

Motional Dynamics in Polythiophenes: A Solid-State ^1H NMR Study

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Abstract: We have investigated, via solid-state ^1H NMR, the morphology and dynamics in polythiophene, poly(3-alkylthiophene), and viologen-functionalized poly(3-alkylthiophene). We identify rigid and mobile phases in polythiophene and have evidence for a doping-induced change in the morphology of the polymer. Two distinct types of side chain motion are identified in the substituted polythiophenes. In poly(3-alkylthiophene), these side chain motions are unaffected by doping of the polymer backbone, whereas in viologen-functionalized poly(3-alkylthiophene), an immobilization of the side chain motion, upon doping of the backbone, is observed. These results are explained via a model proposing a counterion complexation between the polymer backbone and the viologen side group upon doping.

Introduction

Research on conducting polymers has been the focus of great attention in the last decade, with the aim of providing new materials for modern technology.¹ The prototype of π -conjugated polymers, polyacetylene (CH_n), with the highest electrical conductivity observed in these compounds, nearly 10^6 S/cm, falls quite short of the technological requirements for stability and processibility. Consequently most synthetic efforts have centered about developing materials with improved physical characteristics and chemical stability.¹⁻³ The first generation of such compounds is the polyaromatics, among these polythiophene (PT), which have good conductivity and stability, but low processibility.¹ The second generation of conducting polymers involves the attachment of an alkyl chain, as in poly(3-alkylthiophene) (PAT) and poly(3-alkylpyrrole), resulting in improved solubility and processibility.⁴ The poly(3-alkylthiophenes) have conductivities ranging from 10 to 100 S/cm, are soluble in common organic solvents, and show technological application potential.⁵⁻⁷ In an attempt to continue to expand the range of physical, electrical, and chemical properties of these materials, recent synthetic efforts have brought about the third generation of conducting polymers by attaching a functional group to the alkyl chain. In this way, specific properties such as additional redox activity,^{8,9} molecular recognition for biosensor applications,¹⁰ conductive-state solubility,¹¹ and optical activity¹² can be introduced into the polymer. With this approach, molecular engineering, by introducing a specific property via functionalization, becomes possible, opening up a wide range of possible technological applications.

The presence of motion, in conducting polymers in the solid state, and its changes upon doping has become a critical issue, as several effects are proposed to depend upon it. The ring rotational angle has been proposed as an important parameter determining the electronic properties of polyaniline.¹³ Small angle neutron scattering data show a backbone stiffening of poly(3-alkylthiophenes) upon doping.¹⁴ This behavior should cause a higher mobility of charge carriers within the conjugation length. The thermochromic effects observed in poly(3-alkylthiophenes) are supposed to arise from structural effects of the flexible side chains on the electronic structure of the, presumably rigid, polymer backbone.¹⁵

Solid-state NMR has proven to be an important tool for examining motions in polymers.^{16,17} Most typically ^{13}C magic angle spinning (MAS)^{18,19} or ^2H experiments are employed,^{16,20-24} with ^1H NMR being utilized much less frequently.^{25,26} The reasons sited for this are the high resolution of ^{13}C MAS and the high specificity of ^2H NMR, when isotopic labels are incorporated. The large ^1H - ^1H couplings present in most systems generally obscure all chemical information in the ^1H spectra, while rapid spin diffusion among ^1H 's yields single values for relaxation parameters

solely due to the dominant motion at the frequency being measured. There are, however, some advantages to performing ^1H experiments to monitor motion. ^1H are 100% naturally abundant and have a high gyromagnetic ratio, yielding a high-sensitivity NMR spectrum without the need for isotopic labeling, as in the case of ^2H . Secondly, the second moment of the peak pattern can be used as an indicator of polymer motion, similarly to the way one uses the quadrupole splitting of a ^2H powder pattern. Finally, rapid spin diffusion equalizes all relaxation rates, allowing, in some cases, a relaxation sink involving a small number of protons to have a large effect on the ^1H relaxation behavior. One such example is the well-known spin-lattice relaxation of the ^1H 's in a large organic molecule by a few rotating methyl groups.²⁷ An excellent probe of slow motions is the spin-lattice relaxation rate

