

Study of Conformational Changes in Poly(3-dodecylthiophene) Dependent on Backbone Stereoregularity Using a Spin-Probe Technique

F. Šeršeň,¹ G. Čík,² P. Veis³

¹Institute of Chemistry, Faculty of Natural Sciences, Comenius University, 842 15 Bratislava, Slovak Republic

²Department of Environmental Science, Faculty of Chemical and Food Technology, Slovak University of Technology, 812 37 Bratislava, Slovak Republic

³Department of Plasma Physics, Faculty of Mathematics and Physics, Comenius University, 842 48 Bratislava, Slovak Republic

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ABSTRACT: Poly(3-dodecylthiophene) (P3DDT), with different amounts of head-to-head configuration defects, was characterized by ultraviolet-visible, ¹H-NMR, photoluminescence, and Raman spectra. The heat-induced conformational sample changes were studied by electron paramagnetic resonance (EPR). For the study of these changes, a spin-probe technique was used, in which 5-doxyl-stearic acid methyl ester was applied as a spin probe. From the EPR spin-probe spectra, rotational correlation times and order parameters were calculated. The heat-induced conformational changes of P3DDT were accompanied by a monotonic decrease in the rotational

correlation time up to approximately -33°C (240 K) and then by an increase in the range of the glass-transition temperatures, with the maximum being near room temperature and depending on the effective conjugation length. Afterward, the rotational correlation times had a decreasing tendency up to 90°C (363 K). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2215–2223, 2003

Key words: conducting polymers; conjugated polymers; conformational analysis; ESR/EPR

INTRODUCTION

In past years, poly(3-alkylthiophene)s (P3ATs) have extensively been studied because of their high processability induced by the alkyl substitution of polythiophenes, which makes them interesting in various applications.¹ Moreover, some interesting thermochromic and solvatochromic effects unobservable in other substituted polymers have been reported for this class of materials.^{1–3}

In our previous works,^{4,5} we found that at the optimum concentration of Fe³⁺, a high diamagnetism of the polymer system ($\chi'_{1/(4\pi)} = -0.89$ SI units) and a high alternating-current conductivity ($\sigma_{ac} > 10^8$ S m⁻¹) in poly(3-dodecylthiophene) (P3DDT) could be achieved by oxidative doping of the backbone with FeCl₃. Both parameters depended on the heat-induced conformational changes of the backbone and side alkyls.

This work presents some results obtained by the electron paramagnetic resonance (EPR) study of the

heat-induced conformational changes of P3DDT with respect to the contents of configurational head-to-tail (H-T) and head-to-head (H-H) dyads. The first sample (P1) contained 61% H-T and 39% H-H dyads, and the second one (P2) contained 74% H-T and 26% H-H dyads. For sample characterization at room temperature, absorption spectroscopy, analysis of photoluminescence (PL) spectra, Raman spectrometry, and ¹H-NMR spectrometry were used. The heat-induced conformational changes in both polymer samples were studied by EPR (spin-probe technique).

It is known from literature data that P3ATs with a side alkyl chain that is larger than an octyl have the properties of liquid crystals at certain temperatures.⁶ It is possible that a spin-probe technique could be suitable for the study of conformational changes in these polymers. The derivatives of fatty acids, with a spin label in their alkyl chains, are employed as spin probes. It can be assumed that the spin probe is built into the polymer (because of hydrophobic interactions), so its spin label will be placed among side alkyl chains of the polymer. The EPR spectrum of the located spin probe will reflect the properties of its close surroundings. From the EPR spin-label spectra, the rotational correlation time (τ) and the order parameter (S) can be calculated. These parameters may be computed on the basis of relations applied to liquid crystals or lipid membranes known from the literature.^{7–10}

Correspondence to: G. Čík (cik@chtf.stuba.sk).

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The rate of molecular spin-probe orientation is characterized by τ . For the spin-probe rotational correlation time within the limit of the fast spin-label motion, that is, for $10^{-11} \text{ s} < \tau < 3 \times 10^{-9} \text{ s}$, the following relations have been derived from parameters of the applied spin-probe EPR spectrum:^{8,9}

$$\tau_B = \Delta H_0 2.8 \times 10^6 (3\pi)^{1/2} [8b\Delta\gamma H_0]^{-1} \times [(I_0/I_{-1})^{1/2} - (I_0/I_{+1})^{1/2}] \quad (1)$$

$$\tau_C = \Delta H_0 2.8 \times 10^6 (3\pi)^{1/2} [b^2/4]^{-1} \times [(I_0/I_{-1})^{1/2} + (I_0/I_{+1})^{1/2} - 2] \quad (2)$$

$$-\Delta\gamma = \beta [g_{zz} - 0.5(g_{xx} + g_{yy})]h^{-1}$$

$$b = 4\pi (A_{\parallel} - A_{\perp})/3$$

where ΔH_0 is the half-width of the central ($M = 0$) EPR line (Gauss), H_0 is the magnetic-field induction in the position of the central line (Gauss), I_M is the amplitude of the EPR lines for the magnetic quantum number M , β is Bohr's magneton, \hbar is Planck's constant, g_{ii} is a component of the diagonalized g factor measured in the crystal, and A_{\parallel} and A_{\perp} are \mathbf{A} tensor components of the hyperfine interaction in units of the frequency (s^{-1}). Relations (1) and (2) imply two different procedures for the calculation of the same rotational correlation time. If conditions of the quick motion are carried out, the deviations between them is minimal.

