Effects of molecular weight on the electrical properties of electrochemically synthesized poly(3-hexylthiophene)

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The relation between molecular weights and electrical properties was investigated for electrochemically prepared poly(3-hexylthiophene) (PHT). The PHT films with weight-average molecular weight (M_w) in the range 12500–58000 were prepared by controlling the polymerization conditions. For $M_w < 25000$, the electrical conductivities (σ) of as-polymerized PHT films increased rapidly from 10^{-1} to 10^1 S cm^{-1} with increasing M_w. For $M_w > 25000$, the increase in σ with M_w was minor. The visible absorption maximum (π–π^* absorption band) of the neutral PHT films shifted to the red side as M_w increased. The shift was more prominent in the samples with low M_w (<25000). Wide-angle X-ray analyses of the films showed that the increase in M_w resulted in an increase in regularity of supermolecular structure in the as-polymerized PHT films, which enhanced the development of a π-conjugated system in the sample.

(Keywords: conducting polymers; molecular weight; electrical properties; polyhexylthiophene; electrochemical polymerization)

INTRODUCTION

The electrochemical polymerization of thiophene is an excellent method for obtaining flexible polythiophene films with high electrical conductivity[1–3]. The electrical properties of as-polymerized films are greatly affected by dopant concentration, morphology and structure[4–7]. It is expected that the molecular weight is also one of the fundamental factors for controlling electrical properties since it can be related to the π-conjugating length in the polymer chain[8]. Although the relation between molecular weight and π-conjugation length has been reported for polythiophene[9], the molecular weight utilized in previous study has been limited to low values since high molecular weight materials are insoluble in common organic solvents. It is reported[10–12] that electrochemically prepared poly(3-hexylthiophene) is soluble in common organic solvents such as THF and chloroform. Further, the poly(alkylthiophene)s retain the preferable properties of polythiophene[7,11]. It is also reported[13,14] that the conductivity of poly(alkylthiophene) is strongly affected by the conditions for polymerization and alkyl chain length. However, effects of molecular weight on the electrical properties of these materials are still not clear.

In this study, PHTs with various molecular weights were prepared electrochemically by controlling polymerization conditions. The effects of molecular weight on dopant concentration, conjugation length and supermolecular structure of the PHT films have been investigated. Based on the results, the relation between molecular weight and electrical properties are discussed.

EXPERIMENTAL

Hexylthiophene (HT) monomer was prepared according to the method by Chiem *et al.*[15]. The HT was characterized by i.r. and H-n.m.r. spectra. PHT films were generated electrochemically on a platinum electrode in a beaker-type cell under an atmosphere of dry nitrogen. The electrolyte used was a mixture of HT monomer and 0.03 M of tetrabutylammonium-perchlorate (TBAClO$_4$) in dehydrated nitrobenzene (NB). The electrolyses were made at a constant current density, temperature and monomer concentration in the ranges 0.7–10 mA cm^{-2}, 5–25°C and 0.1–0.65 M, respectively. In each electrolysis, the electrolytic charge passed through the cell was adjusted to 2.4 C cm^{-2}. The dopant concentration was calculated from the weight of the doped and neutral films. Since the neutral film was soluble in the electrolytic solution, films as-polymerized were chemically reduced to the neutral state in an aqueous solution of ammonia (28 wt%) at room temperature for a week. The neutral films were dissolved in THF for several months.

The molecular weight was determined by the g.p.c. method, calibrated with standard polystyrene. The electrical conductivities of the samples were measured by a four-probe method at room temperature. The films for absorption spectroscopy have been prepared from the same reaction medium on an indium–tin oxide (ITO) electrode by using the electrolytic charge of 200 mC cm^{-2}. Wide-angle X-ray diffraction (WAXD) analyses were made with a Rigaku RAD-III X-ray generator with Ni-filtered Cu Kα radiation. The diffraction profiles were obtained by step-scan mode (step width of 0.05°).

