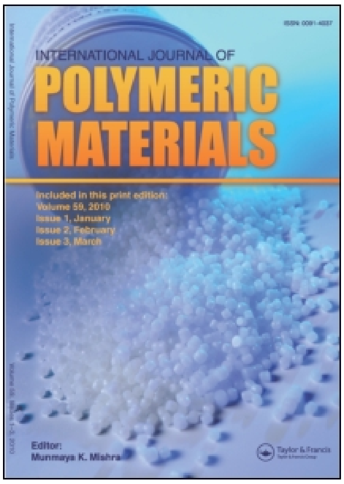

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ENDOR Spectroscopic Study of Macroradicals in Irradiated Oriented Nylon-6

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Macroradicals formed by hydrogen atom elimination in uniaxially and biaxially oriented nylon-6 have been investigated at low temperature using a Q-band ENDOR technique. Hyperfine coupling constants were obtained from the observed ^{1}H ENDOR spectra for the protons located at α-, β-, and γ-positions relative to the unpaired electron in the radical $-CO-NH-\dot{C}H-CH_2-CH_2-$. Principal values for α-proton anisotropic coupling tensor have been determined. A degree of angular disorientation of the radical centers $-\dot{C}H-$ along the axes of biaxially oriented polymer was evaluated. The protons of the β-methylene group were found to be magnetically nonequivalent and therefore the plane of the free carbon was twisted. The deviation from the ideally planar transconfiguration corresponds to the rotation around the C_α–C_β bond on average angle 11°. A change in β-proton ENDOR spectrum has been revealed under mechanical loading of oriented specimens. The results obtained evidenced for the appearance of reversible torsional deformation in stressed macroradicals.

KEY WORDS Free radicals, nylon-6, ENDOR, hyperfine coupling, conformation, orientation.

INTRODUCTION

Irradiation of polymers frequently leads to a hydrogen atom elimination and the formation of middle type free radicals. These radicals in many respects retain properties of native macromolecules inherently related to the polymer structure and mechanical behavior. The radiation induced radicals in polymers were the subject of ESR studies in numerous works.[1–3] In the case of nylon, the predominant type of radical[4,5] trapped in irradiated polymer samples at room temperature was found to be

$$-CO-NH-\dot{C}H-CH_2-CH_2-.$$

Fundamental limitation of the ESR is its resolution. Since the ENDOR method excels ESR in high resolution, it has some advantages in studying radicals in polymers. The ^{1}H ENDOR spectra of macroradicals produced by X-ray irradiation in some unoriented solid polymers including nylon-6 have been reported earlier.[6] In the present work, the ENDOR technique has been used to investigate conformational structure and orientational ordering of radicals in oriented nylon-6.

EXPERIMENTAL

Free radicals were created by X-ray irradiation of uniaxially and biaxially oriented specimens of nylon-6 at room temperature during 1–2 h, absorbed energy was not exceeding 50 kJ kg^{-1}. Uniaxially oriented specimens with 1 mm in diameter had a draw ratio about 5. Biaxially oriented samples were prepared by pressing of uniaxially oriented ones with subsequent annealing at 190°C for 20 min. The maximum press ratio was about 3.

ENDOR spectra were recorded with a laboratory Q-band spectrometer[7] which was built up using Varian-4503 EPR spectrometer operating at 35 GHz with magnetic field modulation at 100 kHz. A magnetic RF field, necessary for the excitation of nuclei transition, was generated in a cavity resonator where a single turn coil was placed. An RF current passed through the coil was amplitude modulated at frequency of 200 Hz. When the double resonance was recorded the amplifying channel of the EPR spectrometer was included in the circuit so as to provide the amplification and separation of signals at the both modulation frequencies (100 kHz and 200 Hz). The ENDOR spectra were obtained by slow sweeping of the frequency in the range of 45–120 MHz with a fixed tuning to the maximum of the derivative of the outermost component of the ESR spectrum in the presence of a saturating level of the microwave power.