- (1) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 2.
- (2) *Science and Application of Conducting Polymers*; Salaneck, W. R., Clark, D. T., Samuelsen, E. J., Eds.; Adam Hilger: Bristol, 1990.
- (3) Bryce, M. R.; Chissel, A. D.; Smith, N. R. M.; Parker, D.; Kathirgamanathan, P. *Synth. Met.* **1988**, *26*, 153.
- (4) Eisenbaumer, R. L.; Jen, K. Y.; Obvodi, R. *Synth. Met.* **1986**, *15*, 169.
- (5) Sato, M.; Tanaka, S.; Kaeriyama, H. *J. Chem. Soc., Chem. Commun.* **1986**, 873.
- (6) Jen, K. Y.; Miller, G.; Eisenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
- (7) Hotta, S.; Rughooth, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.
- (8) Moutet, J. C.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1989**, 188.
- (9) Bäuerle, P.; Gaudl, K.-U.; Götz, G. In *Electronic Properties of Conducting Polymers 4*; Kuzmany, H., Mehring, M., Rotlu, S., Eds.; Springer: 1991; in press.
- (10) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1989**, 679.
- (11) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.
- (12) Delabouglise, D.; Garnier, F. *Synth. Met.* **1990**, *39*, 117.
- (13) Ginder, J. M.; Epstein, A. J. *Phys. Rev. B* **1990**, *41*, 10674.
- (14) Aime, J. P.; Rawiso, M.; Schott, M. *Springer Ser. Solid-State Sci.* **1987**, *76*, 58.
- (15) Winokur, M. J.; Spiegel, D.; Kim, J.; Hotta, S.; Heeger, A. J. *Synth. Met.* **1989**, *8*, C419.
- (16) Bovey, F. A.; Jelinski, L. W. *J. Phys. Chem.* **1985**, *89*, 571.
- (17) Jones, A. A. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; R. A. Komoroski, Ed.; VCH: Deerfield Beach, FL, 1986, p 247.
- (18) Andrew, E. R.; Bradbury, A.; Eades, R. G. *Nature* **1958**, *182*, 1659.
- (19) Lowe, I. J. *Phys. Rev. Lett.* **1959**, *2*, 285.
- (20) Schaefer, J. In *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; Wiley: New York, 1974; Vol. 1, p 149.
- (21) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.
- (22) Schaefer, J.; Stejskal, E. O. In *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; Wiley: New York, 1979; Vol. 3, p 284.
- (23) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
- (24) Spiess, H. W. *J. Mol. Struct.* **1983**, *111*, 119.
- (25) Inglefield, P. T.; Jones, A. A.; Lubianez, R. P.; O'Gara, J. F. *Macromolecules* **1981**, *14*, 288.
- (26) Jones, A. A.; O'Gara, J. F.; Ingelfield, P. T.; Bendler, J. T.; Yee, A. F.; Ngai, K. L. *Macromolecules* **1983**, *16*, 658.
- (27) Fedotov, V. D.; Schneider, H. *Structure and Dynamics of Bulk Polymers by NMR-Methods*; Springer: Berlin, 1990; p 107.

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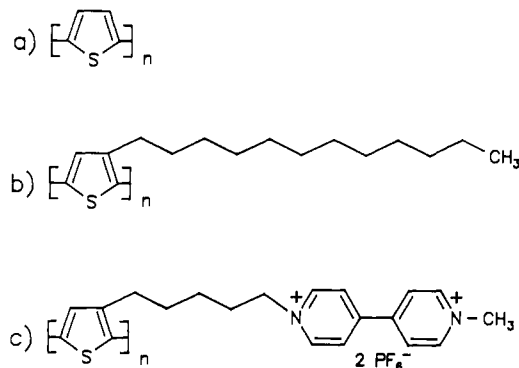


Figure 1. Schematic diagram of the unit structures for the polymers in this study: (A) polythiophene, (B) poly(3-dodecylthiophene), (C) viologen-functionalized poly(3-pentylthiophene).

