Macromolecules 1987, 20, 212–215

Spectroscopic Studies of Soluble Poly(3-alkylthienylenes)

S. Hotta,† S. D. D. V. Rughooputh, A. J. Heeger,* and F. Wudl

Department of Physics and Institute for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, California 93106. Received May 29, 1986

ABSTRACT: It is demonstrated that the conjugated poly(3-alkylthienylenes) can be processed from solution and subsequently used as semiconducting and metallic polymers. These polymers were synthesized by electrochemical polymerization and characterized by high-pressure liquid chromatography (HPLC) and infrared (IR) spectroscopy. The HPLC data indicate a mean (weight average) molecular weight of about 48000, i.e., approximately 300 monomer units. The IR spectra show that these soluble polythienylenes have a well-defined molecular structure; the data are completely consistent with linear chains of poly(3-alkyl-2,5-thienylene). Both as-synthesized and solution-cast films can be readily doped, with resulting electrical conductivities that are quite high; for example, $\sigma \approx 40$ S/cm for films of poly(butylthienylene). UV–visible absorption spectra of these soluble polythienylenes have been obtained for solid films (as-synthesized and solution-cast) and for the polymers in solution. The spectral characteristics of the solution-cast films are essentially identical with those of the as-synthesized films both in the neutral state and after doping.

I. Introduction

Recent years have witnessed the emergence of a growing class of conductive polymers with π-conjugated electronic structures.[1–5] In particular, polymers involving monomers that are heterocycles such as polypyrrole, polyfuran, polythiophene (or polythienylene) (PT), and poly(3-methylthienylene) (P3MT) have received considerable attention. PT and P3MT can be prepared as powders by chemical coupling[6] or as free-standing films through oxidative electrochemical polymerization.[7–10] These films are relatively heavily doped from in situ doping with anions of the supporting electrolyte during electrochemical polymerization. Consequently, the as-synthesized films have relatively high electrical conductivities, with values as high as 500 S/cm reported in the literature.[10] The films can be reversibly undoped (and subsequently redoped) by electrochemical reduction (oxidation); standard chemical doping techniques can also be used.

To be potentially useful in electronic applications, a material must have excellent electronic and mechanical properties, and it should be solution or melt processible with high environmental stability. Although the delocalized electronic structures of π-conjugated polymers tend to yield relatively stiff chains with little flexibility and with relatively strong interchain attractive interactions, solubility can be achieved through addition of appropriate side groups.[11] Thus, whereas neither PT nor P3MT is soluble, the addition of relatively long, flexible, hydrocarbon chains to the thiophene ring might be expected to enhance the solubility and processibility of this conjugated polyheterocycle. Poly(3-alkylthienylenes) (P3ATs) have recently been synthesized and characterized as materials that are highly conndutive and environmentally stable and that are soluble in common organic solvents in both their neutral and conductive (doped) forms.[11]

In this paper, we present an initial study of the poly(3-alkylthienylenes), with emphasis on poly(3-hexylthienylene) (P3HT) and poly(3-butylthienylene) (P3BT). The polymers were synthesized by electrochemical polymerization and characterized by high-pressure liquid chromatography (HPLC) and infrared (IR) spectroscopy. Both as-synthesized and solution-cast films can be readily doped, with resulting electrical conductivities that are quite high. For example, we have found $\sigma = 40$ S/cm for as-synthesized films of P3BT and $\sigma = 30$ S/cm for as-synthesized films of P3HT. UV–visible absorption spectra of these soluble polythienylenes have been obtained for solid films (as-synthesized and solution-cast) and for the polymers in solution. The spectral characteristics of the solution-cast films are essentially identical with those of the as-synthesized films, in both the neutral and the doped states. The transport and spectroscopic data imply that these relatively high molecular weight conjugated polymers can be processed from solution with no change in electronic structure or electrical properties.

