spin distribution shown in figure 3*b*, suggesting that the actual spin is slightly more delocalized. There is also a relatively small diamagnetic component in the asymmetry (*ca.* 20%) (cf. figure 2*d*).

It is interesting to note that at room temperature there is no observable decay of the asymmetry of the radical emission in cis-polyacetylene (figure 4*a*) (see also results for other polymers below). This result may be compared with the

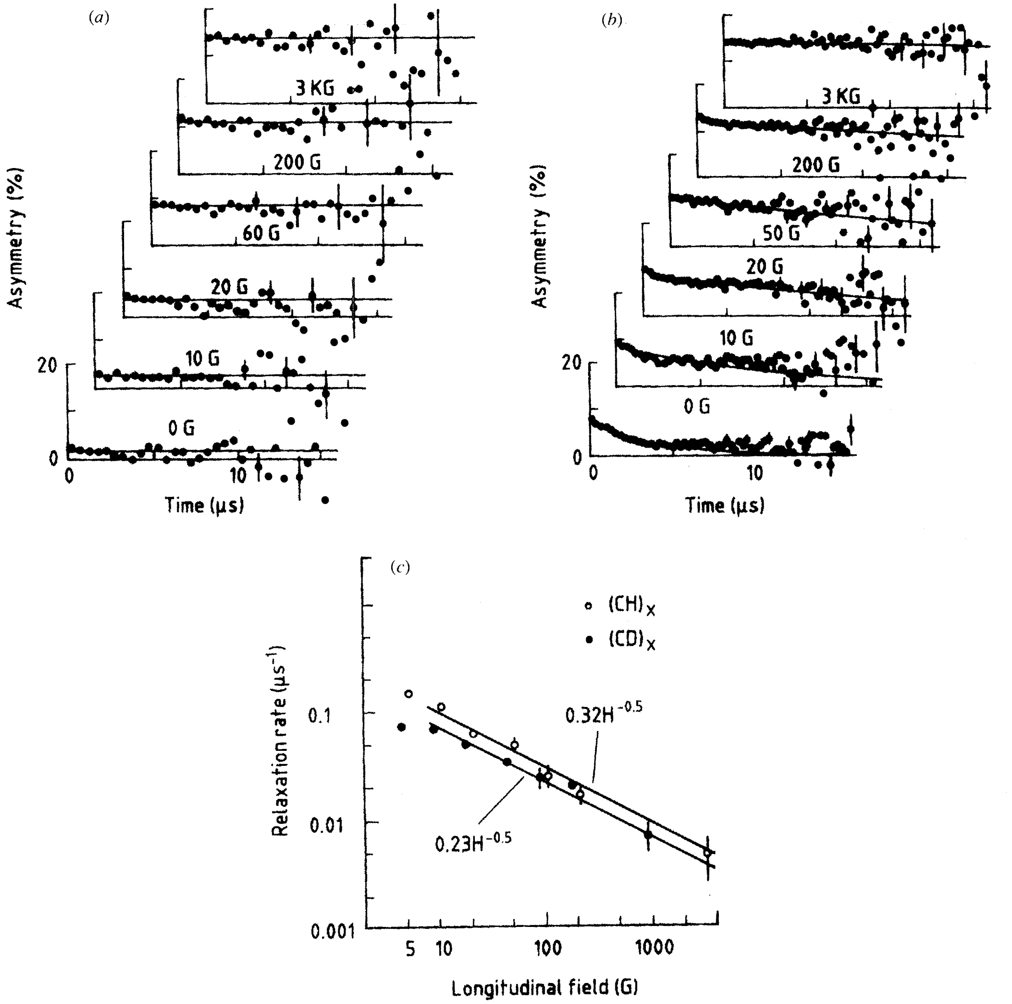

Figure 4. Magnetic field dependence of longitudinal muon spin relaxation in (*a*) cis-polyacetylene and (*b*) trans-polyacetylene and (*c*) relaxation rates for trans-$(CH)_x$ and for trans-$(CD)_x$; all measurements at 293 K (after Nagamine & Ishida 1986).

relatively rapid decay of a muonium-substituted ethyl radical in the gas phase (Fleming *et al.* 1990), due to motional effects of gas molecules.

The data for trans-polyacetylene show that a substantial fraction of the muons are in a diamagnetic state (cf. figure 2*b* and figure 3*a*). However, a significant fraction repolarizes under the effect of an applied magnetic field indicating that there is also a substantial paramagnetic radical component. We have no clearcut explanation for this other than to suggest a confining effect of defects, e.g. chain ends (see § 1).