From the parameters of these spectra, S , which characterizes the degree of crystallinity, can also be calculated:^{8,9}

$$S = f_A(A_{\parallel} - A_{\perp})/[A_{zz} - (A_{xx} + A_{yy})/2] \quad (3)$$

$$f_A = (A_{\parallel} - 2A_{\perp})/(A_{xx} + A_{yy} + A_{zz})/$$

$$A_{\perp} = A_{\min} + 1.4(1 - S_{\text{app}})$$

$$S_{\text{app}} = (A_{\parallel} - A_{\min})/[A_{zz} - (A_{xx} + A_{yy})/2]$$

where A_{ii} is a component of the diagonalized \mathbf{A} tensor measured in the crystal and f_A is the polarity correction factor. If the spin probe is incorporated into the perfect crystalline surroundings, S is 1, and its spectrum can be characterized by g and \mathbf{A} tensors with axial symmetry.

The aim of this work was to ascertain by means of the spin-probe technique how the heat-induced conformational changes in P3DDT depended on the content of H-T and H-H configurational dyads.

EXPERIMENTAL

P3DDT with different contents of H-T dyads was synthesized with two procedures. P3DDT containing 61% H-T and 39% H-H (sample P1) was synthesized according to ref. 11 through Grignard reaction intermediates of monomers. P3DDT containing 74% H-T and 26% H-H (sample P2) was synthesized by oxidative polymerization with FeCl_3 according to ref. 12. The dedoping of FeCl_3 was accomplished by the addition of ammonia to the chloroform solution of P3DDT. The dedoping was performed three times, each procedure lasting 40 min at room temperature. The chloroform extract layer was finally rinsed out three times with distilled water, and P3DDT was precipitated into methanol. After the reflux in methanol (1 h), the product was filtered off and dried out in a desiccator.

The content of H-T dyads was determined from the $^1\text{H-NMR}$ spectra according to ref. 13. These spectra were measured with an FT NMR VXR-300 (Varian, Palo Alto, CA) spectrometer in CDCl_3 .

The ultraviolet-visible (UV-vis) spectra were measured with a PU-8800 (Philips Analytical, Cambridge, UK) spectrophotometer with an accuracy of $\pm 0.3 \text{ nm}$. The polymer film samples were prepared by a spin-coating method on quartz glass from a chloroform solution. The thickness of the film was measured with a Talysurf apparatus (Rank Taylor Hobson, Leicester, UK) based on the principle of apical contact surface scanning. The thickness of the polymer films was within $500 \pm 50 \text{ nm}$.

The Raman spectra were obtained in the backscattering geometry with a LabRaman micro-Raman spectrometer (Jobin Yvon-Dilor-Horiba, Lille, France) and HeNe laser excitation at 632.8 nm. The laser beam was focused onto the sample surface with a completely stigmatic optic microscope (BX 40, Olympus, Hamburg, Germany). As the polymer surface showed a relatively high roughness, the use of an objective with maximal enlargement ($50\times$) had to be chosen. With a confocal hole of $1000 \mu\text{m}$, it was possible to scan the upper layer of the polymer sample, which had a thickness of about $10 \mu\text{m}$. The microscope parameters enabled us to scan the Raman spectra from a spot about $1 \mu\text{m}$ in diameter. The spectrometer was equipped with an X-Y moving table for sample positioning. As the polymer was highly sensitive to the laser exposition (showing remarkable changes in the Raman spectrum due to the full energy of 50 mW during 10 s), $100\times$ attenuated laser energy and an exposition of only 1 s were used. To obtain reasonable spectra, we needed to perform an accumulation 15 times in different X-Y positions with a moving table. The displacement of different scans placed in a circle was $2 \mu\text{m}$. It was impossible to achieve a higher accumulation because of the roughness of the sample surface and the

TABLE I
UV-Vis, PL, and Raman Spectra of P3DDT

Sample	λ_{\max} (nm)	λ_{em} (nm)	Stokes shift (nm)	PL ratio	Raman shift (cm^{-1})	Gauss/Lorentz ratio
P1	501	663	162	0.38	144.4 ^a	0.95 ^d
P1		714	213		138.0 ^b	0.60 ^d
P1					726 ^c	
P2	511	664	153	0.53	1449.1 ^a	0.95 ^d
P2						
P2		721	210		1379.8	0.60 ^d
P2						

^a C=C symmetry ring stretching.

^b C—C ring stretch.

^c C—S—C bending.

^d The error was 5%.

defocalization of the scan volume. The spectrometer was equipped with a holographic grating (1800 grooves/mm) and a charge coupled device (CCD) detector. With a 150- μm slit, the wave-number accuracy was within 0.5 cm^{-1} . From the recorded spectra, after the background caused by PL was subtracted, the locations of the peaks were fit with LabSpec software (Lille, France). The polymer films were prepared by the Si support plate being poured from a chloroform solution (5 mg/cm^3). The thickness of the films was within $50 \pm 5 \mu\text{m}$.