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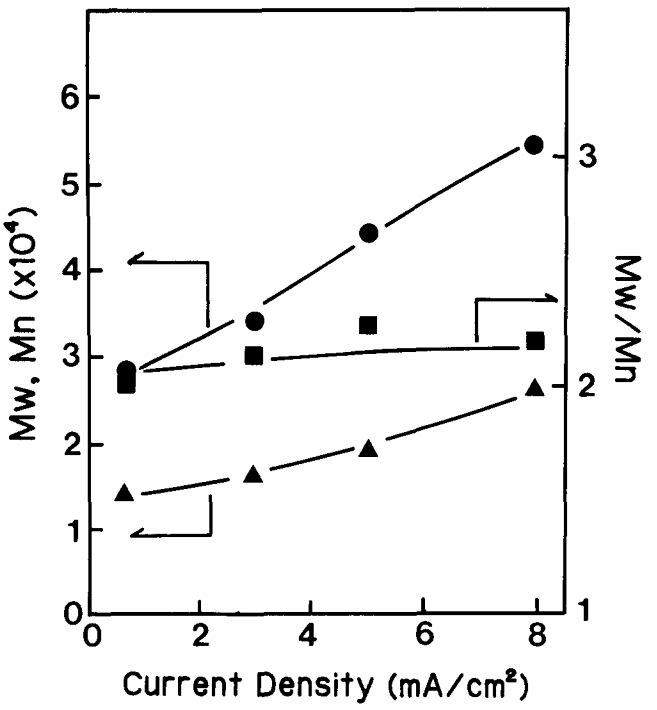

Figure 1 Molecular weights against electrolytic current density: (●) M_w; (▲) M_n; (■) M_w/M_n

RESULTS AND DISCUSSION

Preparation of PHT films with various molecular weights

Under a constant polymerization charge of 2.4 C cm^{-2}, the molecular weights of the resultant PHT films were greatly affected by polymerization temperature (T_p), electrolytic current density (I_d) and monomer concentration (C_m). *Figure 1* shows weight-(M_w) and number-(M_n) average molecular weight and their ratio M_w/M_n as a function of I_d. The electrolyses were made at 5°C with a NB solution containing 0.3 M of HT monomer. Both M_w and M_n increase with increasing I_d. On the other hand, M_w/M_n is almost independent of I_d and shows a value of about two. This value was also reported by Hotta *et al.*[7]. At a high I_d (>8mA cm^{-2}), the as-polymerized products were heterogeneous and sometimes powdery. Masuda *et al.* reported[13] that the M_n of poly(3-dodecylthiophene) increased linearly and M_w and M_w/M_n increased exponentially with increasing I_d. They pointed out that crosslinking took place at high I_d. As will be shown in the following section, PHT films obtained below 8 mA cm^{-2} in our experimental conditions were composed by 2,5 linkage of thiophene rings. Further, the conjugation length also increased with increasing M_w. The crosslinking would be minor in *Figure 1*. In *Figure 2*, M_w and M_n are plotted against T_p. The I_d applied for a NB solution containing 0.3 M of HT monomer was adjusted to a low value of 0.7 mA cm^{-2}. M_w as well as M_n increases with decreasing T_p. In *Figure 3*, M_w and M_n are plotted against C_m in NB solution. I_d and T_p were chosen to be 0.7 mA cm^{-2} and 5°C, respectively. M_w and M_n increase with decreasing C_m. By controlling I_d, T_p and C_m, PHT films with M_w in the range 12 500–58 000 could be obtained.

Recently, Wang *et al.* reported[14] the relation between polymerization conditions and conductivities of poly(3-alkylthiophene)s. Although the reaction species and polymerization conditions utilized in this study were different from those used by Wang *et al.*, a similar relation between conductivities and the conditions was obtained for PHT films. In this study, the relation was quite similar to the tendencies of the molecular-weight–conditions relationship, which indicates that the molecular weight is an important factor for controlling electrical properties of as-polymerized PHT films.