II. Experimental Section

Monomers (3-hexylthiophene and 3-butylthiophene) were synthesized following Kumada's method[12] and were distilled under dry nitrogen. The solvent (nitrobenzene) was distilled over phosphorus pentoxide under a reduced pressure of about 0.05 Torr. The electrolyte (Bu_4NClO_4) was recrystallized from methanol/water (1:1 volume ratio) and was dried at about 100 °C under a reduced pressure of about 0.05 Torr for 20 h. The monomers, the solvent, and the electrolyte were stored under dry argon for further use. P3HT and P3BT films, heavily doped with ClO_4^- ions, were synthesized on an indium/tin oxide (ITO) surface from nitrobenzene solutions containing 0.2 M 3-alkylthiophene and 0.02 M Bu_4NClO_4 under nitrogen.[13] The polymerization was carried out at 5 °C by applying a constant current density of 2 mA/cm^2 for periods ranging from 40 s (thin films) to 40 min (thick films). The preparation and handling techniques differ from previously reported synthetic methods in that during synthesis, the electrochemical cell operates in an oxygen-free and moisture-free environment.[14] These more rigorous conditions result in significant improvement of the quality of the resulting polymer films; for example, we find electrical conductivities of such films to be 3–5 times higher than previously reported, with values up to 500 S/cm.[10,14]

The polymer films (typically about 10-μm thickness) used in this study were undoped to the neutral state after synthesis by the reversal of cell polarity immediately following the polymer preparation (see ref 13 for details), and they were subsequently carefully cleansed by Soxhlet extractions with methanol and acetone, successively. Elemental analyses of the undoped P3BT and P3HT films yield chemical compositions in agreement with theoretical values[15] and set an upper limit on the number of remaining ClO_4^- ions of less than 0.03 per thiophene ring (i.e., less than 0.01 per carbon atom along the pseudo-polyene backbone). A correspondingly weak broad-band absorption due to the residual dopant could be seen at wavelengths beyond the interband transition (see discussion below); the resistivity of the as-synthesized neutral films was $\rho \approx 10^9$ Ω cm, consistent with the small residual dopant concentration. The residual ClO_4^- content in the films cast from solution was considerably lower; the broad-band absorption below the gap was unobservable. For physical measurements, the neutral P3AT films were subsequently doped and/or undoped electrochemically.

Polymer solutions were prepared by dissolving the neutral films in purified solvents (e.g., chloroform, dichloromethane, toluene,

† Permanent address: Central Research Laboratories, Matsushita Electric Industrial Co., Ltd., Moriguchi, Osaka 570, Japan.

Table I
Infrared Band Positions (cm^{-1}) and Their Assignments for Undoped P3ATs

sample	arom C–H str	aliph C–H str			ring str			methyl def	arom C–H out-of-plane
PTh[a]	3063				1491	1453	1441		788
P3MT[a]	3059	2965	2919	2857	1514	1456	1442	1377	819
P3BT	3055	2955	2928	2858	1512	1458	1439	1377	829
P3HT	3055	2959	2930	2858	1512	1458	1439	1377	825

[a] See ref 8 and 9.

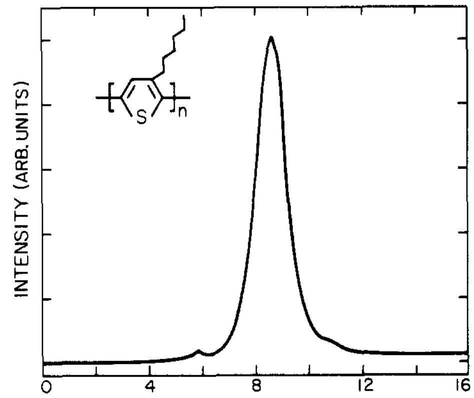

Figure 1. HPLC trace of P3HT; the flow rate of the polymer solution (≈10^{-4} M/L in THF) was 1.2 mL/min. The inset shows the chemical structure of poly(3-hexylthienylene).

and tetrahydrofuran (THF)) at about 60 °C. We found that P3AT films could be readily cast onto glass (or ITO-coated glass) substrates from solution by evaporation of the solvent. The solution-cast films were electrochemically doped by using an electrolytic solution of lithium perchlorate (0.1 M) in propylene carbonate (in which the P3AT films are insoluble).