The results obtained showed that in spite of the considerable sensitivity decrease (as compared to the ESR method), ENDOR spectra were reliably recorded at moderately low temperatures with signal-noise ratio exceeding 10.

RESULTS AND DISCUSSION

Magnetic resonance spectra

Figures 1 and 2 show the ESR spectra of macroradicals in irradiated nylon-6, obtained for various orientations of drawn samples in the magnetic field. Here we denoted L is draw direction, l is transverse direction, H is magnetic field direction. The resolved hyperfine structure of spectra is produced by unpaired electron coupling to the three protons located in α- and β-positions with respect to the radical center $-\dot{C}H_\alpha-CH_{\beta_1}H_{\beta_2}-$. Interactions with the other protons result in a broadening of ESR lines only (linewidth is about 35 MHz). Changes in the ESR spectrum observed for various directions of the magnetic field (different number of lines, their separation and their relative intensities) are produced through the variation of doublet splitting due to the α-proton anisotropy.[5] In the case when $L \parallel H$, α- and both β-methylene protons seem to be magnetically equivalent, though more detailed analysis predicts some nonequivalence of β-protons.[3,8]

The ENDOR spectra of macroradicals in oriented nylon-6 presented in Figures 3 and 4 exhibit sufficient improvement in resolution as compared to that of the ESR. ENDOR bandwidths measured at one-half of line height are much less than in ESR and equal to several MHz. ENDOR spectra allow to separate individual absorption bands for strong and weak interacting protons in the macroradical. Assignments of bands to α-, β-, and γ-protons in $-CO-NH-\dot{C}H-CH_2-CH_2-$ are depicted in Figure 3. There is also an absorption band in the ENDOR spectrum in the region of free nuclear magnetic resonance from more distant protons.

A double resonance spectrum can be treated as a magnetic resonance of nuclei surrounding the unpaired electron in a radical detected by ESR signal increasing at particular radio-frequencies. A shift of the magnetic resonance frequency ν_{END} from the frequency ν_0 of free NMR reflects the hyperfine interaction between the appropriate nucleus and

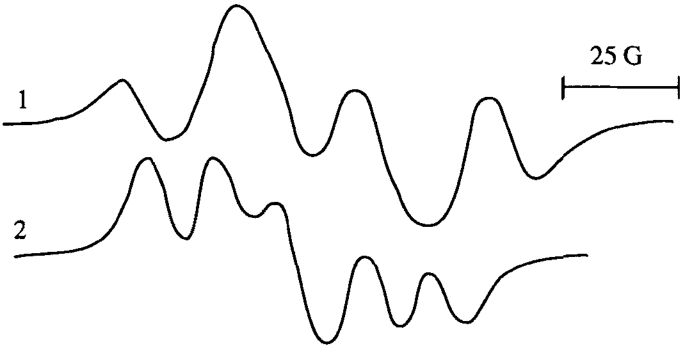

FIGURE 1 First derivative Q-band ESR spectra of radicals in uniaxially oriented nylon-6. Orientation of the specimens in the magnetic field: $L \parallel H$ (curve 1), $L \perp H$ (curve 2).

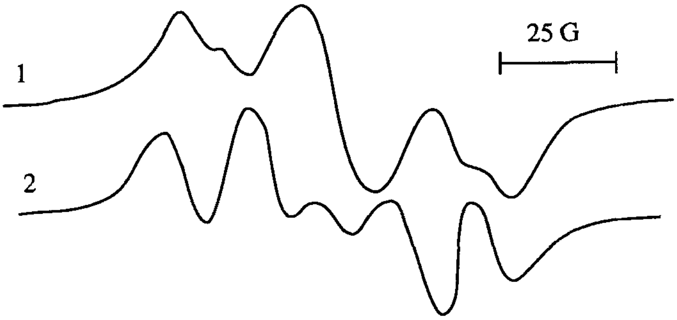

FIGURE 2 ESR spectra of radicals in biaxially oriented nylon-6. Orientation of the specimens in the magnetic field: $L \perp H$ and $l \parallel H$ (curve 1), $L \perp H$ and $l \perp H$ (curve 2).