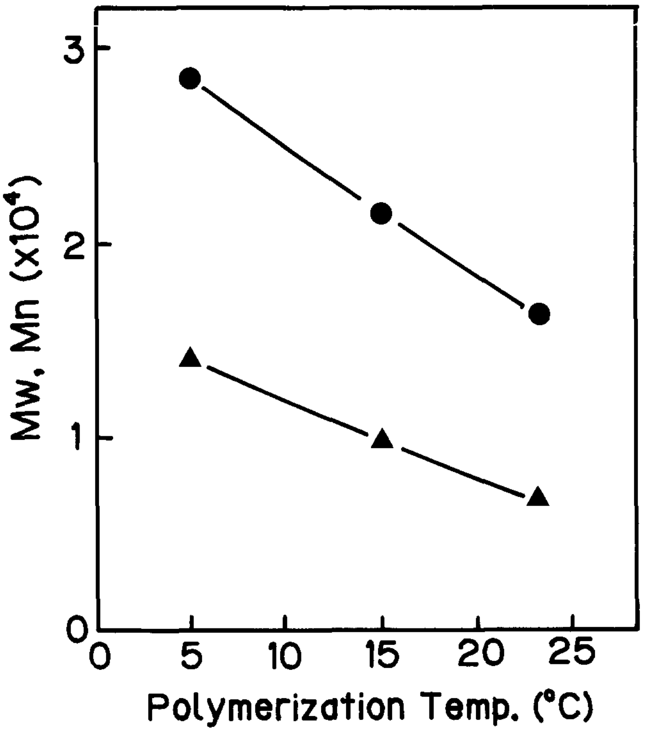

Figure 2 Molecular weights against polymerization temperature: (●) M_w; (▲) M_n

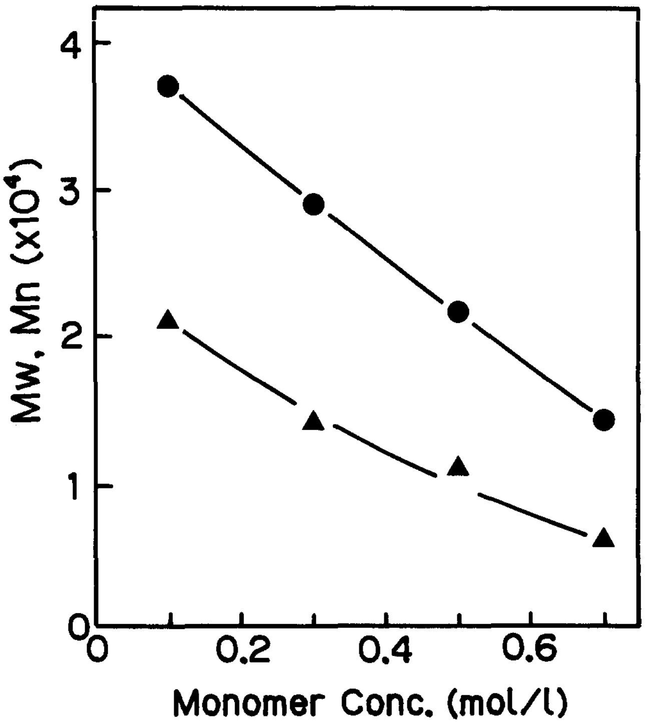

Figure 3 Molecular weights against monomer concentration: (●) M_w; (▲) M_n

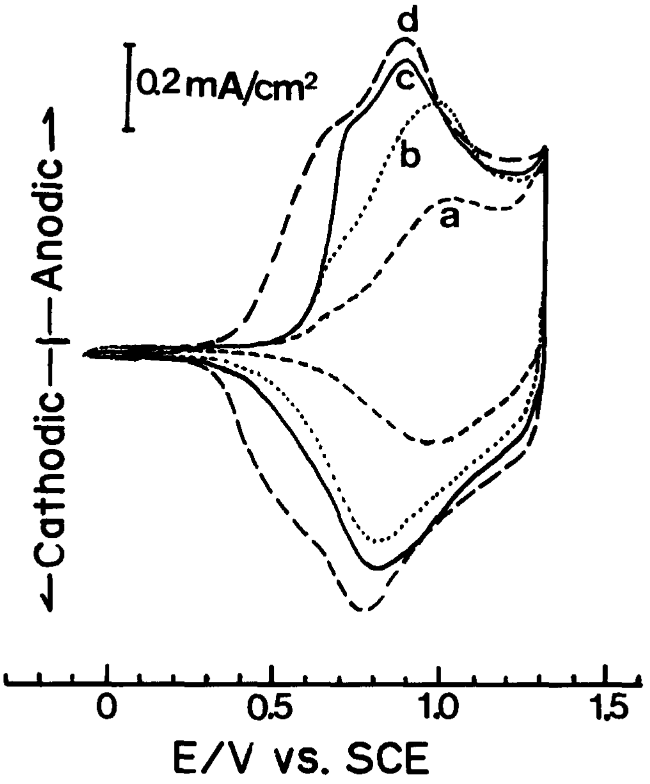

Figure 4 Cyclic voltamograms of PHT films with several molecular weights: a, $M_w = 16000$; b, $M_w = 21500$; c, $M_w = 28000$; d, $M_w = 58000$