The measurement of the PL spectra was carried out with the same LabRaman spectrometer and under the same experimental conditions used for the measurement of the Raman spectra. The PL spectra were less sensitive to the exposition of the laser beam (the position of the peaks and their radii and half-widths). For this reason, the higher power output (50 mW) of the laser with a spot dimension of approximately $10 \mu\text{m}$ at a $10\times$ magnification was applied for the excitation of the PL spectra. The scanning of the spectra was accomplished in several spots (six points total with an X-Y step of $2 \mu\text{m}$). The character of the scanned spectra did not change (in this work, the PL spectra from the first registration are indicated). For the decomposition of the PL spectra, the standard program for deconvolution (LabSpec) was used. Inasmuch as the 100% Gauss/Lorentz decomposition did not correspond exactly to experimental shapes, the linear combination of both kinds of line shapes (the Gauss/Lorentz ratio is indicated in Table I) was used for fitting. The accuracy of the peak location was within $0.1 \pm 0.05 \text{ nm}$ for both fitted peaks.

The EPR spectra were measured with an ERS-230 apparatus (ZVG, Academy of Sciences, Berlin, Germany) in the X region at a microwave output of 5 mV and at a modulation amplitude of 0.1 mT. For the measurement of the changes in the arrangement of the polymer samples caused by temperature, the EPR spectra of the spin probe built into the polymer matrix

were recorded. 5-Doxyl-stearic acid methyl ester (5-DSAME; Sigma, St. Louis, MO) was used as a spin probe. The P3DDT films of samples P1 and P2 with the probe 5-DSAME were made as follows: 5 mg of P3DDT was dissolved in 1 cm^3 of chloroform with the necessary amount of the spin probe (the molar ratio of the monomer of dodecylthiophene to 5-DSAME was 100:1). The solution of the polymer and spin probe was applied by being poured onto the Teflon support plate, and after the evaporation of chloroform, the film was pulled down. The thickness of the film was approximately $30 \mu\text{m}$. After drying out in a desiccator, the film was transferred into a glass measuring tube, in which the drying was finished (ca. 2 h) in a vacuum of 1 Pa, and then the cell was sealed under the vacuum.

From the parameters of the 5-DSAME spin probe, the following formulas for the calculation of the rotational correlation times (s) were obtained:⁸⁻¹⁰

$$\tau_B = 6.208 \cdot 10^{-10} \Delta H_0 [(I_0/I_{-1})^{1/2} - (I_0/I_{+1})^{1/2}] \quad (4)$$

$$\tau_C = 5.805 \cdot 10^{-10} \Delta H_0 [(I_0/I_{-1})^{1/2} + (I_0/I_{+1})^{1/2} - 2] \quad (5)$$

where ΔH_0 is required in Gauss. For the calculation of S , hyperfine splitting constants of 5-DSAME in the crystal phase were used: $A_{xx} = 6.3 \text{ G}$, $A_{yy} = 5.8 \text{ G}$, $A_{zz} = 33.6 \text{ G}$, $g_{xx} = 2.0068$, $g_{yy} = 2.0061$, and $g_{zz} = 2.0027$.⁸⁻¹⁰

RESULTS AND DISCUSSION

The influence of the content of H-H dyads on the conjugated length was characterized with UV-vis PL and Raman spectra. Figure 1 illustrates absorption spectra of the polymer films of both investigated samples of P3DDT. It follows from the figure that λ_{\max} in the sample with a higher proportion of configurational

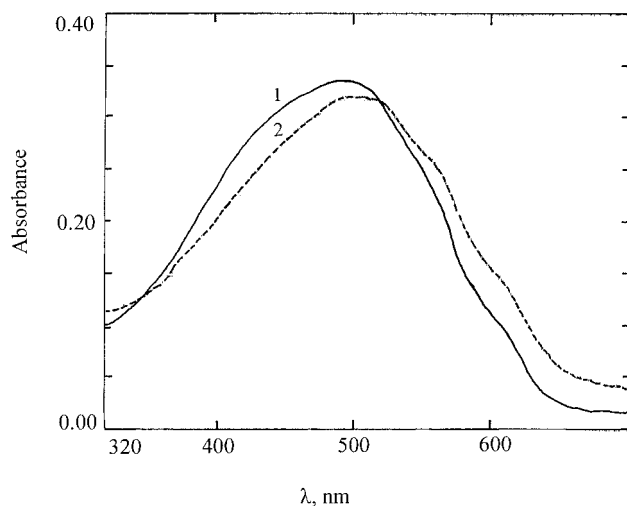


Figure 1 UV-vis spectra of P3DDT films: (1) P1 and (2) P2.

defects (P1 containing 39% H-H) was shifted, in comparison with that of sample P2 (26% H-H), to higher energies (from 511 to 501 nm) by 10 nm. Moreover, the shape of the absorption spectra points to the fact that P1 had a higher proportion of the subchains with a shorter conjugated length. Figure 2 provides PL spectra of films of both samples. The analysis of the decomposed spectra is demonstrated in Table I.