unpaired electron of a free radical

$$|a + b| = 2(\nu_{\text{END}} - \nu_0).$$

Isotropic a and anisotropic b components of hyperfine coupling (HFC) can be derived from ENDOR spectra of oriented polymer samples. HFC calculated for different protons in the radical at low temperature are given in Table I.

The strongest anisotropy is typical of the α-proton HFC. Figure 4 shows ENDOR spectra of α-protons in uniaxially and double axially oriented nylon-6 radicals measured at different sample positions in the magnetic field. It is seen that the spectrum obtained from the uniaxially oriented sample with the draw axis being placed perpendicular to the magnetic field differs from the similar spectrum for the biaxially oriented specimen. The ENDOR intensity in the second case increases while the band width decreases. If the plane of the biaxially oriented sample is parallel to the magnetic field, the band is concentrated on the low-frequency absorption edge. At the perpendicular sample orientation, the band is displaced to the high frequency edge. These changes are associated with the anisotropy of the α-proton HFC and may be considered as characteristic of orientational ordering of radicals along the transversal axis. An ENDOR bandwidth depends on disordering of radical arrangements. In the case of regularly arranged free radicals, trapped in irradiated

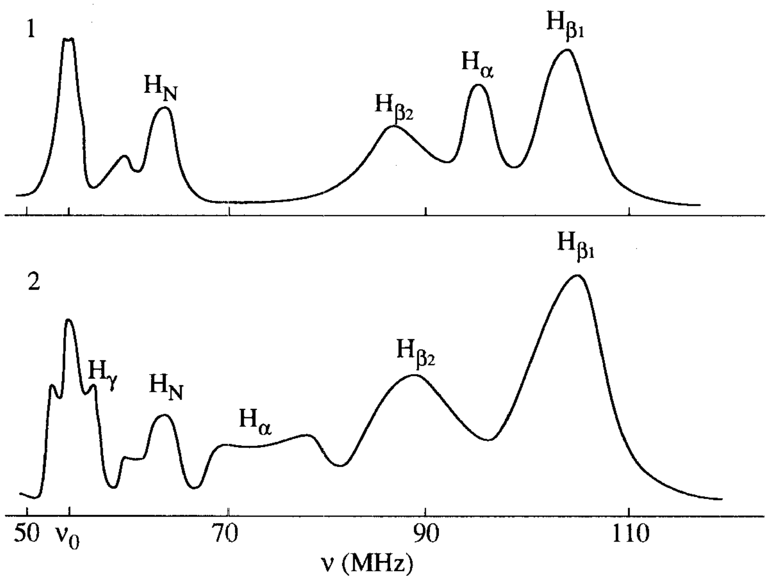

FIGURE 3 Absorption ENDOR spectra of radicals in uniaxially oriented nylon-6. Orientation of the specimens in the magnetic field: $L \parallel H$ (curve 1), $L \perp H$ (curve 2).

TABLE I
Hyperfine couplings at −100°C

Proton	Hyperfine couplings (MHz)	
	$L \parallel H$	$L \perp H$
H_α	84	25–50†
H_{β_1}	98	100
H_{β_2}	64	67
H_N (1)	19	17
H_N (2)	12	10
H_γ	—	4.2

† Boundaries of the ENDOR line.

organic monocrystals, linewidth is rather small (0.1 MHz).[9] Such a narrow ENDOR line of the radical $-CO-NH-\dot{C}H-CH_2-$ in ε-caprolactam single crystal, measured at an arbitrary orientation of the sample in the magnetic field, is shown in Figure 4.