Molecular weights of P3BT and P3HT films were determined by high-pressure liquid chromatography (HPLC) with a Varian 5000 liquid chromatograph equipped with a MicroPak TSK exclusion column (Type GMH6) of length 30 cm. The molecular weights were obtained in the usual manner from the retention time calibration curve using a series of polystyrene standards (supplied by Gasukuro Kogyo Inc., Japan, with molecular weights spanning the range from 4000 to 612000). The quoted values should be considered as approximate, since the precise quantitative applicability of the polystyrene calibration to the conjugated P3ATs is uncertain. Infrared (IR) transmission spectra were obtained with a Perkin-Elmer Model 1330 spectrophotometer using KBr pressed disks in which fine P3AT particles were dispersed. For UV–visible measurements, solid films (≈10-nm thickness) were deposited onto ITO glass; absorption spectra were obtained from a Perkin-Elmer Lambda 5 spectrophotometer. Electrical conductivities were measured by using standard two-probe techniques at room temperature.

III. Results and Discussion

Figure 1 shows the molecular weight distribution of P3HT (the corresponding curve for P3BT is essentially identical). The absorbance of the eluted material at 360 nm is plotted as a function of retention time, and the retention time has been calibrated in terms of equivalent molecular weight (of polystyrene) as noted in the Experimental Section. The absorbance at a given elution time (or at a given molecular weight, M_i) is proportional to the mass of alkylthiophene chains in the elution volume at that time; i.e., $\alpha_i = kN_iM_i$, where N_i is the number of P3HT chains of molecular weight M_i in that fraction, and k is a constant. From Figure 1, the peak in the distribution curve occurs at $\bar{M}_w \approx 20000$, corresponding to approximately 150 monomer units. The weight-average molecular weight ($\bar{M}_w$) can be calculated[16] directly from the data of Figure 1. We find $\bar{M}_w \approx 48000$, corresponding to approximately 300 monomer units in a typical P3HT chain in solution. Since the number-average molecular weight ($\bar{M}_n$) is greater than $\bar{M}_w$, the polydispersity index is estimated to be ($\bar{M}_w/\bar{M}_n$) ≈ 2. The measured molecular weights are about an order of magnitude greater than those reported for P3ATs by Jen et al.[11] and also about an order of magnitude greater than that estimated (from end-group analysis) for the chemically coupled polythiophene.[6a] We conclude that the electrochemical synthesis described above can yield soluble conjugated poly(3-alkylthienylenes) with relatively high molecular weight and with moderate polydispersity.

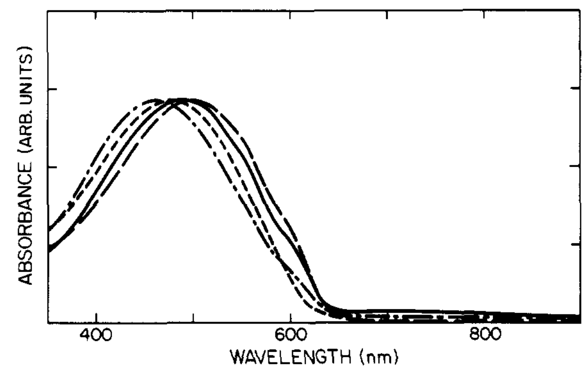

Figure 2. Absorption spectra of PT and a few alkyl derivatives of 3-substituted PTs: (-·-) PT; (– – –) P3MT; (-·-·-) P3BT; (—) P3HT.

The principal IR absorption bands observed in the poly(3-alkylthienylenes) and their assignments are listed in Table I together with the corresponding results for PT. The methyl, butyl, and hexyl derivatives show major absorption peaks that are in close correspondence to one another. In particular, the ring stretching vibrations in the vicinity of 1520–1440 cm^{-1} and the C–H out-of-plane vibrations at about 820 cm^{-1} are characteristic of the 2,5-disubstituted thiophene. These observations show that these alkyl derivatives have a well-defined chemical structure indicating that straight-chain macromolecules of poly(3-alkyl-2,5-thienylene) (with negligible cross-linking) are dominant. The IR data, the molecular weight data, and the solubility are thus fully consistent.

The electrical conductivities obtained from the as-synthesized films were 40 and 30 S/cm for P3BT and P3HT, respectively. The results of detailed electrical measurements on P3AT films will be reported separately. We simply note here that the measured values for the heavily doped samples are about 10 times higher than those reported by Jen et al.,[11] consistent with the above described observation of the order of magnitude increase in molecular weight resulting from the improved method of synthesis and sample preparation.