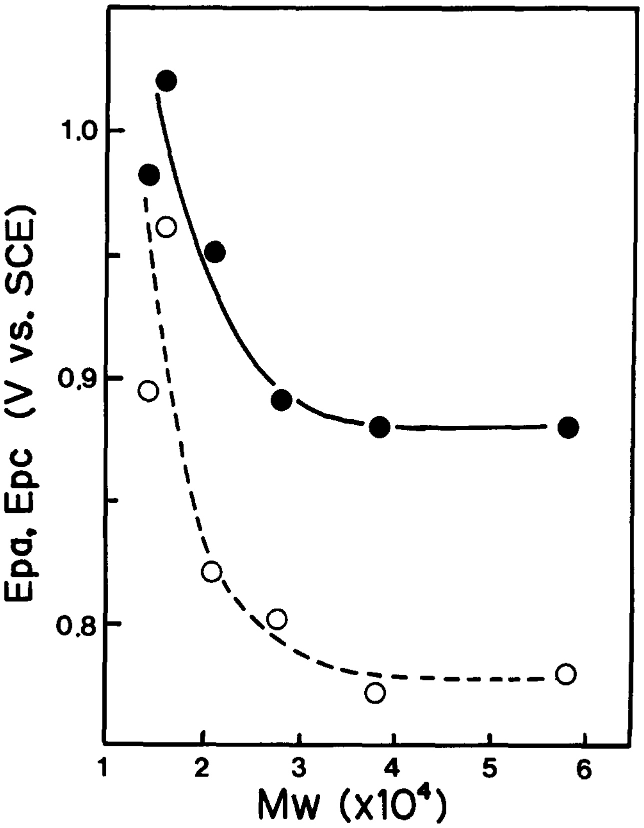

Figure 5 E_{pa} (●) and E_{pc} (○) against M_w from voltametrical measurements

Electrical properties

Figure 4 shows cyclic voltamograms of PHT films with several molecular weights. The measurements were made in acetonitrile solution containing 0.1 M $LiClO_4$. The sweep rate was $10\ mV\ s^{-1}$. These curves show that the difference in the molecular weight exhibits two major effects on the electrochemical behaviour of the polymers.

The first effect is that the potentials of anodic peak (E_{pa}, oxidation potential of polymer) and cathodic peak (E_{pc}, reduction potential of polymer) decrease with increasing M_w. The decreases are more prominent in the low M_w region (<25000), as shown in *Figure 5*. It is reported[14,16] that the peak potential also depends on the alkyl chain length in poly(3-alkylthiophene) due to the steric effect of the alkyl chain. In this study, the alkyl chain length was constant. Therefore, the difference in potential shift is due to the difference in the molecular weight. The oxidation potential of the electroconductive polymer decreases with increasing the π-conjugated system (L) in the polymer network.[16,17].

In order to investigate the relation between the molecular weight of PHT and L, the visible absorption maximum (λ_{max}) due to π–π^* transition was measured as a function of M_w and the results are shown in *Figure 6*. It is clearly seen that λ_{max} shifts to the red side as M_w increases. Further, the shift is more prominent in the low M_w region (<25000). The results indicate that L exactly increases with increasing M_w. The increase in L raises the energy level of the highest occupied molecular orbital in the conductive polymer[17]. As a result, the oxidation and reduction potentials are lowered in accordance with the results shown in *Figure 5*.