α-proton coupling tensor

ENDOR spectra of macroradicals in oriented samples of nylon-6 provide data to calculate the principal values of the α-proton coupling tensor. The principal values B_x, B_y, B_z of the anisotropic coupling tensor were evaluated in accordance with the equation for dipole–dipole hyperfine splitting

$$b = B_x\cos^2\alpha + B_y\cos^2\beta + B_z\cos^2\gamma.$$

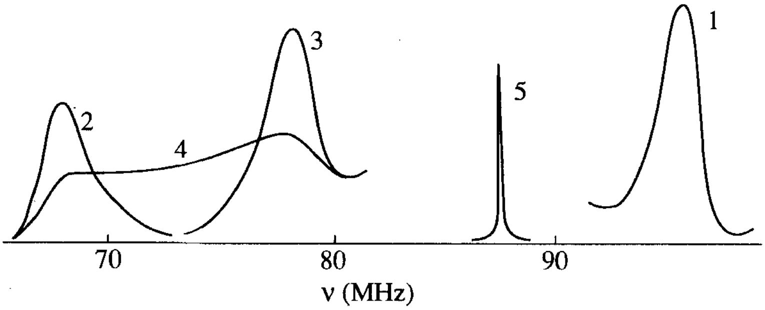

FIGURE 4 ENDOR spectra for α-proton of radicals in biaxially (curves 1–3) and uniaxially (curve 4) oriented nylon-6. Specimens orientation: $L \parallel H$ (curve 1); $L \perp H$, $l \parallel H$ (curve 2); $L \perp H$, $l \perp H$ (curve 3); $L \perp H$ (curve 4). ENDOR line of radicals in irradiated crystal of ε-caprolactam (curve 5).

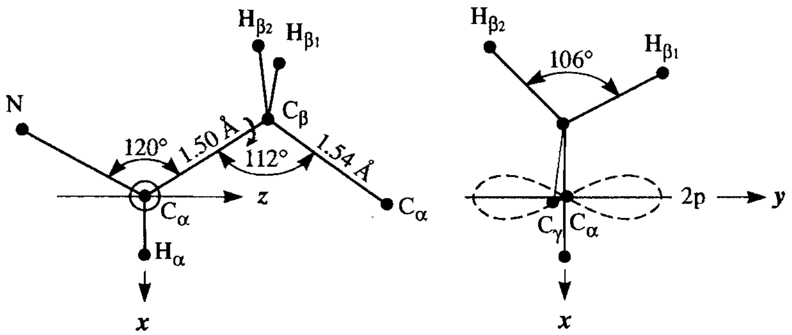

FIGURE 5 Radical geometry.

Here cosα, cosβ, cosγ are the direction cosines of the magnetic field to the principal axes of the tensor (X is along the C$_\alpha$–H$_\alpha$ bond, Y is along the 2p-orbital of unpaired electron, Z is the third axis of ortogonal system (see Figure 5)).

It is reasonable to assume that in an oriented polymer there is some amount of free radicals having an ideal alignment along the orientational axes when axis Z coincides with L, and axis X coincides with l. Ideally oriented radicals should define the appropriate values of anisotropic hyperfine splitting ($b_1 = B_x$ at $L \perp H$ and $l \parallel H$, $b_2 = B_y$ at $L \perp H$ and $l \perp H$, $b_3 = B_z$ at $L \parallel H$) and hence the boundaries of ENDOR spectra.

The fact that any drawn polymer sample contains a significant amount of radicals oriented not parallel to the draw direction results in the smoothing of the absorption bands edges. Therefore, boundary frequencies ν_1, ν_2, ν_3 may be defined with some approximation. For the sake of simplicity, frequencies ν_1 and ν_3 were evaluated by linear extrapolation of the central slope of the appropriate band edges to the base line and the intermediate frequency ν_2—by its extrapolation up to the top level of the resonance line. These frequencies were found to be $\nu_1 = 66.3$ MHz, $\nu_2 = 78.7$ MHz, $\nu_3 = 96.7$ MHz at $\nu_0 = 54.3$ MHz. The average meaning ν is of 80.57 MHz. Isotropic component of HFC tensor taking into account its sign for α-proton was determined to be $A_\alpha = -2(\bar{\nu} - \nu_0) = -52.5$ MHz.