The existence of π-conjugation in these materials is implied by their colors and their electronic spectra. The electronic absorption spectra of the P3ATs (see Figure 2) indicate that the band edge (the onset of the π–π^* transition) occurs at about 2 eV, a value that is typical for the

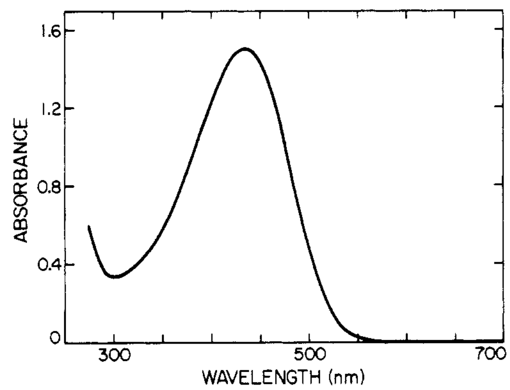

Figure 3. Absorption spectrum of P3HT/THF solution (≈2 × 10^{-4} M/L) at room temperature.

entire P3AT series. Although slight shifts in the edge and in the weak shoulder just above the edge are observed, the data of Figure 2 indicate that the electronic structure of the P3ATs is essentially independent of the alkyl substituent.

Figure 3 shows the UV–visible absorption spectrum of a P3HT/THF solution. The maximum extinction coefficient (at 435 nm) is found to be approximately 8800 M L^{-1} cm^{-1}. On dissolution, a major shift of the π–π^* absorption band is observed (see Figures 2 and 3), analogous to that observed in a number of soluble poly(diacetylenes) (PDAs).[17-20] For the soluble PDAs, the conformation of the yellow phase of the polymers in solution is that of a coil with a small effective conjugation length, and that of the red-shifted phase is that of a rodlike structure with more extensive electronic delocalization.[17-20] Dissolution causes localization of the electronic wave functions as a result of the disorder brought about by the (random) coil conformation. On the basis of the similar spectral shifts observed for the P3ATs (see Figures 2 and 3), we suggest that the chains of the yellow P3AT in solution are in a disordered conformation, whereas casting into solid film restores a more ordered backbone with an associated more extensive delocalization of the π-electron wave functions. More detailed experiments on both the solutions and on oriented films are needed to test these initial conclusions. We have, in addition, observed thermochromic spectral shifts,[21] again analogous to the poly(diacetylenes).

The absorption spectra of P3HT for as-synthesized and solution-cast films are compared in Figure 4 (the corresponding spectra for the P3BT are essentially the same as those of P3HT). The spectral characteristics of the solution-cast films are nearly identical with those of the as-synthesized films, both in the neutral case and after droping (with ClO_4^- ions). Note in particular that the π–π^* absorption edge is neither shifted nor significantly broadened. In addition, the residual absorption below the interband transition is extremely weak for the solution-cast films, indicating the absence of impurity or disorder induced states in the gap.

IV. Conclusion

We have demonstrated that the relatively high molecular weight, conjugated poly(3-alkylthienylenes) can be processed from solution and subsequently used as semiconducting and metallic polymers. Analysis of the IR spectra has demonstrated that these soluble polythienylenes have a well-defined molecular structure; the available data are completely consistent with linear chains of poly(3-alkyl-2,5-thienylene). Both as-synthesized and solution-cast films can be readily doped, with resulting electrical conductivities that are quite high; for example, $\sigma \approx 40$ S/cm

