

## Electron Nuclear Double Resonance Observation of $\pi$ -Electron Defect States in Undoped Poly(Paraphenylene Vinylene)

S. Kuroda

*Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan*

T. Noguchi and T. Ohnishi

*Tsukuba Research Laboratory, Sumitomo Chemical Co. Ltd., Tsukuba, Ibaraki 300-32, Japan*

(Received 20 September 1993)

Electron nuclear double resonance spectra in stretch-oriented undoped poly(paraphenylene vinylene) films show clear anisotropy of an unpaired  $\pi$  electron on the polymer chain. The maximum value of the spin density reaches 0.09, which corresponds to the half-width of the spatial extension of the spin over several phenyl rings. Comparison between the dark and photoinduced ESR signals strongly suggests that the observed spins are trapped polarons.

PACS numbers: 76.70.Dx, 71.50.+t, 75.20.Ck

Conjugated polymers have been attracting much attention as one-dimensional electronic systems which are capable of generating nonlinear excitations such as solitons and polarons [1]. These excitations give rise to characteristic absorptions in optical, magnetic resonance, and other spectroscopic measurements [1-6]. Among them, poly(paraphenylene vinylene) (PPV) with nondegenerate ground-state structure has been extensively studied [4-6] in relation to the role of polarons, excitonic polarons, and bipolarons in determining the mechanism of the intense electroluminescence [7,8] observed in this system. These studies as well as others have indicated the existence of the polarons in PPV; their stability has recently been the subject of theoretical interest [9]. To identify the existence of the polarons, their spatial extension, or in other words, the wave function, is another essential microscopic quantity. Electron nuclear double resonance (ENDOR) spectroscopy can directly measure the spin density distribution of the paramagnetic excitation in the conjugated polymers through the study of hyperfine coupling [1,10,11].

In this Letter, we report the first high-resolution ENDOR spectra of paramagnetic species observed in the dark state of undoped PPV using stretch-oriented samples. The spectra have shown a clear anisotropy of a  $\pi$  electron on the conjugated chain. Three distinct spectral turning points have been resolved for the spectra of stretch direction. The maximum spin density reaches 0.09, corresponding to the spatial extension of the spins over several phenyl rings. The resemblance between the dark and photoinduced ESR signals at low temperatures strongly suggests that the observed  $\pi$ -electron spins are trapped polarons.

Figure 1 shows the chemical structure of PPV. Block letters from A to F show the eight carbon sites in one PPV monomer unit. The principal axes of hyperfine coupling of an unpaired  $\pi$  electron due to the proton are also defined in the figure, where the  $x$  and  $z$  axes are parallel to the C-H bond axis and the  $p\pi$  orbital axis, respectively. When the direction cosines of the external magnetic

field to the hyperfine axes are given by  $p, q, r$ , for a proton bonded to a particular carbon site with a spin density  $\rho$ , the ENDOR frequency is given as [10],

$$\nu_{\pm} = \nu_p \pm \frac{1}{2} \rho A(p, q, r). \quad (1)$$

Here  $\pm$  represent the two branches of the ENDOR frequency and  $\nu_p$  is the free proton frequency.  $\rho A(p, q, r)$  is the hyperfine coupling due to the proton and  $A(p, q, r)$  is given by the following equation [10,11]:

$$A^2(p, q, r) = A_{xx}^2 p^2 + A_{yy}^2 q^2 + A_{zz}^2 r^2. \quad (2)$$

Here  $A_{xx}$ , etc., are the principal hyperfine tensor components of a  $\pi$  electron due to a C-H proton and they are approximately expressed as  $A_{xx} = -(1-\alpha)A$ ,  $A_{yy} = -(1+\alpha)A$ , and  $A_{zz} = -A$ . Here  $A$  is the so-called McConnell's constant, of magnitude 56-84 MHz (or in magnetic field units, 20-30 G).  $\alpha \sim 0.5$  represents the relative magnitude of the anisotropic coupling. Among these tensor components  $A_{yy}$  has the largest absolute magnitude.