From the PL spectra presented, it follows that in both samples they could be fit by two bands, the relative intensity of which, given by the ratio of the

first and second bands, probably depended on the existing proportion of H-H dyads. By comparing the Stokes shifts, given by the difference between the λ_{\max} values of the absorption and emission spectra,¹⁴ we observed that they were larger in the sample with a higher proportion of the configurational H-H dyads (sample P1). This also agreed with the results of ref. 14, according to which P3ATs with a higher proportion of H-H defects assume a quinonoid (coplanar) arrangement in the excited state, which leads to a more distinctive shift of the main emission maximum in the direction of lower energies. However, the shift of maxima in the PL spectra to lower energies with a loss of the H-H defects (sample P2) confirmed the well-known fact from the literature¹⁵ that in P3DDT with a higher content of H-T dyads, the emission maximum is shifted to higher wavelengths, as was observed in our case. The vibronic shape of the PL spectra suggests that the samples contained chains with various conjugated lengths depending on the content of H-H dyads. The vibronic shape of the PL spectra could be explained by a previous work,¹⁶ the authors of which studied the influence of thiophene-based regioregular polymers on luminescence spectra. By virtue of the model dialkyl dimers of thiophene, the authors discovered that the vibronic shape of the luminescence spectra was caused by the presence of H-H dyads that could be oriented in the space, similarly to H-T dyads, in the shape of syn- and anti-

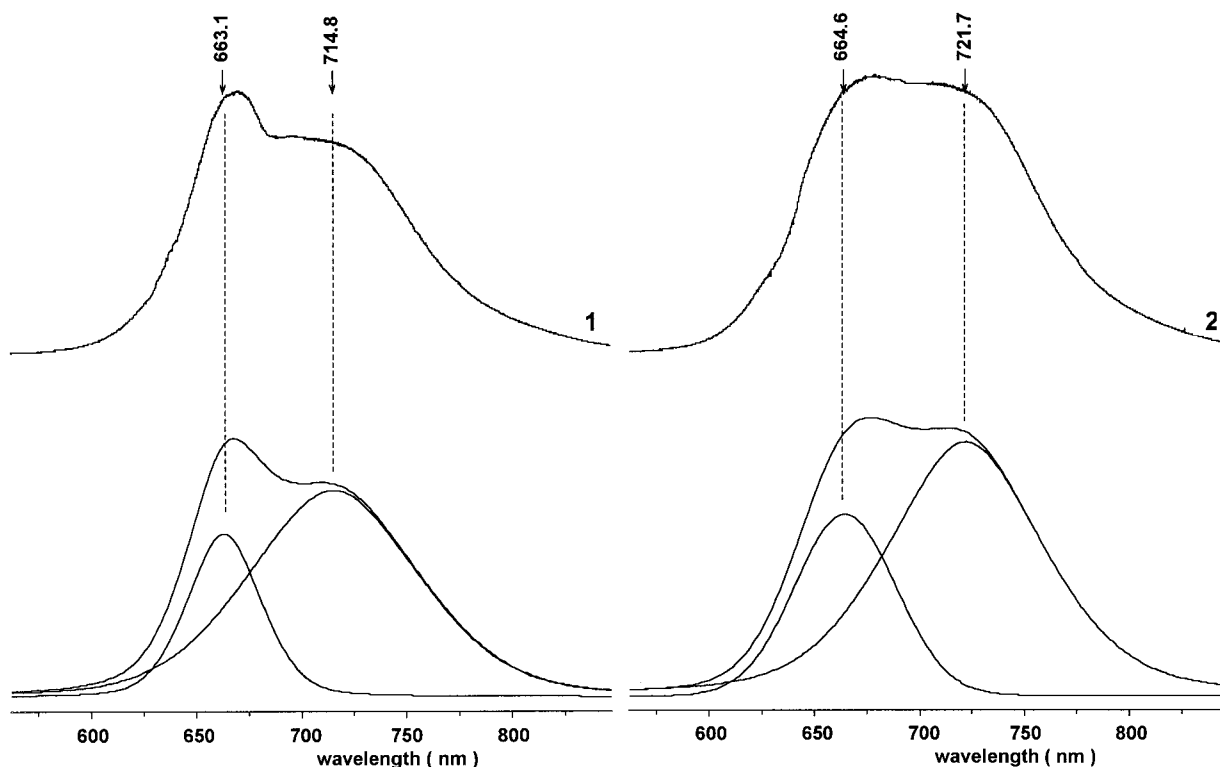


Figure 2 PL spectra of P3DDT films: (1) P1 and (2) P2.