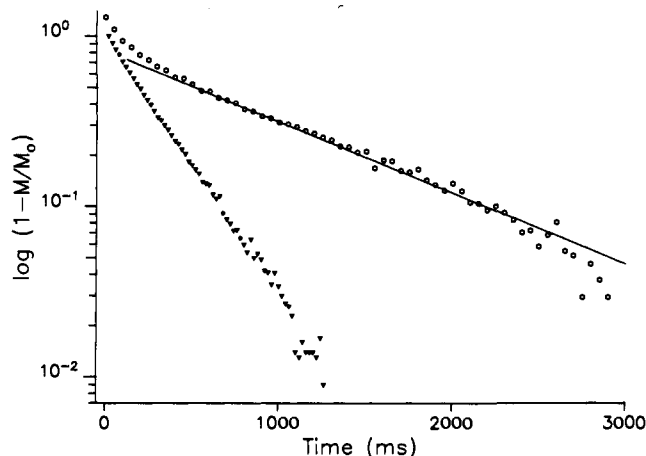


Figure 2. Signal intensity versus time for the recovery of inverted magnetization for undoped (open circles) and doped (solid triangles) PT. Note the biphasic relaxation of undoped PT, indicating amorphous and crystalline regions.

in the rotating frame, $1/T_{1\rho}$. When $T_{1\rho}$ is dominated by slow motions, a peak in the relaxation rate should occur when the correlation time of the motion $\tau_c \approx 1/2\omega_1$, in which $\omega_1/2\pi$ is the radiofrequency field strength, typically on the order of 50 kHz.²⁸

In this paper, we report a ^1H solid-state nuclear magnetic resonance (NMR) investigation of the motional dynamics of members from all three generations of polythiophenes represented by polythiophene (PT), poly(3-dodecylthiophene) (PAT), and 4,4'-bipyridinium (viologen) functionalized poly(3-pentylthiophene) (PTV²⁺).²⁹ While it is often difficult to attribute the relaxation rate maxima to specific motions, for a given system, a comparative study of structurally related systems, here PT, PAT, and PTV²⁺ (Figure 1a–c, respectively), in both the undoped and conducting states, should make the assignment possible and provide valuable information on the dynamics in these systems.

Local Order in Polythiophenes

Nuclear spin–lattice relaxation, in the laboratory and rotating frames, is an excellent probe of the degree of local order in semicrystalline polymers.³⁰ Crystalline regions will have an entirely different set of restrictions upon the topology and rates of motions available, and will therefore exhibit relaxation times that are quite different from those of the amorphous regions of the polymer. Figure 2 illustrates the recovery of magnetization, following a π inversion pulse, versus time for undoped (open circles) and doped (solid triangles) PT at 300 K. The undoped PT sample clearly

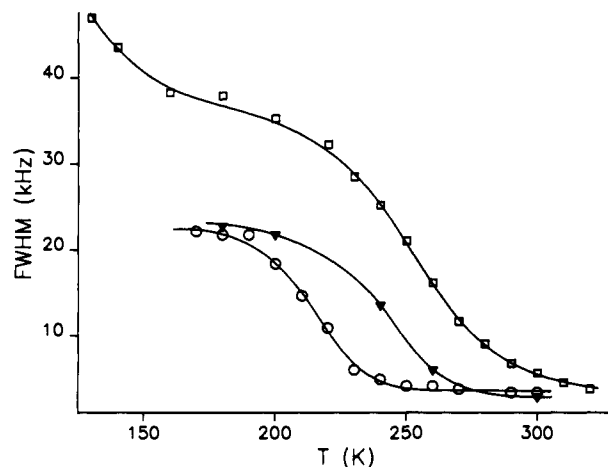


Figure 3. ^1H line widths (full widths at half-maximum) vs temperature for the amorphous component of undoped PT (open circles), doped PT (solid triangles), and undoped PAT (open squares). The solid lines are guides to the eye.

