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Light-induced ESR (LESR) has been employed to study optically-generated polarons in two dialkoxy derivatives of poly(*p*-phenylene vinylene) (PPV), MEH-PPV and CN-PPV. A clear reduction of LESR linewidth is observed in CN-PPV compared with MEH-PPV and also with PPV previously reported, providing direct evidence that the polaron spin density predominantly reside on vinyl sites. This feature can be reproduced by the linewidth analysis based on a theoretical spin distribution of a polaron extending over approximately 4 phenyl rings.

Keywords light-induced ESR; polarons, spin density distribution; conjugated polymers; poly(*p*-phenylene vinylene) and its derivatives

INTRODUCTION

Polarons in poly(*p*-phenylene vinylene)s (PPV) attract much attention in relation to their electroluminescent properties[1]. In PPV, ESR and electron-nuclear double-resonance (ENDOR) spectroscopies have been successful in detecting the spatial extension of the polaron over several phenyl rings through the study of proton hyperfine coupling[2, 3]. The observed spin distribution of the polaron has been

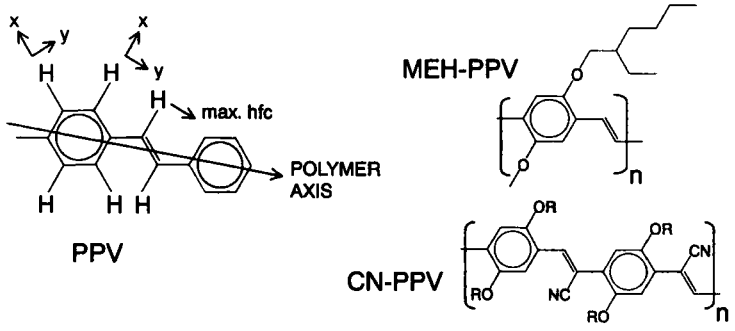

FIGURE 1 Chemical structures of PPV, MEH-PPV and CN-PPV.

well reproduced by the PPP (Pariser-Parr-Pople) model in the case of finite electron-electron interactions[4,5]. Recently, we have been successful in observing significant reduction of light-induced ESR (LESR) linewidth in CN-PPV compared with that of MEH-PPV, where half of protons attached at the vinylic carbon sites are substituted by cyano groups in the former[6]. Chemical structures of these polymers are shown Fig. 1. The result has been well explained by the theoretical spin distribution of the polaron. It is thus of interest to compare the LESR spectra of these derivatives with those of PPV itself. In this paper, we report on the LESR width of these PPV polymers and the analysis based on the theoretical model.

RESULTS AND DISCUSSION

The middle and lower curves in Fig. 2(a) show the observed first derivative LESR spectra of cast films of CN-PPV and MEH-PPV, respectively. The upper curve shows the LESR spectrum of PPV in unoriented case for comparison[3]. The ESR spectrum of CN-PPV has a much narrower spectral span than PPV and MEH-PPV. Asymmetry of the line shape, more pronounced in PPV and MEH-PPV, can be

explained in terms of the anisotropic properties of g-value and the linewidth due to hyperfine coupling of the π-electrons. Full-widths at half maximum of the integrated forms of these spectra in Fig. 2 are 6.7 ± 0.2 Gauss, 6.6 ± 0.2 Gauss and 4.5 ± 0.1 Gauss for PPV, MEH-PPV and CN-PPV, respectively, showing a clear reduction of the linewidth in CN-PPV.

The LESR linewidths in these polymers can be calculated by using the theoretical spin distribution of the polaron previously obtained for PPV by ENDOR, as shown in Fig. 2(b). The calculated width of 4.9 Gauss in CN-PPV is considerably reduced from the width of 6.4 Gauss in PPV and 6.1 Gauss in MEH-PPV, consistent with the observation. This provides evidence for the theoretical prediction that the major spin density of the polaron resides on the carbons at vinyl sites at half of

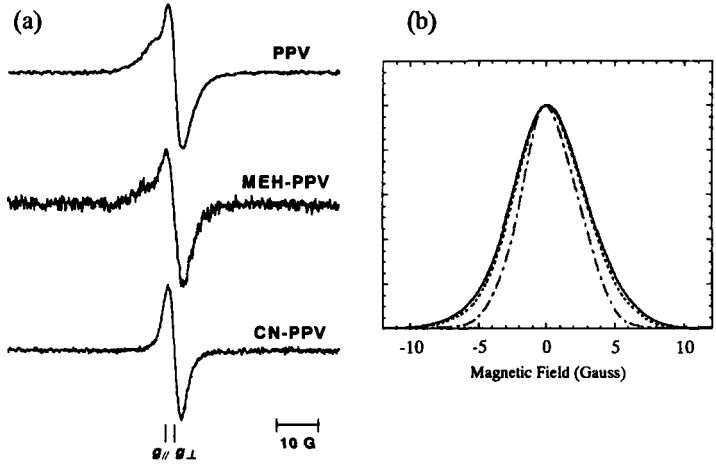

FIGURE 2 (a) First derivative light-induced ESR spectra of cast films of PPV, MEH-PPV and CN-PPV at 80 K under 300 nm light illumination. (b) Calculated ESR spectra, in integrated form, of PPV (solid line), MEH-PPV (dotted line) and CN-PPV (half-dotted line).

which the protons are substituted by the CN group in CN-PPV. Nearly equal widths of MEH-PPV and PPV shows that the spin density at phenyl carbons of which the protons are substituted by alkoxy side chains in MEH-PPV is not significant, as previously predicted. The above agreement of LESR width between the experiment and calculation also supports the polaron extension over approximately 4 phenyl rings. We note that these results are consistent with previous optically-detected magnetic resonance (ODMR) studies of the polaron signal in PPV and CN-PPV, where a considerable reduction of ESR linewidth was observed for CN-PPV compared with PPV[7].

The excitation spectrum of the LESR signal of CN-PPV shows an interesting behavior with a clear threshold, that compares well with the photocurrent action spectrum in MEH-PPV. More details are described elsewhere[6]. Our present work shows that the LESR is a useful technique in elucidating spin distributions as well as the excitation spectra of polarons in conjugated polymers.

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