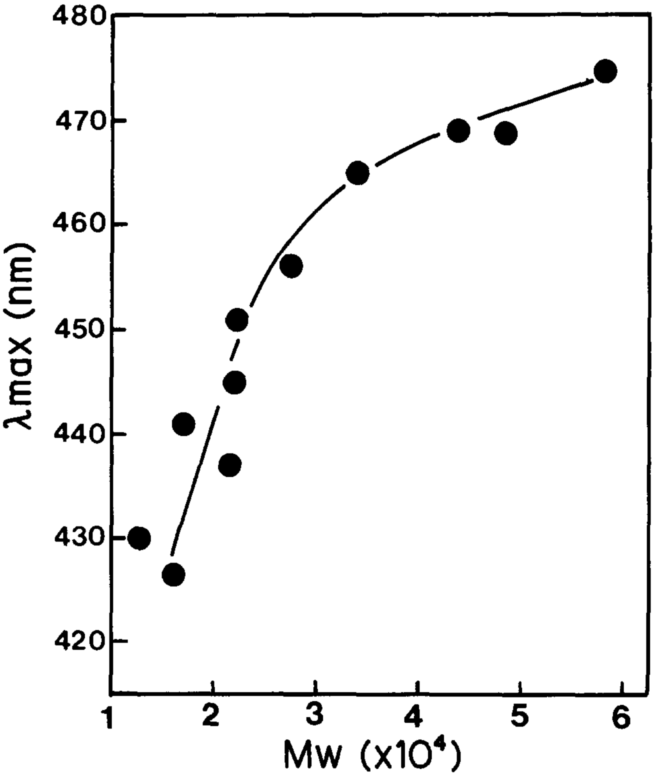

Figure 6 The visible absorption maximum of the neutral PHT films as a function of M_w

The second effect is that the integrated anodic and cathodic charges increase with increasing M_w. The integrated charges are proportional to the number of dopants associated with the doping (oxidation) and undoping (reduction). In fact, as shown in *Figure 7*, the dopant concentration calculated by the method described in the experimental section increases with increasing M_w.

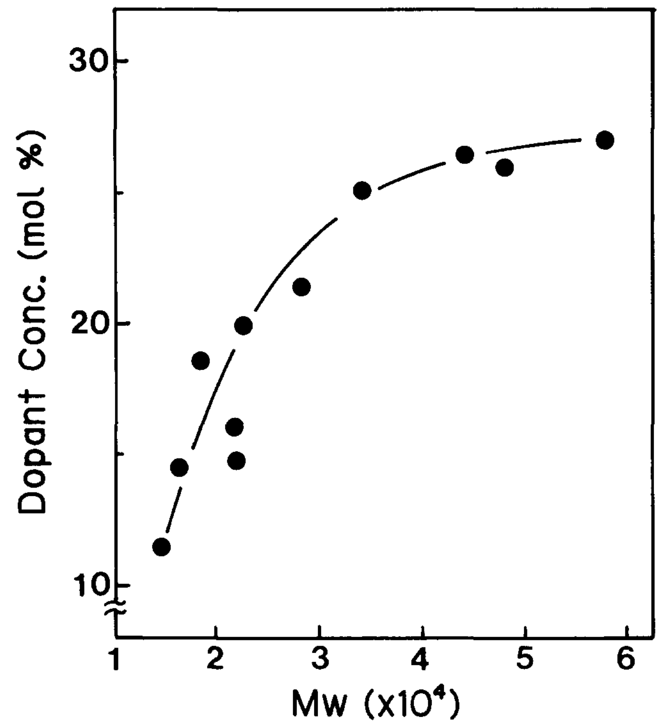

Figure 7 Dopant concentrations as a function of M_w for as-polymerized films prepared under various conditions

As was discussed above, the mean length of the π-conjugated system increases with increasing M_w, which results in a decrease of the oxidation potentials of the polymer. The lower the oxidation potential, the higher the dopant concentration of the as-polymerized films can be expected to be.

Figure 8 shows the electrical conductivities (σ) of as-polymerized films (series I) and controlled films that have constant dopant concentration of *ca.* 15 mol% (series II) as a function of M_w. For series II, the dopant concentration was controlled by varying the polar charge of electrochemical reduction. It is reported[13,18] that σ for electrochemically prepared film is strongly affected by the film thickness and charge density. In this study, to minimize these dependencies on σ, the charge density was adjusted to 2.4 C cm^{-2} and the film thicknesses were 14–18 μm. At $M_w < 25\,000$, σ for both series increases rapidly from *ca.* 10^{-1} to 10^1 S cm^{-1} with increasing M_w. As was seen in *Figure 7*, the dopant concentration increased with increasing M_w. Thus, the increase in σ for series I cannot be simply related to M_w. However, for series II, the dopant concentrations for all the samples were adjusted to the value of 15 mol%. This means that the increase in σ for series II is not due to the increase in dopant concentration, but to the increase in M_w.

At a given dopant concentration, it is expected that the increase in molecular weight produces two effects on σ. The first is the decrease of a polymer chain resistance due to the increase in the mean conjugation length, as was indicated in *Figure 6*. The second is the decrease in bulk resistance due to the decrease in the number of polymer chain ends. The conduction mechanism of the polymer is thought to be complex. However, the conduction is expected to be governed mainly by a resistance of the polymer chain itself and interchain resistance. We showed in our previous paper[19] that the electrical conductivity of drawn polythiophene films both perpendicular and parallel to the draw direction increased with increasing draw ratio. By drawing, the development of the π-conjugation system became dominant, which resulted in an increase in σ for all directions of the neutral polythiophene films. As was shown in *Figure 6*, λ_{max} in the low molecular weight region ($<25\,000$) shifted to the red side with increasing molecular weight. This tendency was quite similar to that observed in σ-M_w relations. These results imply that the mean length of π-conjugation in the molecular chain is directly related to the conductivity of the sample.