Figure 2 shows the orientation dependence of ESR spectra at room temperature in an undoped film stretched up to 10 times. The samples were prepared with a new precursor polymer containing cyclic sulfide [12] instead of the one originally developed [13]. The average of the  $g$

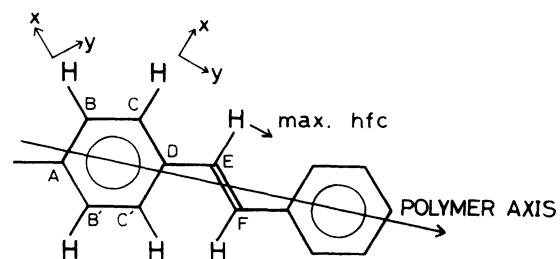


FIG. 1. Chemical structure of poly(paraphenylene vinylene), PPV. Principal axes of proton hyperfine coupling of a  $\pi$  electron are also shown for two inequivalent C-H bond orientations.

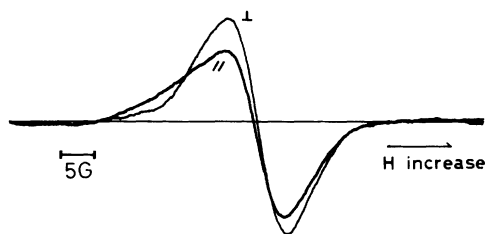


FIG. 2. Anisotropy of ESR spectra at room temperature in a 10-times stretched undoped PPV film. The external field is parallel and perpendicular to the stretch direction for the curves marked by  $\parallel$  and  $\perp$ , respectively.

values of the two orientations in Fig. 2 is 2.003. The spin concentration of about 1 spin per  $10^6$  PPV monomer units and the anisotropy of the  $g$  value and linewidth (both larger for the stretch direction) are similar to those reported previously in a 7-times stretched film prepared by the original method [14]. On the other hand, the marked difference between the present and previous spectra is that the unknown structure observed when the external magnetic field is parallel to the stretch direction in the previous case is completely absent in the present spectra. This difference may be reasonably attributed to the improved quality of the present film obtained by the new synthetic method, which almost completely eliminates  $sp^3$  defects [12] that possibly give rise to unknown signals with different  $g$  values. Observed anisotropic behavior of the  $g$  value and the linewidth is qualitatively similar to those reported in stretch-oriented polyacetylene films [15] and is understood as that of  $\pi$  electron on the polymer chain [14]. In particular, the linewidth anisotropy suggests the dominance of the unresolved proton hyperfine structures of a  $\pi$  electron, which can arise from the interactions of the distributed  $\pi$ -electron spin with the protons on the polymer chain. The situation has been found to be exactly the case by the direct measurement of the hyperfine coupling using ENDOR spectroscopy, as below.

Figure 3 shows the anisotropy of the proton ENDOR spectra at 4 K in a 10-times stretched undoped PPV film. The spectra were recorded with a Bruker ER-200D spectrometer with the microwave and rf power settings of  $-25$  and  $-10$  dB, respectively. No significant distortion of the spectra was observed around these power levels or below. The external magnetic field is parallel to the stretch direction for the curves in Fig. 3(a) and perpendicular to the stretch direction for those in Fig. 3(b). In each figure the thick-line curve represents the spectrum which was obtained by integrating the observed frequency-derivative spectrum shown by a dotted line. The broad distribution of the spectral frequency up to 19.5 MHz directly shows the distribution of the spin density on the polymer chain [10,11]. An important feature of the spectra in Fig. 3 is that the spectrum taken with the field parallel to the stretch direction shows the larger

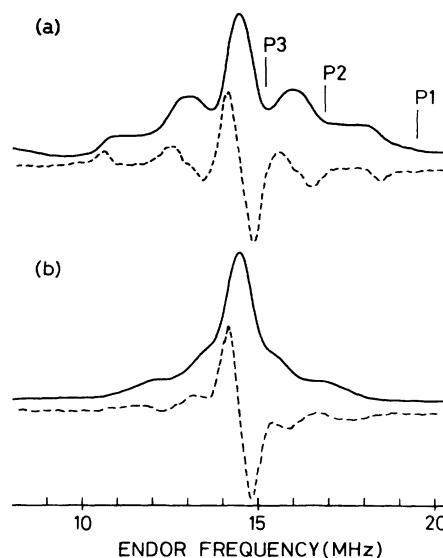


FIG. 3. Proton ENDOR spectra at 4 K in a 10-times stretched undoped PPV film. The external magnetic field is parallel to the stretch direction in (a), and it is perpendicular to that direction in (b). In each figure the thick-line curve represents the spectrum which was obtained by integrating the observed frequency-derivative spectrum shown by a dotted line. Three distinct spectral turning points are marked as  $P1$ ,  $P2$ , and  $P3$  in the spectrum of the stretch direction.