exhibits biexponential relaxation, indicating a highly mobile or “amorphous” phase and a rigid or “crystalline” phase. It should be mentioned that, in this case, we are using the words crystalline and amorphous only to indicate different phases governed by a different set of dynamics, not the presence or absence of any long-range order. Direct fitting of the biexponential decay yields the time constants $T_1(\text{amorphous}) = 144$ ms and $T_1(\text{crystalline}) = 1.2$ s, and the relative amplitudes of the components. The much faster relaxation for the amorphous component is due to the larger free volume available for motions in this phase. Possible imprecision in the relative amplitudes, due to the biexponential fitting process, led us to average the relative amplitudes of the components derived from T_1 curves at different temperatures, and similar biexponential decays from rotating frame relaxation data. These results show that this undoped PT sample is $62 \pm 5\%$ crystalline. The I₂-doped sample, remarkably, yields a monoexponential decay with a time constant $T_1 = 267$ ms. Therefore, either the doped PT is purely amorphous or the spin diffusion rate between the two domains is markedly increased via mediation by the conduction electrons.

PT samples have been found to have varying relative amounts of one phase or the other depending on sample preparation and history. Indeed undoped PT, at least 95% of which is the crystalline phase, has been observed. This sample had a temperature-independent line width and no relaxation rate maxima in the temperature region investigated. Doping with iodine yielded a spectrum with a motionally narrowed component that broadens with decreasing temperature. The destruction of the crystallinity and the creation of an amorphous component illustrate a doping-induced disorder phenomenon.

The PAT and PTV²⁺ samples were purely amorphous in both their undoped and doped states, the doped state T_1 's at 300 K being 136 and 66.5 ms, respectively. Nuclear spin–lattice relaxation in doped conducting polymers is generally considered to result from fluctuations of the motionally averaged hyperfine coupling to the conduction electrons.³¹ The significantly shorter T_1 for doped PTV²⁺ relative to PT and PAT may therefore be due to an increased localization of the polaron on the polymer backbone, which has indeed been seen by in situ spectroelectrochemical methods.^{32,33}

An indication of a degree of order even in the amorphous component of undoped PT is given by the change in the line width of the ^1H spectrum as a function of temperature as illustrated in

(28) Mehring, M. *High Resolution NMR in Solids*, 2nd ed.; Springer: Berlin, 1983.

(29) Bäuerle, P.; Gaudl, K.-U. *Adv. Mater.* **1990**, *2*, 185.

(30) Komoroski, R. A.; Mandelkern, L. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; R. A. Komoroski, Ed.; VCH, Deerfield Beach, FL, 1986; p 1.

(31) Devreux, F.; Lecavelier, H. *Phys. Rev. Lett.* **1987**, *59*, 2585.

(32) Sariciftci, N. S.; Neugebauer, H.; Gaudl, K.-U.; Bäuerle, P.; Grupp, A.; Mehring, M. In *Electronic Properties of Conducting Polymers*, 4; Kuzmany, H., Mehring, M., Roth, S., Eds.; 1991; in press.

(33) Sariciftci, N. S.; Kolbert, A. C.; Mehring, M.; Neugebauer, H.; Neckel, A.; Bäuerle, P.; Gaudl, K.-U. *Chem. Phys. Lett.* **1991**, *182*, 326.

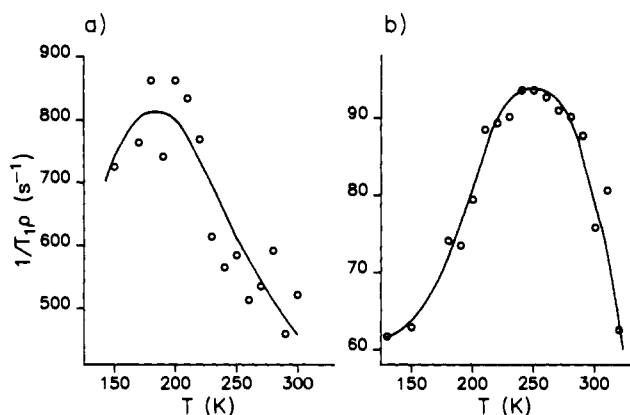


Figure 4. Spin-lattice relaxation rates in the rotating frame versus temperature for (a) amorphous undoped PT and (b) doped PT.