Nagamine *et al.* (1984) have also studied the magnetic field dependence of the longitudinal relaxation time T_1 of the diamagnetic component for both $(CH)_x$ and $(CD)_x$ near room temperature (figure 4*c*). They conclude that the fluc-

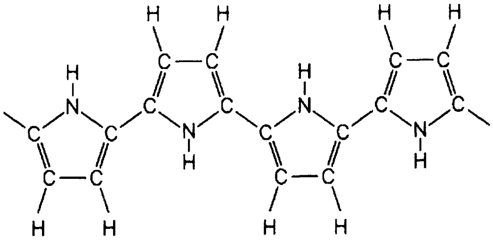

Figure 5. Schematic representation of the structure of polypyrrole.

tuating magnetic field associated with the muon-generated soliton (figure 2*b*) dominates the relaxation rate T_1^{-1}. They assume that the relaxation rate at the Larmor precession frequency ν_μ of the muon is proportional to $\phi(\nu_\mu)$, where $\phi(\nu)$ is the power spectrum of the fluctuating magnetic field at the muon sites (see Butler *et al.* 1976). On an anisotropic three-dimensional random walk picture a $\nu^{-1/2}$ dependence is expected for $\phi(\nu)$ when ν falls between a fast and two much slower jump rates, i.e. when one-dimensional motion predominates. Similarly a $\ln \nu$ dependence is expected for $\phi(\nu)$ when ν falls between two fast and one much slower jump rate, i.e. for two-dimensional motion. In the limit where the Larmor frequency is higher than any characteristic hopping rate in the system a ν^{-2} dependence is predicted for $\phi(\nu)$ (for further discussion see Butler *et al.* 1976).

In general the magnetic field dependence of T_1^{-1} gives the functional form of $\phi(\nu)$ if the applied field does not affect $\phi(\nu)$ directly. Usually one plots the measured T_1^{-1} against H^{-m} and obtains an effective dimensionality d for $d < 2$ from the relationship $m = 1 - \frac{1}{2}d$ (see Derneux & Lecavelier 1987). Fitting their data to an exponential relaxation function, e^{-t/T_1}, Nagamine *et al.* (1984) found that T_1^{-1} varied as $H^{-0.5}$ at 293 K (figure 4*c*), consistent with one-dimensional motion and with the large anisotropy of electrical conductivity of doped stretch-aligned films (see Tsukamoto (1992) for a review and also § 3 *c*).

(*b*) *Polypyrrole*

Undoped polypyrrole (figure 5) is a semiconductor with a bandgap of *ca.* 2.6 eV and as-grown film generally contains paramagnetic defects in high concentration (*ca.* 10^{19} cc; Scott *et al.* 1983). The longitudinal relaxation of implanted muons in undoped polypyrrole at both 15 and 300 K in a range of magnetic fields has been studied by Pratt *et al.* (1993) and is shown in figure 6*a*, *b*. Deuterated samples give similar results and we conclude that relaxation is dominated by electronic spins. About 50% of the muons are in diamagnetic states and about 50% are present as paramagnetic radicals (the behaviour is closer to that found for trans-polyacetylene than for cis polyacetylene (figure 4*a*, *b*) although polypyrrole is a non-degenerate polymer). The existence of both diamagnetic and paramagnetic species in non-degenerate polymers (see also § 3 *a* and discussion of other non-degenerate polymers below) suggests two possible reaction paths for muons (see figure 2*c*, *d*). From the measured decoupling of the electron spin from the muon in the paramagnetic radical it is possible to obtain a rough estimate of *ca.* 500 MHz for the contact hyperfine interaction (a more detailed study of this decoupling, including effects of anisotropic hyperfine interaction, will be published later for polypyrrole and for the other polymers discussed below in § 3 (Pratt *et al.* 1995).