Principal values of α-proton anisotropic coupling tensor at low temperature were determined to be $B_x = +28.5$ MHz, $B_y = +3.8$ MHz, $B_z = -32.3$ MHz. A comparison of these values with those of the theoretical tensor for $-\dot{C}H-$ radical[10] gives a spin density of

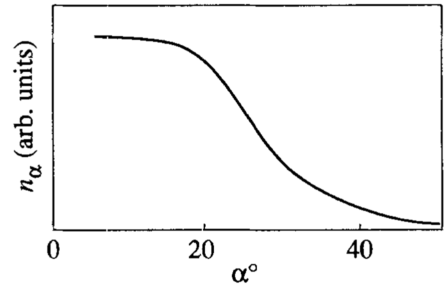

FIGURE 6 Angular distribution of radicals in biaxially oriented nylon-6. α is dihedral angle between Ll and LX planes.

unpaired electron on C_α atom in macroradical to be equal to $\rho_c = 0.75$.

Using the principal values of anisotropic HFC tensor for α-proton and treating band shapes of ENDOR lines, it is possible to estimate a quality of a macroradical orientational order in the drawn polymer sample. The results obtained evidence that the majority of radicals have the Z axis declined with respect to the draw direction L. The inclination takes place in both LX and LY planes. When the Z axis declines from the L axis at the angle γ_x in the plane LX, z and x components of anisotropic tensor differ from principal meanings by values

$$\Delta b_z = (B_z - B_x)\sin^2\gamma_x = -\Delta b_x.$$

When the Z axis declines from L axis at an angle γ_y in plane LY, the appropriate differences are

$$\Delta b_z = (B_z - B_y)\sin^2\gamma_y = -\Delta b_y.$$

The mean values of the angles γ_x and γ_y estimated from the experimental data are equal to 12° and 17°. The angular distribution of radicals along the L axis evaluated from the band width of $L \parallel H$ spectrum (taken at one half of line height) ranges from 7° to 22°.

In the case of biaxially oriented sample, angular distribution along the transverse axis was found to be wider. Approximate curve describing the orientation of radicals in biaxially oriented polymer is shown in Figure 6. This curve was plotted as angular dependence of ratio of resonance absorption intensity for biaxially oriented sample, recorded at $L \perp H$ and $l \parallel H$, to the intensity of the similar band of the spectra for uniaxially oriented polymer. Polymer specimen had draw ratio ~ 5, and press ratio ~ 3.

β-methylene group protons

Magnetic unequivalence of β-protons, obvious from the ^{1}H ENDOR spectra, indicates that the macroradical in irradiated nylon-6 is not planar and carbon atom C_γ is not located in the radical center plane (C_β, C_α, N_β atoms plane). A deviation from the ideally planar tansconfiguration of radical carbon backbone was evaluated assuming that isotropic HFC constants obey the relation[11]

$$a_\beta = A_\beta \cos^2\theta.$$

Here θ is the angle between the 2p-orbital axis and the projection of the C_β–H_β bond onto a plane perpendicular to C_α–C_β bond.

Geometry of the methylene groups in macromolecules slightly differs from the tetrahedral one, valency angle C–C–C is equal to 112° and H–C–H is of 106°. Therefore the dihedral angle between the planes C_α, C_β, H_{β_1} and C_α, C_β, H_{β_2} equals 116° but not 120°. Then

$$a_\beta = A_\beta \cos^2(32° \pm \varphi),$$

where φ is a change of the angle of internal rotation around the C_α–C_β bond. The values a_{β_1} and a_{β_2} deduced from the ENDOR spectra at low temperature give the mean value of this angle equal to 11°.