Figure 3. Doped P has a gradual broadening upon cooling over a range of 100 K from 280 to 180 K. Neutral PT has a much more precipitous rise, over a range of 60 K. Apparently there are varying degrees of order within the phase we call amorphous. As expected, the rigid lattice line width for PAT and PTV²⁺ (not shown) is much larger (~ 50 kHz) than for PT due to the presence of the strongly coupled ¹H's in the CH₂ groups of the alkyl chains. The temperature down to which the ¹H line continues to broaden is ~ 120 K. It is only at this temperature that the free alkyl chain motion freezes out. What was quite surprising was the fact that all three polymers exhibited strongly motionally narrowed ¹H spectra at room temperature. The residual ¹H line widths at 300 K for PT (amorphous component), PAT, and PTV²⁺ were ~ 3 , 5, and 5 kHz, respectively, indicating rapid reorientational motion at rates approaching the rigid lattice line widths, 10^4 – 10^5 s⁻¹. Note that small angle librations are insufficient for this purpose; only motions that significantly change the ¹H–¹H homonuclear interactions will give rise to such extreme narrowing of the ¹H spectra. Included in this class of motions are ring rotations and backbone and side chain reorientation. It was essentially this observation that motivated the rotating frame relaxation measurements of the next section, with the aim of characterizing the type and correlation times of the motions present in these systems.

Rotating Frame Relaxation Measurements

The frequency of the motions responsible for the line narrowing in these systems may be investigated via temperature-dependent measurements of the spin-lattice relaxation rate in an effective field B_1 in the rotating frame. Assuming a Gaussian-Markoff process with a correlation time, τ_c , which causes a modulation of the dipole-dipole interaction, the relaxation rate may be given by

$$1/T_{1\rho} = M_2 \left[\frac{\tau_c}{1 + 4\omega_1^2\tau_c^2} + \frac{5}{3} \frac{\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{2}{3} \frac{\tau_c}{1 + 4\omega_0^2\tau_c^2} \right] \quad (1)$$

in which M_2 is the rigid lattice second moment, ω_1 is the rf field strength, and ω_0 is the Larmor frequency.²⁸ The relaxation rate maximum occurs at $\tau_c = 1/2\omega_1$, which is found by varying the temperature, and therefore the correlation time of the motion. Away from the relaxation maximum, the temperature dependence of $T_{1\rho}$ can be related to the activation energy, E_a , for the motion by plotting $\ln 1/T_{1\rho}$ versus $1/T$ in an Arrhenius fashion.

Figure 4 shows the relaxation rate, $1/T_{1\rho}$, versus temperature for (a) undoped and (b) doped PT. In figure 4a, only the rate obtained for the amorphous component is plotted, to exclude the effect of differences in the free volume available for motion upon comparison with the doped PT. There is substantial scatter, in Figure 4a, due to the biexponential fitting, though a maximum at ~ 180 K is perhaps present. The relaxation rate maximum is more convincing in the curve of Figure 4b, for doped PT in which at the maximum of 250 K, the correlation time for the motion

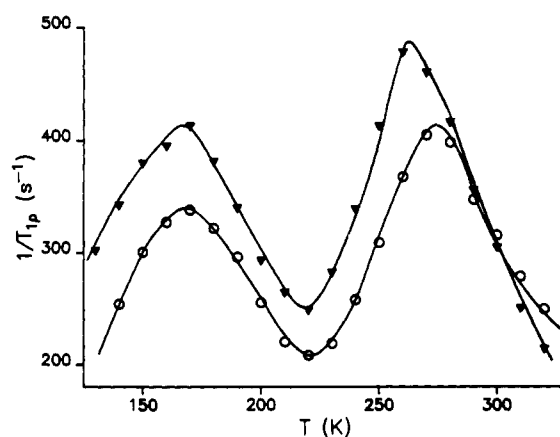


Figure 5. Relaxation rates, $1/T_{1\rho}$, versus temperature for undoped PAT (open circles) and doped PAT (solid triangles). The low- and high-temperature maxima correspond to small and large displacement side chain wagging, respectively. The solid lines are merely guides to the eye.