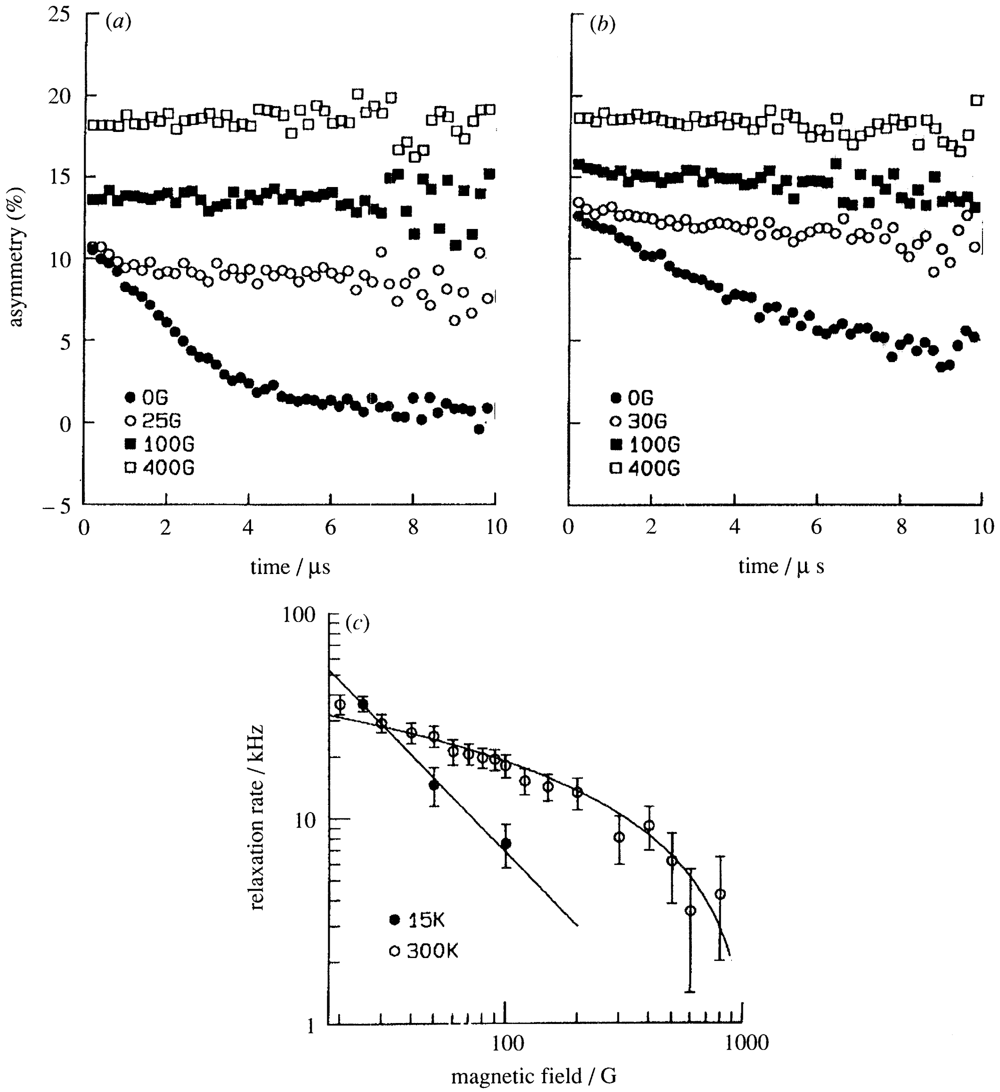

Figure 6. Magnetic field dependence of longitudinal muon spin relaxation in polypyrrole at (*a*) 15 K and (*b*) 300 K and (*c*) of relaxation rates at both temperatures (after Pratt *et al.* 1993).

Figure 6*c* shows the field dependence of the relaxation rate of the diamagnetic muons at both 15 and 300 K, derived by fitting to an exponential relaxation function (see § 3 *a*). The curve fitted to the 300 K data is a $\log H$ fit, consistent with an effective two-dimensional motion of the spins causing relaxation (see § 3 *a* and below). The H^{-m} fit to the data for 15 K gives $m = 1.2$, suggesting restricted motion of the perturbing spin (compare also the data in figure 6*a* for zero field) and possibly only partial polymerization.