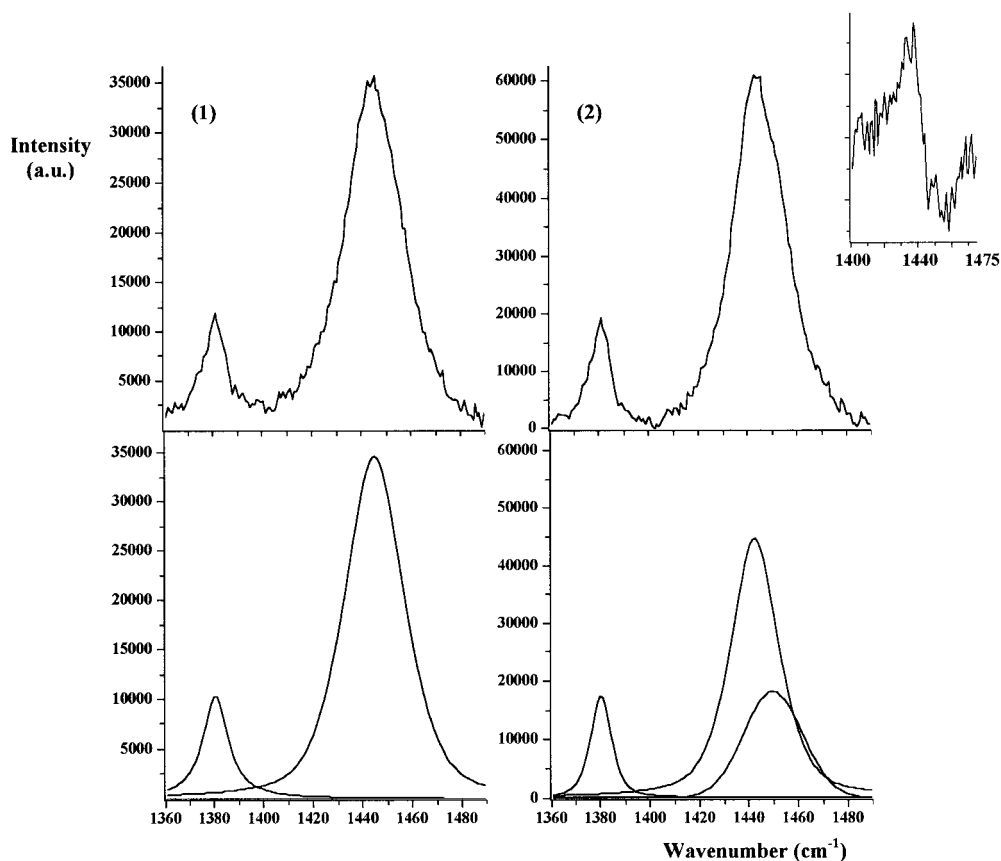


Figure 3 Raman spectra of P3DDT films: (1) P1 and (2) P2.

arrangements. Because the excited syn- and anti-states of H-H dyads have different energies, they can show themselves in a spectrum by two peaks.¹⁶ The other conception was used by the authors of ref. 17, who claimed that syn-arrangements of alkyls in P3ATs exist. Their model is based on the idea that in one macromolecule (with the anti-arrangement of H-T dyads), folded structures with side alkyls in the syn-arrangement occur. In view of the fact that the syn-geometry is most likely less coplanar even in the excited state, the emission peak is shifted from this state to higher energies. In this way, two peaks can appear in the emission spectrum, of which that with the higher energy is caused primarily by the presence of a syn-arrangement. However, according to the aforementioned model, the syn-arrangements (folded structures) are present on subchains formed by H-T dyads.¹⁷ We can also admit such a notion, although, for the time being, it is difficult to decide how the percentage of H-H dyads affects the shape of PL spectra.

In Figure 3 (Table I), Raman spectra (experimental and fit between 1360 and 1490 cm^{-1}) of films of both P3DDT samples are compared. They reveal that the bands in P3ATs, assigned to symmetrical C=C stretching,¹⁷⁻¹⁹ had a different shape in the studied samples. In P1, just one band appeared to be present at

approximately 1440 cm^{-1} , whereas in P2, a weak shoulder could apparently be observed around 1450 cm^{-1} . This fact was also documented by the first derivation of the Raman signal of the studied film [inserted picture in Fig. 3(2)]. This is the reason that the signal in sample P2 was fit with two peaks. The second peak was weaker and shifted by approximately 7.5 cm^{-1} to higher wave numbers (Table I). At this time, we are not able to give an exact explanation for this phenomenon, but we find the reason for it in the different distributions of the conjugation lengths in both studied samples.^{17,20}

Considering the analysis of NMR, absorption, PL, and Raman spectra, we observed that our P3DDT samples differed in the contents of H-H and H-T dyads, and this resulted in the distribution of the conjugated subchain lengths. Of course, this was reflected in the different physical properties of the polymer samples. The next factor influencing the stereoregularity of P3DDT is the spatial arrangement of side alkyls and, in this connection, the coplanarity of the backbones. On the basis of existing studies,²¹ one may state that the three types of conformational changes of P3DDT— γ , β , α —induced by thermal induction can be registered. γ changes occurring below -150°C (123 K) are characteristic of the conformational rotations of the methylene groups of alkyls (e.g., trans-to-gauche

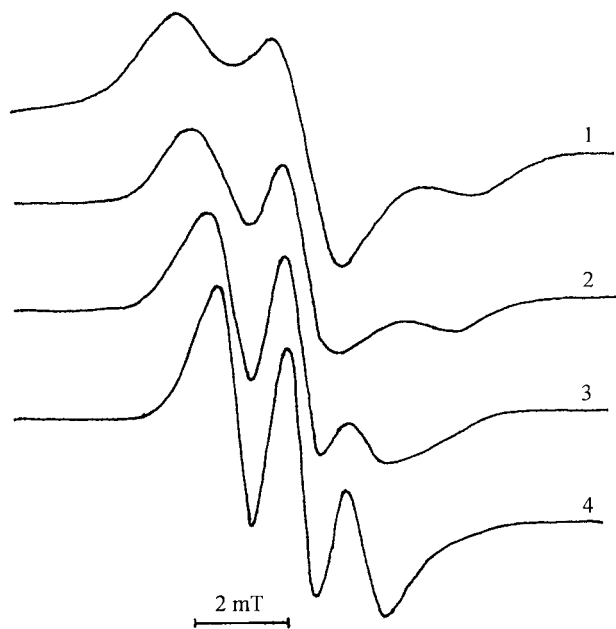


Figure 4 Temperature changes in a spin-probe EPR spectrum for a film of P1: (1) 143, (2) 293, (3) 333, and (4) 363 K.