$\tau_c = 1/2\omega_1 = 1 \times 10^{-5}$ s. Plotting the data in an Arrhenius fashion does not yield strictly linear slopes, so the activation energies could not be reliably calculated. This is generally not surprising, though, as the fractal nature of the amorphous polymer demands a more involved theoretical treatment. Only in the cases below, in which the slopes were properly linear, have we extracted "activation energies" for the motion. Simply by considering the absolute values of the relaxation rates, it is clear that there is substantially less slow motion present in the conducting form of the polymer. Whether this is backbone stiffening leading to a higher activation barrier for polymer motion, or a morphological change that modifies the motional modes available for relaxation, is a question we cannot answer from this data. ²H NMR experiments on *d*₃-labeled polythiophene are currently underway to address these issues.

The relaxation curves for undoped and doped PAT are illustrated in Figure 5. Note the presence of two well-defined maxima at 170 and 265 K. The effect, of doping, on the relaxation is minimal, leading only to a slight increase in the overall rates. Linear regression of the Arrhenius plots yields activation energies of 1.1 and 2.7 kcal/mol for the low- and high-temperature maxima, respectively. We therefore attribute the low-temperature maximum to small displacement side chain wagging, whereas the high-temperature maximum is due to large displacement side chain reorientation. We cannot exclude the possibility of a continuum of complexity of side chain motions; however, if that is the case, they appear to have grouped themselves into two classes with distinct correlation times and activation energies. The possibility that the low-temperature maximum may be due to rotation of the methyl group on the side chain's terminus should be considered, although there are a number of arguments against it. First, the maximum has an unusually low activation energy of 1.1 kcal/mol, whereas methyl groups typically have barriers of around 3 kcal/mol. Second, the spectrum, which is dominated by the 22 ¹H's on the alkyl side chain, continues to broaden substantially in this temperature regime, indicating a slowing of motion involving most of the ¹H's. Finally, there is the absence of such a maximum in this temperature range for PTV²⁺ (shown below), in which the methyl group should move just as freely.

Figure 6 shows the relaxation curves for PTV²⁺. The two side chain maxima are still present in the curve of undoped PTV²⁺, though shifted to higher temperatures of 220 and 320 K, respectively, with E_a for the 220 K maximum being 1.5 kcal/mol. The few points comprising the 320 K maximum prevent an accurate determination of E_a for that motion. Considering the results of Figure 6, in view of the assignment of the side chain maxima in PAT, one may conclude that small displacement side chain wagging is only slightly inhibited by the presence of viologen, due to the increased moment of inertia of the side chain. The activation energy for the motion is correspondingly higher, 1.5 kcal/mol in PTV²⁺ versus 1.1 kcal/mol in PAT. The 320 K maximum is quite

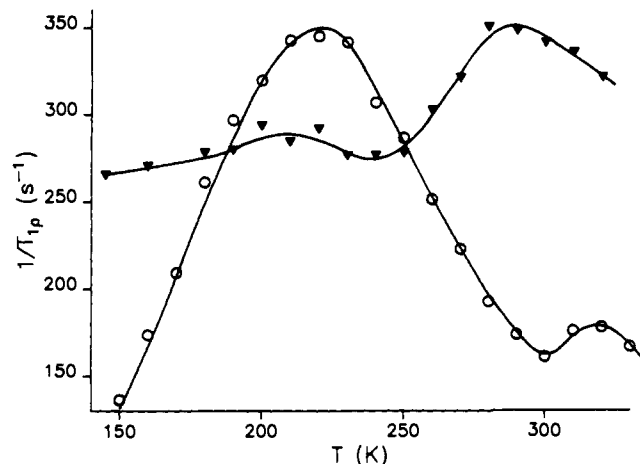


Figure 6. Relaxation rates, $1/T_{1\rho}$, versus temperature for undoped (open circles) and doped (solid triangles) PTV. The solid lines are guides to the eye.