We have also carried out longitudinal relaxation studies of doped polypyrrole (Pratt *et al.* 1990), a highly conducting material with an average carrier density of one carrier for every three pyrrole rings. The conductivity mechanism in this system is complex with, among other mechanisms, variable range hopping between localized states and seems to involve both polarons and bipolarons (Subramanyam *et al.* 1991; Ishiguro *et al.* 1992). About 90% of the muons are in a diamagnetic state and the relaxation at 15 K exhibits the initial fall and subsequent recovery characteristic of a fairly static spin system (Hayano *et al.* 1979). Increasing the temperature leads to a fall in the relaxation rate as the spin (and possibly the muon; see § 2) become more mobile. Similar behaviour has been observed in the more conventional metal Nb containing Ta impurities and has been explained by trapping and thermally induced release at impurity sites (Bokema *et al.* 1982). The present situation is somewhat different, however, because of the relatively localized nature of the carriers. In this connection we point out that the frequency dependence of proton relaxation in doped polypyrrole has been studied by Devreux & Lecavelier (1987) using NMR techniques. Below 150 K they find, using a random walk model of the electron spins causing the relaxation, that the data indicate one-dimensional motion; this gradually changes to two-dimensional motion as the temperature increases to 293 K. At this point we emphasise that although anisotropic random walk theory has significance when indicating one-dimensional motion of electronic spins along polymer chains, assigning meaning to implied dimensionality is less straightforward when more complex motion occurs, involving jumps between chains, and that change from two- to three-dimensional motion is not expected to give clearcut effects (see figure 2 of Butler *et al.* 1976). We also add the cautionary remark that neutron scattering measurements have shown that doped films of polypyrrole possess an anisotropic layered structure in which the planes of the polypyrrole rings lie preferentially parallel to the surface of the film (Mitchell *et al.* 1988).

(*c*) *Polyaniline*

Polyaniline has three stable insulating forms (figure 7), leucoemeraldine base (LEB), the half oxidized form, emeraldine base (EB) and the fully oxidized form, polypernigraniline base (PPG). There is also a highly conducting form, emeraldine salt (ES) hydrochloride (figure 7) and there is general agreement that conductivity in this material is due to polarons and that bipolarons are not involved (for general background see Zuo *et al.* 1987; McCall *et al.* 1990; Monkman & Adams 1991). The fundamental defect carrier in LEB (figure 7*a*) is a ring rotation polaron which has a large effective mass (*ca.* $50m_e$) because of the large moment of inertia involved in rotation of the C_6 rings about the N–N axis. However, in the case of PPG (figure 7*c*), which may be considered to be a Peierls bandgap polymer, a solitonic defect in the bond length order parameter with lower mass (*ca.* $50m_e$) has also been identified. Polyaniline is less crystalline than polyacetylene and the emeraldine salt is not as highly conducting as doped polyacetylene (see Coplin *et al.* 1994).

Results of longitudinal polarization measurements on PPG obtained by Pratt *et al.* (1993) are shown in figure 8*a*, *b*. About 45% of the muons are in diamagnetic states and the remainder are present as paramagnetic radical with a hyperfine interaction comparable to that found for polyacetylene (§ 3 *a*) and polypyrrole (§ 3 *b*). The relaxation rates for the diamagnetic component are fitted quite well on the basis of the random hopping model with an effective dimension of 0.9 at 11 K and 1.8 at 300 K (figure 8*c*). Similar results are obtained for EB (Pratt *et al.* 1993); in this case the relaxation rate at 15 K again indicates one-dimensional motion of the perturbing spin but the room temperature behaviour is complex

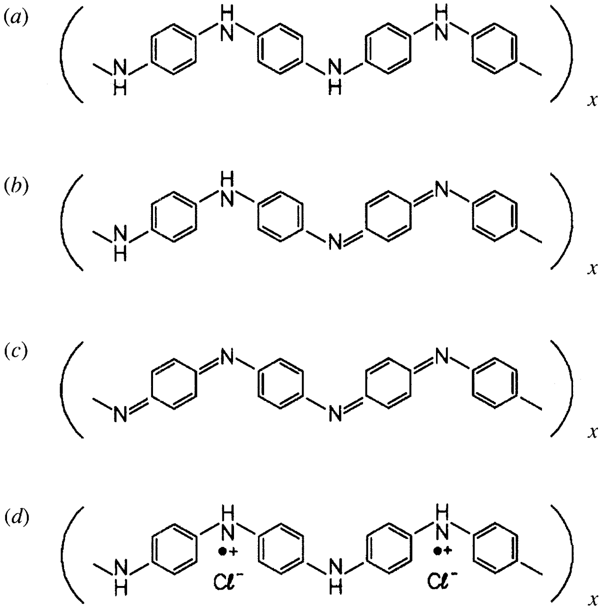

Figure 7. Schematic representation of the structure of (*a*) leucoemeraldine base (*b*) emeraldine base (*c*) pernigraniline base and (*d*) emeraldine hydrochloride salt.

and may involve more than one relaxation component. The fact that the motion of the perturbing spin is less one-dimensional at room temperature than in trans-polyacetylene (§ 3 *a*), despite lower crystallinity, is consistent with the fact that there is a topological constraint on movement of solitons between chains but less so for polarons (Heeger *et al.* 1988; see also § 3 *b*).