groups on short segments beginning from the end of alkyls). α changes are associated with the glass transition in the amorphous phase. According to ref. 21, the glass-transition temperature (T_g) for P3DDT depends on the molecular mass and can be shifted to the region of -40 to 25°C (233–298 K). Between α and γ transitions, the conformational changes take place on larger side alkyl subunits (from 123 to 233 K). In agreement with refs. 21 and 22, the partially arranged, so-called soft conformons, in which the torsion between the two coplanar subchains is distributed over several repeating units, divide the polymer chain into shorter segments, with a distribution of the shorter conjugated length. It has been assumed that the temperature increase is accompanied by a density increase of the conformons as well as a simultaneous decrease of the conjugated length.

The thermochromic properties of P3ATs with different contents of H-T dyads were studied by the authors of ref. 23 by means of the heat-induced changes in UV-vis spectra, DSC measurements, and the X-ray analysis. They proposed a phenomenological model for a macrostructure of P3ATs, according to which the polymers (the mutual ratio of which changes with temperature) contain crystalline, quasi-crystalline (less arranged), and amorphous phases. They also claimed that stereoirregular P3ATs (higher content of H-H dyads) are formally amorphous and contain smaller arranged structures, which are dispersed in the amorphous phase. Both the quasiarranged and unarranged (amorphous) phases are in mutual equilibrium, but the quasiarranged phase at lower temperatures prevails.²⁴ The authors of ref. 24

ascertained that P3ATs with approximately 80% H-T dyads contain 55% of the quasiarranged phase and 45% of the unarranged phase at room temperature.

The heat-induced conformational changes of P3DDT were studied with a spin-probe technique when 5-DSAME was chosen as a paramagnetic probe. The probes derived from the stearic acid have recently been exploited more extensively in the study of complex substances and structures, such as polymer liquid crystals and biological membranes.^{25,26} Inasmuch as this probe had a long hydrophobic alkyl chain, it was assumed that the spin label would be situated predominantly among the alkyl chains of P3DDT. The ratio of the spin probe to the monomeric unit of P3DDT was very low (1 spin probe per 100 monomeric units of 3-dodecylthiophene). In virtue of this fact, it was possible to expect that the polymer matrix structure would be unaffected by the probe, although this possibility could not be completely excluded.

Figures 4 and 5 demonstrate temperature changes of the EPR spectra of the spin probe built in the polymer films of the P1 and P2 samples. Considering the shape of the spectra registered at -130°C (143 K), we can suggest that the spin probe was situated in the surroundings with axial symmetry; this means that the spectra are similar to the EPR spin-probe spectra observed for liquid crystals chaotically distributed in the solid phase.²⁵ With eq. (4), S was calculated for both P3DDT samples with the temperature (Fig. 6). S practically did not change in both samples at low temper-

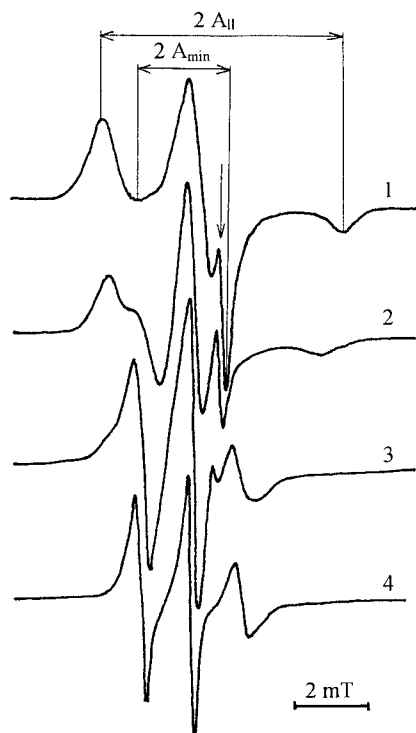


Figure 5 Temperature changes in a spin-probe EPR spectrum for a film of P2: (1) 143, (2) 293, (3) 333, and (4) 363 K.