hyperfine coupling. This provides direct evidence for the  $\pi$ -electron nature of the spin. As pointed above, the proton coupling of a  $\pi$  electron shows the maximum value along the  $y$  axis. Figure 1 shows that the  $y$  axis is more inclined to the direction of the polymer axis for the four protons ( $B', C, E, F$ ), while it points intermediate between the polymer axis and the direction perpendicular to it for the two protons ( $B, C'$ ). Therefore, as a whole, larger proton coupling will be expected for the stretch direction, along which the polymer axis may be preferentially oriented. It should also be noted that the observed anisotropic behavior of the spectral line shape can be reasonably reproduced for a distributed spin density on the PPV chain with an ENDOR spectrum simulation method for a partially oriented system [16] taking the existence of the above two inequivalent sites of the C-H bond orientation into account. Of course, model spin densities are required for a more elaborate comparison between the observed and calculated spectra.

Another important feature of Fig. 3 is that the spectrum along the stretch direction has three distinct spectral turning points,  $P1$  to  $P3$  as marked in the figure. These spectral turning points have been resolved clearly for the first time in the present study and they have been confirmed to the intrinsic structures associated with the single spin species observed by cw ESR, using an ENDOR-induced ESR technique [11]. The coupling constants corresponding to these turning points are summarized in Table I together with the values of the spin

TABLE I. Hyperfine coupling and spin density associated with the three distinct spectral turning points resolved in the ENDOR spectra of the stretch direction shown in Fig. 3(a).

Spectral turning points in Fig. 3(a)	Hyperfine coupling (MHz)	Spin density <sup>b</sup>
P1	9.8	0.09
P2	5.1 <sup>a</sup>	0.05
P3	1.3 <sup>a</sup>	0.01

<sup>a</sup>Approximate value.

<sup>b</sup>Values calculated using the relation,  $A_{\text{obs}} = \rho A_{yy}$ , between the observed hyperfine coupling  $A_{\text{obs}}$  and the spin density  $\rho$ . Here  $A_{yy} = (1 + \alpha)A$  shows the  $y$ -axis component of the hyperfine coupling of a  $\pi$ -electron radical.  $\alpha \approx 0.5$  and  $A = 70$  MHz (or 25 G) are assumed.

density deduced from them by assuming a McConnell's constant of 70 MHz (25 G). The largest spin density, determined from the largest coupling at P1, reaches 0.09. This quantity, defined as  $\rho_{\text{max}}$ , is nearly inversely proportional to the full width at half maximum of the spin density distribution, defined as  $l$  [17,18]. In the case of the soliton in Shirakawa polyacetylene,  $\rho_{\text{max}}$  reaches 0.18 (with  $A = 70$  MHz) corresponding to  $l$  of about 18 carbon sites [11,16,19]. Thus  $l$  of the present species becomes close to 40 carbon sites, corresponding to several PPV monomer units.

The appearance of the structures at P2 and P3 shows that there are three distinct groups in the magnitude of spin density, the largest one with the peak value given by  $\rho_{\text{max}}$ , the intermediate one with the peak value (nearly half of  $\rho_{\text{max}}$ ) obtained from P2, and the group with small spin densities with the peak density obtained from P3. In the case of the Shirakawa polyacetylene, a spectral turning point for the first time resolved in the stretch-oriented samples was postulated to be intrinsically associated with the second group of the spin density, that is the negative spin sites arising from the electron correlation effect [16]. The structure has been confirmed to be intrinsic with the aid of ENDOR-induced ESR [11] and the negative sign has been confirmed by electron-nuclear-nuclear triple resonance [19]. The triple resonance in PPV has not been successful so far because of the sensitivity limitation due to the much smaller concentration of the unpaired electrons compared with the case of polyacetylene. The present detection of the above intrinsic structures, however, at least shows that the variation of the spin density is *not monotonic*. This information would be useful in examining the theoretically calculated spin density distribution of the polaron and other paramagnetic spins in PPV.