As in doped polypyrrole (§ 3 *b*) we find that about 90% of the muons present in the highly conducting ES (figure 7*d*) are in diamagnetic states. Results of longitudinal polarization experiments (Pratt *et al.* 1993) are shown in figure 9 at 13 K and 300 K in fields of up to 40 G. Again, as in the case of polypyrrole (§ 3 *b*) the zero-field relaxation at 15 K shows behaviour characteristic of a fairly static spin distribution. This may be partly due to self-localization of the muon on a polymer chain, perhaps near a dopant Cl^- ion (see § 2). From the reduction in zero-field relaxation in a deuterated sample we estimate that *ca.* 75% of the relaxation is caused by nuclear spins and *ca.* 25% by electronic spins. At 300 K the static features of the relaxation are lost as the polarons become more mobile (see § 2 and Chappert 1984). Preliminary results of a study of the magnetic field dependence of T_1^{-1} (Pratt & Valladares, personal communication, 1994) show complex behaviour which may result in part from diffusion of interacting spins. For detailed understanding further experiments are required involving various levels of doping and possibly different dopants.

(*d*) *β-carotene*

The structure of trans β-carotene (figure 10) is closely related to that of trans-polyacetylene and it can be prepared in crystalline form. The crystals are monoclinic with two molecules in the unit cell. Like trans-polyacetylene the crystals can be doped p-type by exposure to iodine or AsF_5. Optical, EPR and computational

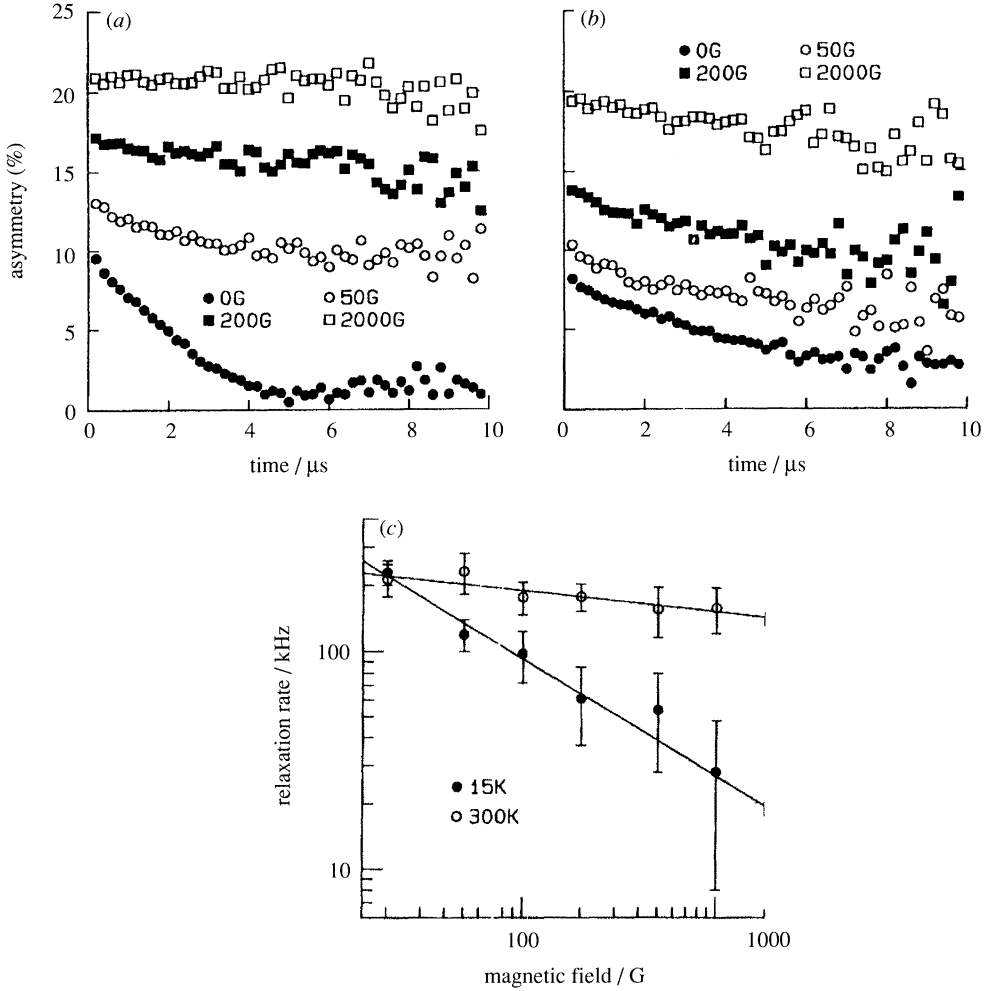

Figure 8. Magnetic field dependence of longitudinal muon spin polarization in polypernigraniline at (*a*) 15 K and (*b*) 300 K and (*c*) of relaxation rates at both temperatures (after Pratt *et al.* 1993).

studies indicate that two charged defects are formed in a molecule, one at each end of the chain, giving a non-magnetic species (Ehrenfreund *et al.* 1992*a*, *b*; Valladares *et al.* 1993). Although not strictly a conjugated polymer it is of interest in the present context because of its relatively well defined structure.