shallow, consistent with steric hinderance to reorienting the side chain attached to the massive viologen group. The effect of doping is quite dramatic with the low-temperature maximum being shifted to 280 K and the high-temperature maximum being shifted beyond the range of our measurements. The nearly temperature independent relaxation rate below 250 K is an indication that the relevant motion is frozen out and the relaxation is dominated by spin diffusion to the paramagnetic polarons induced by doping. These results are consistent with a structural model, derived from in situ spectroelectrochemical data, in which a counterion complexation between the polymer backbone and the viologen moiety occurs in the doped form of PTV^{2+} . This would strongly inhibit viologen motion in the doped state, while continuing to allow small displacement side chain wagging. A fuller explanation and further evidence for this model will be presented elsewhere.³³

It is well known that quantitative interpretation of 1H rotating frame relaxation data is difficult. As has been previously noted, in order for a spectral density interpretation, based upon motion induced fluctuations of the dipole-dipole interaction, to be rigorously valid, spin diffusion to inequivalent 1H 's must be negligible.²⁶ Polythiophene is the only substance in this study that satisfies this condition, as it contains only a single type of 1H . For this reason, the activation energies extracted from the Arrhenius plots may be distorted by cross relaxation to 1H 's moving with similar correlation times. Problems can be avoided by considering only motions with very different correlation times, and relying only on Arrhenius plots with strictly linear slopes. The activation energies reported in this paper were based upon linear regression of at least four $T_{1\rho}$ values with a correlation factor of 0.990 or better.

Experimental Section

All experiments were performed on a home-built pulse spectrometer operating at a 1H frequency of 180 MHz. $T_{1\rho}$ measurements were

performed with a variable spin lock, with $\omega_1/2\pi = 50$ kHz, followed by detection with an echo. Echo decays as a function of the spin locking time were monitored with a boxcar averager interfaced with the ASYST acquisition system (Asyst Software Technologies, Rochester, NY). Typically, 32 values of the spin locking pulse were acquired for each measurement with 4–32 scans/point. Time constants were extracted via direct fits to the exponential decays. Temperature control to ± 0.5 K was accomplished via an Oxford Instruments temperature controller (Oxford, England).

The samples were prepared via electrooxidative polymerization of a 0.05 M solution of the monomers of Figure 1a–c in acetonitrile under argon. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as a supporting electrolyte. The polymerization was performed by applying a potential of 1.5 V (versus 0.1 M $Ag/AgNO_3$) for the monomers of Figure 1b,c, and 1.9 V for the monomer of Figure 1a. After polymerization the films were rinsed with acetonitrile to remove oligomers. The films were then removed from the electrode and chemically reduced in ammonia solution, for PTV^{2+} , or by shaking in dimethylformamide, for PT and PAT. After removing the reducing solution, the films were washed with acetonitrile and dried in vacuo. Doping of the samples was done via exposure to gas-phase I_2 at 60 °C for several hours before use to achieve saturation doping. Experiments were performed entirely in the 24-h period following doping, and no attempt was made to remove excess I_2 from the sample, to ensure that saturation doping levels were maintained during the course of the experiments.

Conclusions

We have investigated the motional dynamics in polythiophene, poly(3-dodecylthiophene), and viologen-functionalized poly(3-pentylthiophene) by solid-state 1H NMR relaxation measurements. We have identified crystalline and amorphous regions in polythiophene and found a $T_{1\rho}$ minimum in the doped state. Two distinct modes of side chain motion were identified in the functionalized polythiophenes, and the activation energies for the motions were determined.

The observed mobility of the side chains may have significant consequences for proposed models of thermochromism, in which the side chains are assumed to be rigid below the temperature at which the thermochromic shift is observed.¹⁵ These experiments were performed on PAT films, which may have a crystalline component, while our PAT samples were purely amorphous, perhaps due to the particular details of the sample preparation. NMR and thermochromic measurements in parallel on the same samples may give insight into this issue.

Doping of PTV^{2+} was shown to have a substantial effect on the side chain motion, in contrast to the case of PAT, in which no significant effect is observed. This result supports a structural model with a counterion complexation between the viologen and the polymer backbone in the doped state that restricts the side chain motion.

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Registry No. PT (homopolymer), 25233-34-5; PAT (homopolymer), 104934-53-4; PTV^{2+} (homopolymer), 130424-51-0; I_2 , 7553-56-2.