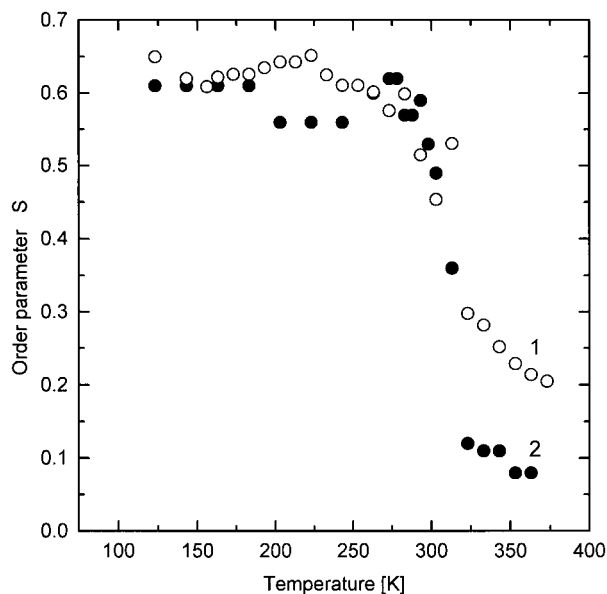


Figure 6 Temperature dependence of the calculated values of S for P3DDT: (1) P1 and (2) P2.

atures up to 0°C (273 K). Above this temperature, it had a decreasing tendency. Therefore, it can be assumed the measure of arrangement of the studied polymer at higher temperatures was lower than the one at a low temperature. This effect may be associated with achieving T_g of the amorphous phase of samples.^{21,27}

Through the elevation of the sample temperature, the line widths of the EPR spin-probe spectra became narrower, and the line intensities of the hyperfine splitting were equalized. From the spectral parameters, the values of τ_B and τ_C at various temperatures

were calculated with eqs. (4) and (5). The values of the rotational correlation times corresponded to the viscosity (η) of the (micro)environment in which the probes occurred according to the Stokes law viscosity relation:⁸

$$\eta = 3k \cdot \tau \cdot T / 4\pi \cdot r^3 \quad (6)$$

where r is the effective radius of the spin probe, k is the Boltzmann constant, and T is the absolute temperature.

Figure 7 shows the temperature course of τ_B for both P3DDT samples. The temperature course of τ_C manifested a similar character; however, the values of τ_C were somewhat higher mainly at lower temperatures (data not given). Because τ_B and τ_C were not equal, the motion of the spin label did not have the character of fast motion. Therefore, τ_B and τ_C were not quite accurate, and their values can be considered only informative. From a comparison of the absolute values of τ_B for both samples, it follows that the polymer with a higher content of H-H dyads (sample P1) represented a more rigid system. In accordance with ref. 28, this may be caused by the fact that a higher content of H-H dyads might disrupt crystallinity less than a polymer sequence with a higher content of H-T dyads. According to ref. 28, the polymer structure of P3ATs with a higher content of H-T dyads resembles a diblock polymer in which the two blocks (created in a sequence of the high length of the right and left sequences) are incompatible in the sense that right-positioning alkyl groups do not fit into a left-positioning lattice. Furthermore, Figure 7 suggests that the spin-probe motion at temperatures below -100°C (173 K) was con-

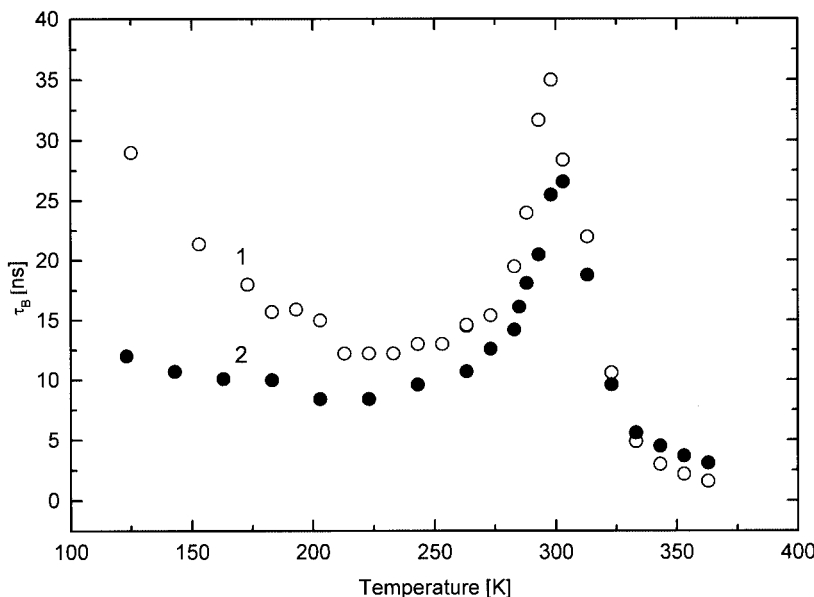


Figure 7 Temperature dependence of the calculated values of τ_B for P3DDT: (1) P1 and (2) P2.

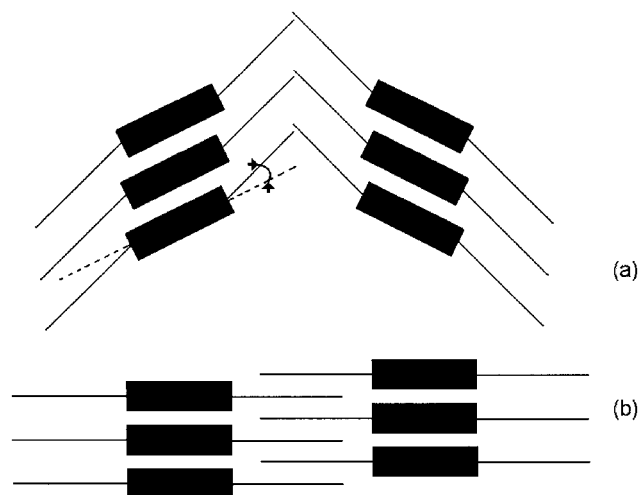


Figure 8 Potential heat-induced structural changes in P3DDT.