Our studies of longitudinal polarization of implanted muons in a magnetic field show that about 50% are in paramagnetic radical states (figure 11*a*; Pratt & Valladares, personal communication, 1994). Using theoretical techniques similar to those used for polyacetylene (§ 3 *a*) the minimum energy configuration for muonium interacting with a β-carotene chain has been obtained (figure 11*b*; Pratt & Valladares, personal communication, 1994). It shows a spin distribution confined to the β-carotene molecule and, in contrast to the situation calculated for trans-polyacetylene (figure 3*a*), the confinement results in a paramagnetic radical state giving a calculated hyperfine interaction with the muon of *ca.* 150 MHz. This may be compared with a rough estimate of *ca.* 400 MHz obtained from the

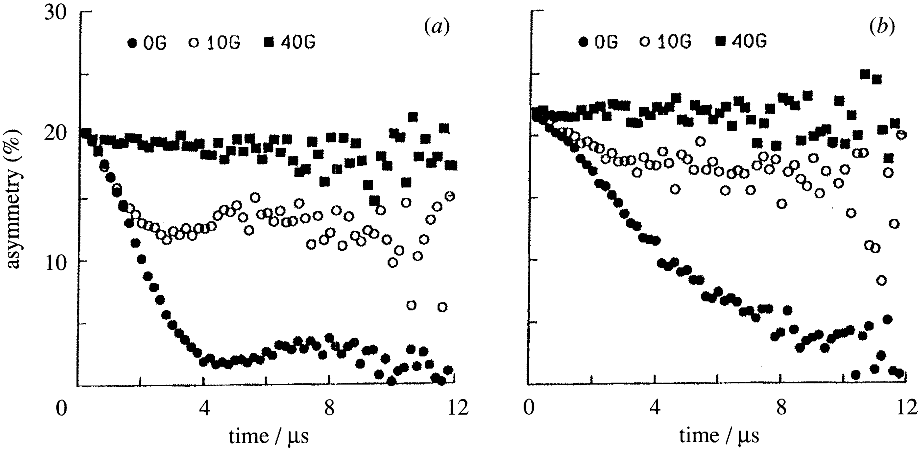

Figure 9. Magnetic field dependence of longitudinal muon relaxation in emeraldine salt at (*a*) 13 K and (*b*) 300 K (after Pratt *et al.* 1993).

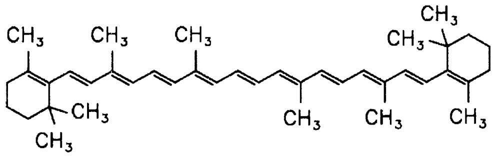

Figure 10. Schematic representation of the structure of trans β-carotene.

repolarization curve at 10 K (figure 11*a*). The magnetic field dependence of the spin lattice relaxation rate of the diamagnetic component at 10 K (figure 11*c*) is consistent with relatively slow spin diffusion ($m = 0.75$; see § 3 *a*) in contrast to the motion observed in longer-chain materials.

4. Charge transfer salts and fullerenes

Conducting polymers are complex systems with a morphology that is not well defined. However, other organic conductors have well defined crystal structures and μSR techniques have recently yielded interesting information about them. Many organic charge transfer salts are metals and some are superconductors (see Kresin & Little 1990). The simplicity of the band structures of such compounds and the relative ease with which they can be calculated and measured makes it possible to show that they have features characteristic of electron–electron interactions in narrow-bandwidth metallic systems and that they have properties intermediate between heavy fermion compounds and cuprate (high T_c) superconductors (see Caulfield *et al.* 1994).

κ-(BEDT-TTF)$_2$Cu[NCS]$_2$ with $T_c = 10.4$ K has been extensively investigated by μSR techniques (BEDT-TTF is bisethylenedithio-tetrathiafulvalene) to obtain information about the ground state symmetry and also to determine the magnetic penetration depth below T_c and hence the ratio of the superconducting carrier density to the carrier effective mass (Harshman *et al.* 1990; Uemura *et al.* 1991; Le *et al.* 1992; Harshman *et al.* 1994). In addition, μSR provides information about the dynamics of local magnetic fields in organic conductors, e.g.