For $M_w > 25\,000$, the increase in σ and the shift of λ_{max} due to the increase in M_w is minor. When a simplified molecular orbital theory reported by Hückel[20] for conjugated polyens is applied to the π-conjugated 2–5 polythiophenes, the lowest π–π^* transition energy of the polymer is given by the equation[8]

$$E_{\pi-\pi^*} = (\alpha_2 - \alpha_1) + 2(\beta_1 + \beta_2)\cos(\pi/(n+1)) \quad (1)$$

where α_1 and α_2 represent the energy of the orbital of an isolated monomeric unit for HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), respectively, β_1 and β_2 represent the exchange integral between the two orbitals in the adjacent two monomeric units for HOMO and LUMO, respectively, and n is the degree of polymerization. From the equation, a large bathochromic shift of the π–π^* absorption is expected only in the low molecular weight regions. In fact, the shift of λ_{max} due to π–π^* transition has been observed only in the low molecular weight regions ($M_w < 1350$) of polythiophene[8,21]. In this study, the shift of λ_{max} in the higher M_w region is minor, as

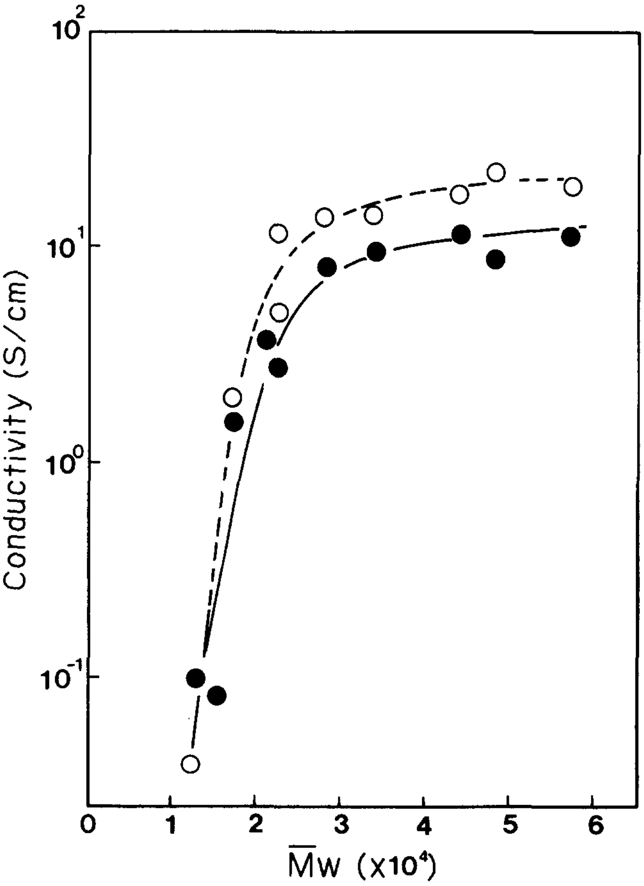

Figure 8 The electrical conductivities of as-polymerized films (○) and *ca.* 15 mol% doped films (●) as a function of M_w