siderably slower and anisotropic and could be characterized by relatively high rotational correlation times ($\tau_B \sim 20$ ns and $\tau_C \sim 30$ – 40 ns). With an increase in the temperature, a release of the spin-probe motion in the polymer matrix took place, probably because of the trans-to-gauche transition of side alkyls.²⁹ This phenomenon led to a decrease in the rotational correlation times when their absolute values for both samples of P3DDT became approximately equal at temperatures above 90°C (363 K) and achieved values of only a few nanoseconds. Figure 7 also suggests that τ_B grew from approximately -33°C (240 K) up to a maximum at approximately 20°C (293 K) for polymer P1 and at approximately 30°C (303 K) for polymer P2. Afterward, their decrease was repeated. The same tendency in the temperature changes was proven also by τ_C (data not given). This mutual growth of the rotational correlation times could be associated either with the increasing viscosity of the spin-probe (micro)environment or with the spin-probe exchange between two or more structurally different phases. In the first case, the alkyl chains, which were arranged in the solid phase shown in Figure 8(a), could pass with an increase in the temperature into the arrangement illustrated in Figure 8(b). The second arrangement [Fig. 8(b)] exhibited the so-called interdigital phase, in which the rotational motion of the probe was restricted by hydrophobic interactions. The same alkyl rearrangement is also considered by the authors of ref. 30 in clarifying some structural changes in the lattice of poly(alkylthiophene)s after iodine doping when the existence of a structure similar to that of Figure 8(b) is assumed at a high doping level. Moreover, conformational changes in the (semi)crystalline cell of nondoped P3DDT with temperatures ranging from -130 to 125°C (143 to 398 K) were studied by the X-ray diffraction method.³¹ These studies showed that up to

approximately 25°C (298 K), the orthorhombic crystalline lattice of P3DDT is similar (insignificant changes of the a parameter and no changes of the interplanar backbone b parameter in the cell). That means the X-ray diffraction studies have not provided adequate information about the conformational changes of polymer chains below room temperature. It is interesting that despite a decline of the order parameter to approximately 10–20% of the initial value (at temperatures greater than 300 K) due to the release of thermal motions, a viscosity increase occurred in this temperature region. Therefore, the second case can also be considered. As shown in Figure 7, an anomaly in the changes of the rotational correlation times (for 240 – 280 K) appeared in the region of T_g of P3DDT.^{4,21} Under these conditions (after T_g was exceeded), a release of the quasicrystalline phase (conformons), which was soaked out in the amorphous phase, and, therefore, a restructuring of semicrystalline centers could occur.⁵ Because the spin probe was built in the aforementioned two phases and the state was dynamic, a part of one phase could pass together with spin probes into the second phase. If in these two phases the parameters of the EPR spin-probe spectra were assumed to be different, then the exchange interaction took place (from the less arranged to the more arranged and vice versa). This, of course, resulted in the lines broadening and, consequently, in higher values of the rotational correlation times.¹⁰ Such an assumption was confirmed also by the shapes of the EPR spin-probe spectra in sample P2 (Fig. 5), in which another peak was noticeable (marked with an arrow in Fig. 5) in the region of the central peak. There also the assumption existed that the former peak was assigned to the central peak of the spin probe built in the other crystalline phase that could be formed, with respect to the higher content of H–T dyads (74%), by coplanar polymer chains. Such stable crystallinities of P3DDT passed into the total amorphous state through the earlier mentioned quasicrystalline phase but not until a temperature of approximately 140°C .⁶ On the basis of the spectra (Figs. 4 and 5), we deduced that the cooperation of the two phases was greater in sample P1 because of its broader lines and lower critical temperature of the temperature anomaly of the rotational correlation times (ca. 293 K). In sample P2, it was approximately 303 K. Inasmuch as the central peak in the EPR spectrum was observable in sample P2 also at higher temperatures [even at 90°C (363 K)], the cooperation of the phases in sample P2 was probably smaller than that in sample P1.

CONCLUSIONS

On the basis of the results obtained in this work, we can summarize that the conformational changes of P3DDT, as one representative of P3ATs, can be stud-

ied by a spin-probe technique with probes of derivatives of stearic acid (5-doxyl-ester stearic acid methyl ester). From the heat-induced changes registered by the EPR spin-probe spectrum, we calculated the rotational correlation times, which depended on the number of H-H conformational defects of the backbone of P3DDT. The values of the spin-probe rotational correlation times permitted us to evaluate the system's phase conversions in connection with the transitions: the arranged and less arranged systems. P3DDT was found to have higher spin-probe correlation times in a sample with a higher content of H-H dyads, and this was caused by a higher content of mutually interacting soft conformers of the backbone. Within T_g (from 240 to 320 K), a remarkable growth of the rotational correlation times was observed as a result of the mutual exchange interactions of two phases existing in the sample or the formation of an interdigital phase. Above room temperature (in the region of the beginning of alkyl melting), the rotational correlation times fell down again, and their values became independent of the number of H-H configurational defects.

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