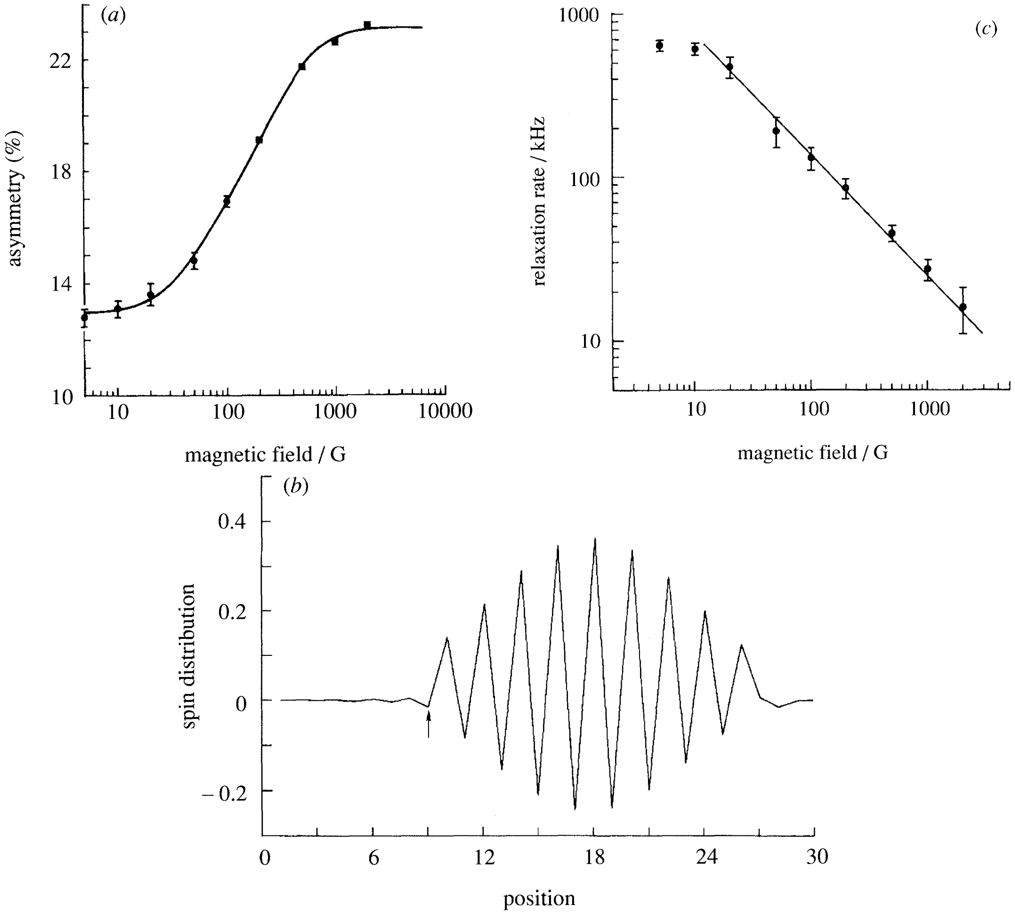

Figure 11. (*a*) Magnetic field dependence of longitudinal muon spin polarization in β-carotene at 10 K (*b*) calculated spin distribution of a muon radical in a β-carotene molecule (*c*) magnetic field dependence of the relaxation rate for diamagnetic muons at 10 K.

in the compound $(\mathrm{TMTSF})_2\mathrm{PF}_6$ spin density wave formation has been observed (TMTSF is tetramethyl tetra selena fulvalene) (Le *et al.* 1991, 1993).

Application of μSR techniques to fullerenes and derivatives has also produced interesting results. In the C_{60} molecule all carbons are equivalent. Above 260 K the structure of crystalline C_{60} is face-centred-cubic and the molecules rotate freely. Below 260 K the structure is simple cubic with four molecules in the unit cell all becoming orientationally inequivalent because of rotation of 98° about $\langle 1\,1\,1\rangle$ directions; in this phase reorientation about the $\langle 1\,1\,1\rangle$ directions occurs by fast hop following relatively long residence times. Below 90 K the C_{60} molecules are frozen into the simple cubic lattice.