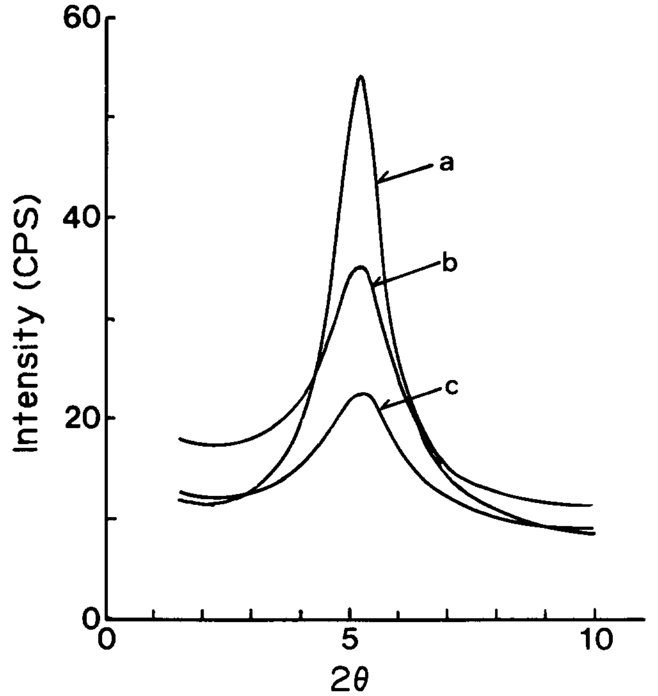

Figure 9 Plots of X-ray intensity versus 2θ for neutral as-polymerized films with various molecular weights: a, M_w = 58 000; b, M_w = 34 000; c, M_w = 28 000

Table 1 X-ray data of poly(3-alkylthiophenes)

	poly(3-methyl-		poly(3-hexyl-		poly(3-dodecyl-	
	d	2θ	d	2θ	d	2θ
As-polymerized	8.6	10.3	18.8	4.7	29.1	3.0
Neutral	7.1	12.5	16.5	5.3	26.7	3.3

expected from the equation. However, a large shift in λ_{max} is observed even in the medium molecular weight region (12 500–25 000). The molecular weight region seems to be higher than that estimated from equation (1). The results suggest that the values of β_1 and β_2 in equation (1) are not constant, but depend on the configuration and/or conformation of the polymer chains.

*FT*i.r. spectra for all the samples utilized in this study showed strong absorption at 830 cm^{-1} and weak, but well defined, absorption at 3060 cm^{-1}, which had been assigned to the C–H deformation vibration of a 2,3,5-trisubstituted thiophene ring and the stretching vibration of the β-C–H bond on the thiophene ring, respectively[22]. The results indicate that the configurational irregularity of the present samples is less. In order to study the conformational irregularity such as distortion and rotation between the thiophene rings of the resultant PHT films, wide-angle X-ray diffraction analyses were made.

Structures

Figure 9 shows the plots of the X-ray diffraction intensity *versus* 2θ for neutral PHT films with various molecular weights. The samples show clear reflections in the angle regions $2\theta = 5.25$–5.35. The peak positions are almost independent of M_w, but the intensity and sharpness of the profiles increase with it. To characterize the diffraction profiles, WAXD analyses were made for three kinds of poly(3-alkylthiophene)s that had been prepared by electrochemical polymerization. The X-ray data of the samples are summarized in *Table 1*. For both neutral and as-polymerized films, the spacings increase proportionally with increasing length of alkyl chain. In addition, the d-spacings of as-polymerized films are about 0.2 nm larger than those of neutral films. Further, WAXD photographs of neutral drawn PHT film exhibited intensity maxima on the equator (data not shown). These results suggest that the spacings corresponding to 2θ = 5.25–5.35 are indicative of the interchain distance perpendicular to the molecular axes. A similar assignment was reported by Winokur *et al.*[23]

The diffraction profiles are relatively sharp, suggesting the existence of partially ordered regions in the sample[23]. It is well known that the relations between the halfwidth of the diffraction profiles and crystallite size in the semicrystalline materials are well explained by using Scherrer's equation[24]

$$D = K\lambda/\beta\cos\theta$$

where D is the mean dimension of the crystallites perpendicular to the molecular axis, β is the halfwidth, K is a constant, and λ is the X-ray wavelength. In this study, the size of ordered regions in the samples (D) was estimated from the equation. The values for D were greatly affected by the history of sample preparation and molecular weight. In *Figure 10*, values for D are plotted as a function of M_w for neutral PHT films and their cast films from THF solution. For both films, D increases