As for the origin of the observed  $\pi$ -electron spins, it may be natural to relate them to certain defect states of the polymer, since there is no intentional generation of spins by doping, photoexcitation, etc., in the present case. If we consider that PPV has a nondegenerate ground state structure, one candidate of the observed  $\pi$ -electron

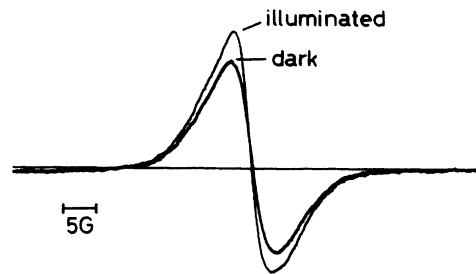


FIG. 4. Comparison of the ESR spectra at 4 K with and without illumination of visible light in a 10-times stretched undoped PPV film. The external field is perpendicular to the stretch direction.

spin is the polaron trapped in the dark state of the polymer. It is interesting to note that the above obtained extension of the spin density, i.e., the maximum value of the hyperfine coupling, is comparable to but slightly smaller than that observed for the anion radical (negative polaron) in the frozen solutions of Li-doped oligomers of phenylene vinylene with the longest case of 7 monomer units [20]. Although the detailed shape of the spin distribution in the reported oligomer naturally does not coincide with the present results obtained in the polymer, the coincidence of the spatial extension further suggests the possibility of polarons.

To investigate the possibility of polarons, we have performed photoinduced ESR measurements at low temperatures, since it is highly possible that the light-induced ESR signal results from positive and negative polarons generated by photoinduced charge transfer between polymer chains. Figure 4 shows an example of photoinduced ESR signal recorded at 4 K under the illumination of visible light (not monochromatic) in a stretched PPV sample with the external field perpendicular to the stretch direction. As is clearly seen, the observed photoinduced signal shows a similar spectral span as the dark ESR signal. This resemblance strongly suggests that the dark species are trapped polarons. The trapped sites of the polarons would be the defects such as chain ends or remaining  $sp^3$  defects in the polymer [9]. Further studies of photoinduced signals such as the signal dependence on the excitation wavelength, requiring enhanced spectral sensitivity and resolution, might provide more detailed information concerning the discrimination of the positive and negative polaron signals and their relation to the dark signal.

- [1] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).
- [2] L. S. Swanson, J. Shinar, and K. Yoshino, *Phys. Rev. Lett.* **65**, 1140 (1990).
- [3] K. E. Ziemelis, A. T. Hussain, D. D. C. Bradley, R. H. Friend, J. R uhe, and G. Wegner, *Phys. Rev. Lett.* **66**, 2231 (1991).

- [4] L. S. Swanson, P. A. Lane, J. Shinar, and F. Wudl, *Phys. Rev. B* **44**, 10617 (1991).
- [5] L. S. Swanson, J. Shinar, A. R. Brown, D. D. C. Bradley, R. H. Friend, P. L. Burn, A. Kraft, and A. B. Holmes, *Synth. Met.* **55-57**, 241 (1993).
- [6] X. Wei, B. C. Hess, Z. V. Vardeny, and F. Wudl, *Phys. Rev. Lett.* **68**, 666 (1992).
- [7] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature (London)* **347**, 539 (1990).
- [8] D. Braun and A. J. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991).
- [9] H. A. Mizes and E. M. Conwell, *Phys. Rev. Lett.* **70**, 1505 (1993).
- [10] S. Kuroda and H. Shirakawa, *Solid State Commun.* **43**, 591 (1982).
- [11] S. Kuroda and H. Shirakawa, *Phys. Rev. B* **35**, 9380 (1987).
- [12] T. Ohnishi, T. Noguchi, T. Nakano, M. Hirooka, and I. Murase, *Synth. Met.* **41-43**, 309 (1991).
- [13] I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Polym. Commun.* **25**, 327 (1984).
- [14] S. Kuroda, I. Murase, T. Ohnishi, and T. Noguchi, *Synth. Met.* **17**, 663 (1987).
- [15] S. Kuroda, M. Tokumoto, N. Kinoshita, and H. Shirakawa, *J. Phys. Soc. Jpn.* **51**, 693 (1982).
- [16] S. Kuroda, H. Bando, and H. Shirakawa, *J. Phys. Soc. Jpn.* **54**, 3956 (1985).
- [17] W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **42**, 1698 (1979).
- [18] K. Yonemitsu, Y. Ono, and Y. Wada, *J. Phys. Soc. Jpn.* **57**, 3875 (1988).
- [19] S. Kuroda and H. Shirakawa, *J. Phys. Soc. Jpn.* **61**, 2930 (1992).
- [20] P. Brendel, A. Grupp, M. Mehring, R. Schenk, K. Müllen, and W. Huber, *Synth. Met.* **45**, 49 (1991).