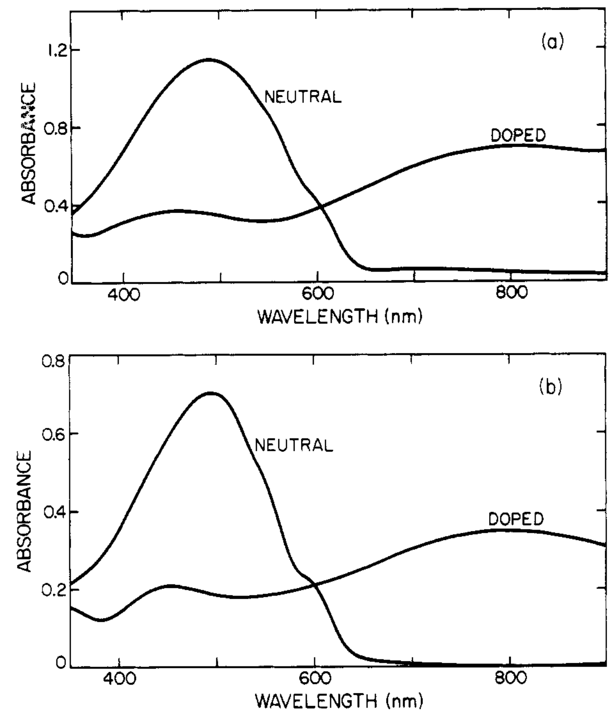

Figure 4. Absorption spectra of neutral (undoped) and conducting (doped) P3HT films at room temperature: (a) as-synthesized film; (b) solution-cast film.

for films of poly(butylthienylene). UV–visible absorption spectra of these soluble polythienylenes have been obtained for solid films (as-synthesized and solution-cast) and for the polymers in solution. The spectral characteristics of the solution-cast films are essentially identical with those of the as-synthesized films both in the neutral state and after doping. From the comparison of the spectra of the as-grown and solution-cast films, we conclude the following: (1) The electronic structure of the P3ATs is unchanged after dissolution and subsequent processing into thin solid films. (2) The solution-cast films have a well-defined electronic structure that is equivalent in overall features to that of the most highly crystalline polythiophene (in fact, the absorption edge is even sharper and the residual absorption below the edge is even weaker than observed for chemically coupled, annealed polythiophene; see ref 6). These conclusions imply weak interchain electronic transfer interactions; i.e., the electronic structure is highly anisotropic or quasi-one-dimensional. This quasi-one-dimensionality is consistent with the good solubility of the alkyl-substituted polymer. In this context, the excellent electrical conductivities found after doping are particularly interesting. The combination of high conductivity and weak interchain coupling implies that electronic motion along the conjugated chains is the dominant transport mechanism. The results on the poly(3-alkylthienylenes) therefore suggest that for conducting polymers in general, solubility (and processibility etc.) and excellent electrical and optical properties are not at all mutually exclusive.

Acknowledgment. This research was supported by the Office of Naval Research. We thank Dr. F. Garnier for a discussion on work carried out in his laboratory on the P3ATs.

Registry No. P3HT, 104934-50-1; P3BT, 34722-01-5.

References and Notes

(1) Etemad, S.; Heeger, A. J.; MacDiarmid, A. G. *Annu. Rev. of Phys. Chem.* **1982**, *33*, 443–469.

(2) Ivory, D. M.; Miller, G. G.; Sowa, J. M.; Shacklette, L. W.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1979**, *71*, 1506.

(3) Kossmehl, G.; Chatziheodorou, G. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 551.
(4) Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Rabolt, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1980**, 348.
(5) Gibson, H. W.; Bailey, F. C.; Epstein, A. J.; Rommelman, H.; Pochan, J. C. S. *J. Chem. Soc., Chem. Commun.* **1980**, 426.
(6) (a) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717. (b) Mo, Z.; Lee, K.-B.; Moon, Y. B.; Kobayashi, M.; Heeger, A. J.; Wudl, F. *Macromolecules* **1985**, *18*, 1972.
(7) (a) Diaz, A. *Chem. Scr.* **1981**, *17*, 145. (b) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173. (c) Bargon, J.; Mohmand, S.; Waltman, R. J. *IBM J. Res. Dev.* **1983**, *27*, 330. (d) Kaneto, K.; Kohno, Y.; Yoshino, K.; Inuishi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 382.
(8) Hotta, S.; Shimotsuma, W.; Taketani, M. *Synth. Met.* **1984/1985**, *10*, 85.
(9) Hotta, S.; Shimotsuma, W.; Taketani, M.; Kohiki, S. *Synth. Met.* **1985**, *11* 139.
(10) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 713.
(11) Jen, K. Y.; Oboodi, R.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1985**, *53*, 79; *Synth. Met.* **1986**, *15*, 169.
(12) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.
(13) Hotta, S.; Hosaka, T.; Soga, M.; Shimotsuma, W. *Synth. Met.* **1984**, *9*, 381.
(14) Hotta, S., to be published.
(15) Elemental analysis for P3BT (after synthesis and electrochemical compensation): Calcd: C, 69.51; H, 7.29; S, 23.20 ($C_8H_{10}S$). Found: C, 69.56; H, 7.59; S, 21.68; Cl, 0.68; N, 0.20 ($C_8H_{10.4}S_{0.93}Cl_{0.026}N_{0.020}$); total C + H + S + Cl + N = 99.71.
(16) $\bar{M}_w = \sum M_i(M_iN_i)/\sum(M_iN_i) = \sum M_i(kM_iN_i)/\sum(kM_iN_i) = \sum\alpha_iM_i/\sum\alpha_i$; the unknown constant k cancels out.
(17) Lim, K. C.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 522.
(18) Wenz, G.; Muller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837.
(19) Patel, G. N. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 607.
(20) Rughooputh, S. D. D. V.; Phillips, D.; Ando, D. J.; Bloor, D. *Polym. Commun.* **1984**, *25*, 242; *Chem. Phys. Lett.* **1984**, *106*, 247.
(21) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