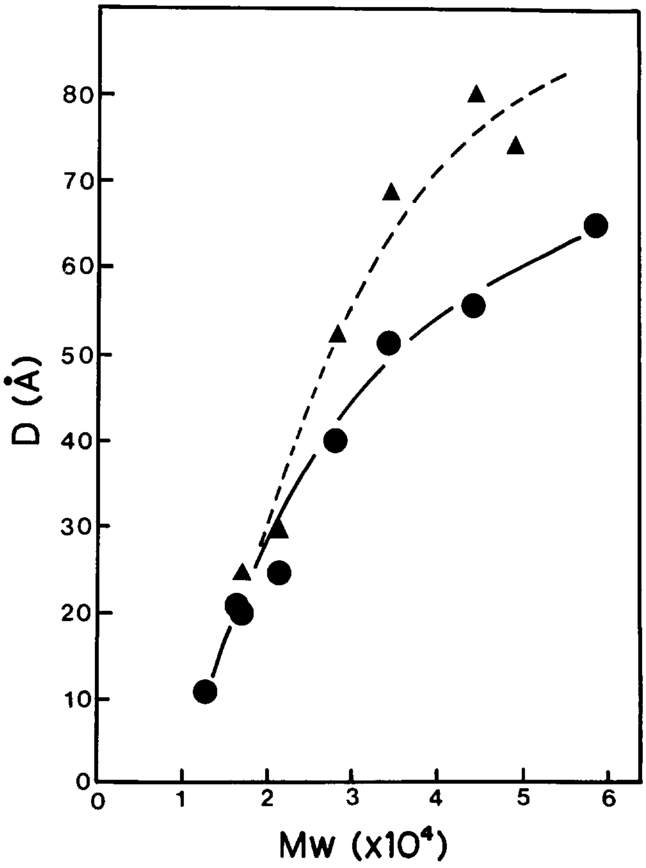

Figure 10 Values for D as a function of M_w for neutral PHT films (●) and their cast films (▲)

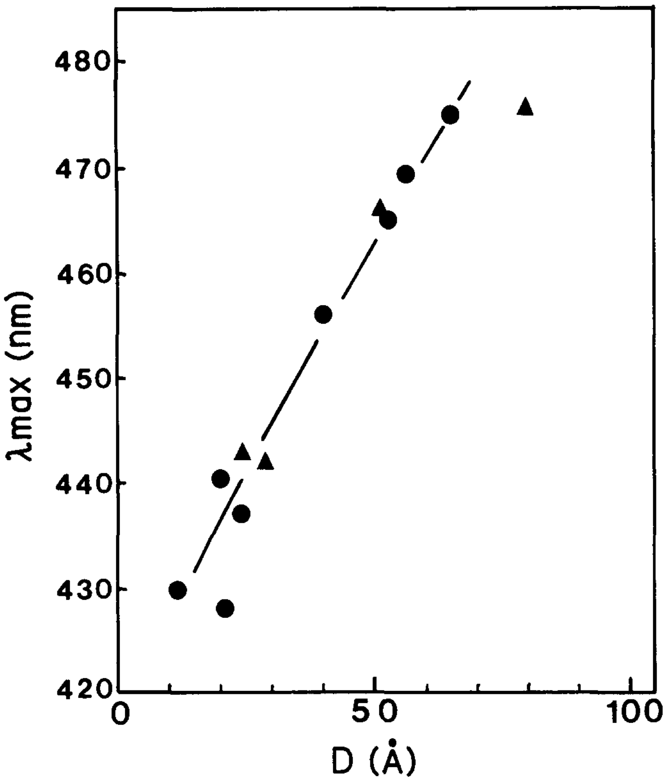

Figure 11 The λ_{max} of the neutral as-polymerized (●) and cast films (▲) as a function of D (1 Å = 10^{-10} m)

with increasing molecular weight, with this tendency being more prominent in the solution-cast films at higher M_w regions. Thus, the difference in D between as-polymerized films and solution-cast films increases with increasing molecular weight. It is generally recognized that chain molecules in the solution-cast films have thermodynamically stable conformation due to the slow evaporation rate of the solvent. During electrochemical polymerization, the growth rate of as-polymerized films is very fast compared with that for films obtained by the solution-casting method. With increasing molecular weight, periodic bend and twist may be introduced in the chain molecules along the aromatic unit during film growth of as-polymerized films, which might suppress the increase in D of as-polymerized films at higher M_w regions.

The values for D can be directly related to λ_{max}, as shown in *Figure 11*. With increasing D, λ_{max} increases almost linearly. This means that mean conjugation length can be controlled by M_w and supermolecular structure of PHT. The higher the regularity of chain conformation and M_w, the longer the length of conjugation that can be expected.

CONCLUSION

The increase in M_w resulted in an increase in the regularity of supermolecular structure in the as-polymerized PHT film, which enhances the π-conjugation length in the film. The dopant concentration increased with increasing conjugation length. At a constant dopant concentration, the conjugation length is directly related to the electrical conductivity of the PHT sample.

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