A change of stereoconfiguration observed is induced by the modification in electron structure and local geometry of the chain resulted from the hydrogen atom elimination. As this takes place the lengths of the C_α–C_β and C_α–N_β bonds slightly decrease but the valence angle N_β–C_α–C_β increases from 112° to 120° that will be followed by bending of the macromolecule backbone in the plane of polymer chain. Easily accessible torsion type deformation through the internal rotation around various bonds in macroradicals may be expected as a compensation of unrealized bending. It is noteworthy that in the case of polyethylene macroradical which has two methylene groups, the angles of twisting in each of them appeared to be less by half than it is in nylon-6 radical with one flexible methylene group and the second rigid amide group.

Anisotropic component of the HFC to β-protons is small, thus the rotation of the oriented sample in the magnetic field produces a shift of several MHz in ENDOR spectrum. According to the ESR study of radicals in organic monocrystal,[12] the principal values of the β-proton anisotropic coupling tensor are as follows $B_1 = +8$ MHz, $B_2 = -1$ MHZ, $B_3 = -7$ MHz. The axis of positive principal value is directed very nearly along the C_α–H_β.[12] As it follows from theoretical investigations, directions of the others depend on conformation of the radical.[13]

We have estimated β-proton ENDOR bandwidth using the principal values B_1, B_2, B_3, mentioned above and taking angular disorientation data which have been found for α-proton of radicals. A comparison of these calculated and experimental values evidences that experimental bands for β-protons are broader and cannot be explained as resulting from the HFC anisotropy and radical disordering only. We can conclude that macroradical conformer distribution exists in an irradiated polymer. Deviation of the twist angle from the average value $\bar{\varphi} = 11°$ is as large as ±3°.

NH-group

Resonance absorption band in the frequency region of 56–64 MHz has been ascribed to β-proton, bonded to the nitrogen atom. The dual component ^{1}H ENDOR spectrum can be accounted for by the difference in the stereoconfigurations of amide part of the radical –CO–NH–ĊH–.

Noncoplanar arrangement of polymer chains connected by hydrogen bonds[14] enables out of plane deformation of amide group of radicals in polyamide matrix. Magnitude of this deformation depends on the way of polymer chain packing, polymer structure (crystallite) and locations of free radicals (crystallites, intercrystallite regions, etc.). Isotropic HFC of the unpaired electron to the H_N proton arising in the planar radical results from the occurrence of the spin density on the 2p-orbital of the nitrogen atom and subsequent spin polarization of N–H bond.

In the deformed nonplanar radical with H_N not lying in the plane of $-N_\beta-C_\alpha-C_\beta-$, the isotropic component is to be larger because of additional overlap of the unpaired electron orbital with the orbital of N–H bond.

Some difference in values of hyperfine splitting observed in ^{1}H ENDOR spectrum may be attributed to variation of amide group nonplanarity in macroradicals trapped in the polymer matrix.

Macroradical mechanics

ENDOR spectroscopy opens up opportunities for investigating mechanically deformed macroradicals. A procedure for recording the ENDOR signal of samples stretched directly in a resonator of the spectrometer has been developed. Irradiated oriented specimens were loaded at low temperatures. We have revealed some changes in β-methylene proton ENDOR spectrum under mechanical loading of nylon-6. The results obtained reveal the torsional type deformation in elastically strained macroradicals. The twist angle φ decreases from initial value under uniaxially tension according to the empirical equation

$$\bar{\varphi}(\sigma) = \bar{\varphi}_0 - b\sigma,$$

here σ is tensile stress, $\bar{\varphi}_0 = 11°$, $b = 2$ deg GPa^{-1}.

CONCLUSION

Successful ENDOR experiments have been performed on irradiated oriented nylon-6 at moderately low temperatures illustrating the type of information that can be obtained from the ENDOR measurements which is obscured in the electron spin resonance.

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