Mobility of Spin Probes in Nylon Films. 2. Anionic Spin Probes

Kunihiro Hamada and Toshiro Iijima*

Department of Polymer Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Ralph McGregor

Department of Textile Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8302.

Received July 23, 1986

ABSTRACT: The mobility of anionic spin probes in dried nylon films was investigated by means of electron spin resonance (ESR) measurements. The effects of methylene chain length and drawing of the nylon were focused on. The mobility of the spin probes increased with increasing methylene chain length of the nylon, suggesting that the mobility of the nylon chain molecule increased with an increase in the number of methylene groups of the nylon. In the Arrhenius plots of the rotational correlation times, two or three crossover points were defined within the temperature range examined. The spin probe containing a carboxylate group (ASPI), in the nylons having 10 and 11 methylene groups in their repeating units (NY-11 and NY-12), gave three crossover points. These three crossover points, progressing from low temperature to high temperature, can be assigned to (a) the temperature where rotation around a single bond (or around an axis between the negative charge of the spin probe and the positively charged amino end groups of the chain molecules) occurs with cooperative fluctuation of the end methylene chains (T_n'), (b) the temperature at which the rotation of the spin probes becomes coupled with the rotation of the end methylene chains, including the amino groups (T_n), and (c) the temperature at which the free isotropic rotation of the probe molecules themselves occurs (T_n''), respectively. The existence of T_n'' for ASPI in NY-11 or NY-12 is attributed to the weak electrostatic interaction in the systems. The activation energy for rotation determined from the Arrhenius plots decreased with increasing methylene chain length of the nylon. This indicates that the increase of the methylene chain length makes the rotational movement of the end methylene chains easier. The effects of drawing on the mobility of the anionic spin probes were very small; i.e., the mobility of the end methylene groups was hardly affected by drawing.

Introduction

We have investigated the mobility of spin probes in nylon films by means of electron spin resonance (ESR) measurements.[1-4] The mobility was strongly affected by water in the nylon films,[2,3] by drawing of the nylon films,[4] and by the methylene chain length of the nylons.[4] In these studies we focused our attention on the interactions between the spin probes and the nylon chains and explained the above-mentioned effects on the basis of these interactions. Many investigators, however, have discussed the mobility of spin probes in relation to the mobility of polymers without considering interactions. Kumler and Boyer[5] and Törmälä et al.[6,7] discussed the correlation of the glass transition temperature, T_g, with T_{50G}, the temperature at which the extrema separation of ESR spectra becomes 5 mT (50 G). Kusumoto et al.[8] and Bullock et al.[9] interpreted these relations by using Bueche's free volume theory[10] and evaluated the segmental volume of the polymer concerned in the motions. Recently Hlouskova et al.[11] analyzed the T_g–T_{50G} relations for cross-linked isotropic polypropylene by considering the shapes of spin probes. Miles et al.[12] and Noël et al.[13] also evaluated the segmental volumes of poly(vinyl acetate) and poly(vinylidene fluoride), respectively, by using these relations. These relations are thought to be applicable to systems where the spin probe–polymer interaction is rather weak. On the other hand, the interaction between the spin probes and the nylon chains can hardly be neglected, as was pointed out in our previous papers.[2-4] Our results could not be explained by these analyses.

In the present work the mobility of anionic spin probes, which are expected to interact electrostatically with the

0024-9297/87/2220-0215$01.50/0