Muons implanted in C_{60} exist in two forms, as endohedral muonium (within the C_{60} cage), with a contact hyperfine interaction of 4256 MHz, close to the value of 4463 MHz for free muonium, and as a paramagnetic radical with a contact hyperfine interaction of 325 MHz (Ansaldo *et al.* 1991). A subsequent study by Kiefl *et al.* (1992*a*) showed that the radical dynamics are strongly coupled to those of its C_{60} neighbours, rotating freely at room temperature and changing discontinuously at 260 K. Further μSR studies by Kiefl *et al.* (1992*b*) on K_4C_{60} and K_6C_{60} at low temperatures show that they are not conductors and that endohedral muonium is present but formation of the radical is suppressed; the majority of the muons form diamagnetic centres with a precession frequency close to that of the free muon. Kiefl *et al.* (1993) have studied muons implanted in metallic Rb_3C_{60}, which becomes superconducting at 29 K. They found that not only are diamagnetic muons formed in the superconducting state (at a concentration about 70% of that formed in a normal metal such as Al) but also endohedral mounium (accounting for about 15% of the muons).

The free C_{70} molecule has D_{5h} symmetry with five inequivalent carbons. Crystals of C_{70} grown by sublimation have a complex mixture of phases but after annealing at 573 K for 17 days it was found that the structure becomes predominantly face-centred-cubic (Green *et al.*, personal communication, 1992). Chandrabhas *et al.* (1993) concluded that the C_{70} molecules are completely orientationally disordered above 330 K, disordered along the long axis of the molecule between 330 and 270 K and orientationally ordered below 270 K. Muons implanted in solid C_{70} also give rise to endohedral muonium and to three radical states with hyperfine interactions of 278, 342 and 364 MHz (Niedermeyer *et al.* 1993), less than the number of inequivalent carbons (see above). Zero-field relaxation studies of the muonium as a function of temperature show orientational ordering of the fullerene at 270 K (Prassides *et al.* 1994).

5. Conclusions

In all the semiconducting polymers studied implantation of muons gives rise to two muon species, one diamagnetic and one a paramagnetic radical with relative concentration dependent on the material. The existence of the paramagnetic radical may be explained by reaction of thermalized muonium with a double bond on the polymer chain. This reaction may be sufficiently energetic to give rise to the escape of an electron in some cases, necessary for the formation of diamagnetic centres (but see § 3 *a* for a discussion of trans-polyacetylene).

Longitudinal muon relaxation measurements of some diamagnetic centres at low temperatures in external magnetic fields show a characteristic $H^{-1/2}$ dependence of the frequency of relaxation suggesting perturbation of the muon nucleus by an electron spin diffusing in one dimension. At higher temperatures the magnetic field dependence suggests increased dimensionality of the spin motion (the $H^{-1/2}$ dependence is also observed at room temperature for trans-polyacetylene, consistent with topological constraint on movement of solitons between chains).

The paramagnetic radicals relax very slowly over a time scale of *ca.* 5 μs, in contrast to the relatively rapid relaxation observed for radicals in the gas phase. It appears that relaxation is more effective in gases because of molecular motions.

In polymers doped to metallic conductivities muons are present primarily in diamagnetic states and at 15 K show longitudinal muon spin relaxation characteristic of a relatively static system. On warming motional effects are observed.

Some organic charge transfer salts are superconductors and muons may be used to determine the magnetic penetration depth, a property of considerable significance for understanding of the superconducting state. Muon spectroscopy has also shown the existence of endohedral muonium and radical states in solid C_{60} and C_{70}, giving information about molecular dynamics in the solids. Both endohedral muonium and diamagnetic muons are found in the superconducting Rb_3C_{60}.

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Discussion

P. Day (*The Royal Institution, London, U.K.*). A straightforward way to vary the dimensionality of spin diffusion in conjugated polymer samples is to make the muon measurements on partially oriented material prepared by stretching. Have any results of this type been obtained?

W. Hayes. No, but stretched polyaniline samples are now available from Durham with large conductivity anisotropy and these will be studied in the near future.

R. Jones (*Department of Physics, Exeter, U.K.*). What is the nature of the pinning centres for charged solitons in trans-polyacetyline?

W. HAYES. Although it is possible to see effects of pinning in infrared spectra, the nature of the pinning defects continues to be elusive.

A. M. STONEHAM (*Harwell Laboratory, Oxfordshire, U.K.*). If the paramagnetic and diamagnetic fractions depend on polymer defects (chain ends, network topology, etc.), surely this could be changed systematically by radiation-induced cross linking?

W. HAYES. Yes, and it is desirable that this should be done.