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Viscometric and Light Scattering Analyses of $CHCl_3$ Solutions of Poly(3-alkylthiophene-2,5-diyl)s

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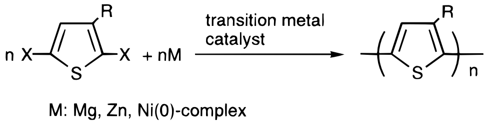
Introduction

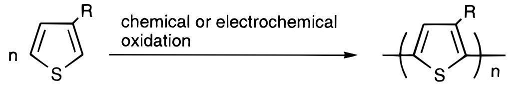
π-Conjugated polymers have been the subject of many recent papers.[1] Extensive studies have been especially carried out on polythiophene[2] and its 3-alkyl derivatives[2c,3] because of their high chemical stability, good electrical conductivity, and other interesting properties. However, solution properties of the polymers have received much less attention.[4] We here report results of viscometric, GPC, and light scattering analyses of $CHCl_3$ solutions of fractionated poly(3-alkylthiophene-2,5-diyl), P3RTh. Several optical properties of the fractionated P3RTh are also reported.

Results and Discussion

Poly(3-alkylthiophene-2,5-diyl)s, P3RTh's, have been prepared by various methods including organometallic polycondensation of dihaloalkylthiophenes (eq 1)[3a−e] and oxidation polymerization of alkylthiophenes (eq 2).[3f−h]



(1)

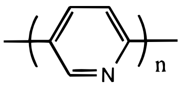


(2)

Solubility of P3RTh depends on the R group as well as the polymerization method, and P3RTh with a hexyl group, P3HexTh, has the highest solubility in $CHCl_3$ among P3RTh's prepared according to eq 1 using an Ni(0) complex. On the other hand, poly(3-dodecylthiophene-2,5-diyl), P3DodTh, has the highest solubility in $CHCl_3$ among P3RTh's prepared by the oxidation polymerization using $FeCl_3$ (eq 2). Other P3RTh's contained insoluble fractions (20−50 wt %) in $CHCl_3$.

Viscosity and Light Scattering. Table 1 summarizes GPC and light scattering (LS)[5] results of fractionated P3HexTh(Ni) and P3DodTh(Fe), which are prepared by using the Ni(0) complex and $FeCl_3$, respectively. The data shown in Table 1, including M_n (number average molecular weight), M_w (weight average molecular weight), R_g (radius of gyration), and ρ_v (degree of depolarization), reveal the following features of the $CHCl_3$ solution of P3RTh.

(i) The M_w value determined by GPC, M_w(GPC), roughly agrees with the M_w value determined by the light scattering method, M_w(LS). Better agreement of the two values is observed with P3DodTh(Fe), indicating that P3DodTh(Fe) takes an effective volume comparable to that of polystyrene. On the other hand, fractions I and II of P3HexTh(Ni) (runs 2 and 3) give M_w(GPC) considerably larger than M_w(LS), presumably due to the stiffer structure of P3HexTh(Ni). The presence of the π-conjugation system seems to make P3HexTh(Ni) more rigid and linear; however, its rigidity and linearity seem not to be as high as those observed with poly(pyridine-2,5-diyl), PPy[6] (PPy with M_w of 3800 gives a ρ_v value of 0.33 and a $[\eta]$ value of 0.85, respectively), presumably due to the hexyl substituent in P3HexTh(Ni).



PPy

(ii) P3HexTh(Ni) and P3DodTh(Fe) exhibit relatively small ρ_v values; however, the non-zero ρ_v values indicate that they do not adopt a complete random-coil structure in $CHCl_3$. The normal R_g values (runs 7, 10, and 13) also indicate that the polymers do not take a rigidly linear structure.

(iii) Plot of log $[\eta]$ ($[\eta]$ in dL g^{-1}) against log M gives the linear correlation shown in Figure 1, to give the following viscometric equations

$$[\eta] = KM^a \tag{3}$$

$$K = 2.56 \times 10^{-6} \text{ and } a = 1.14 \text{ for P3HexTh(Ni)} \tag{4a}$$

$$M = M_n(\mathrm{GPC})$$

$$K = 2.82 \times 10^{-6} \text{ and } a = 1.17 \text{ for P3HexTh(Ni)} \tag{4b}$$

$$M = M_w(\mathrm{LS})$$

$$K = 90.2 \times 10^{-6} \text{ and } a = 0.80 \text{ for P3DodTh(Fe)} \tag{5a}$$

$$M = M_n(\mathrm{GPC})$$

$$K = 49.0 \times 10^{-6} \text{ and } a = 0.78 \text{ for P3DodTh(Fe)} \tag{5b}$$

$$M = M_w(\mathrm{LS})$$

The plot of log $[\eta]$ *vs* log M_w determined by GPC gives the *a* values of 1.0 and 0.77 for P3HexTh(Ni) and P3DodTh(Fe), respectively.

Bi, Ying, and Qian reported an *a* value of 0.77 for P3HexTh prepared by the oxidation polymerization using $FeCl_3$.[4] The *a* value obtained for P3DodTh(Fe) is almost the same as that reported by Qian and his coworkers. On the other hand, the larger *a* value of P3HexTh(Ni) suggests its more linear structure, and the difference between P3RTh's prepared by the two methods may be attributed to the presence of irregular units (e.g., thiophene-2,4-diyl bonding[7]) and/or branching in P3RTh prepared by the oxidation polymerization.[4] In the case of the organometallic polycondensation (eq 1), the polymerization is considered to proceed selectively at the position of the C−X bond, and P3RTh thus prepared will not contain such irregularities.

Effect of Iodine Doping. Addition of I_2 to the $CHCl_3$ solution of P3HexTh(Ni) in $CHCl_3$ causes only a

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Table 1. GPC and Light Scattering Data of Fractionated P3HexTh(Ni) and P3DodTh(Fe)

			GPC data (x 10^{-3})^a			light scattering				
run	fraction	wt %	M_n	M_w	M_w/M_n	M_w ($\times 10^{-3}$)	R_g, nm^b	$\rho_v{}^c$	[η],^{d} dL g^{-1}	λ_{max}, nm^a
					Polymer = P3HexTh(Ni)					
1	original	100	7.6	24.1	3.19					410
2	P3HexTh(Ni)-I	12.8	4.1	5.6	1.36	2.7		0.065	0.031	392
3	P3HexTh(Ni)-II	38.7	11.0	15.3	1.39	7.3		0.026	0.105	406
4	P3HexTh(Ni)-III	15.4	29.3	39.5	1.35	22		0.017	0.31	412
5	P3HexTh(Ni)-IV	1.3	*e*	*e*	*e*					
6	P3HexTh(Ni)-V	31.8	56.9	152	2.68				0.70	416
					Polymer = P3DodTh(Fe)					
7	original	100	66	141	2.14	144	37.8	0.011		430
8	P3DodTh(Fe)-I	17.0	7.1	26.5	3.73	26.5		0.041	0.108	418
9	P3DodTh(Fe)-II	2.0	*e*	*e*	*e*					*e*
10	P3DodTh(Fe)-III	20.5	53.9	167	3.09	120	30.5	0.012	0.57	431
11	P3DodTh(Fe)-IV	20.4	85.5	151	1.76				0.89	430
12	P3DodTh(Fe)-V	3.7	*e*	*e*	*e*					*e*
13	P3DodTh(Fe)-VI	12.1	127	497	3.92	515	68.5	0.0045	1.04	429
	P3DodTh(Fe)-VII	24.4	223^e	4540^e	20.4^f					432

[a] In $CHCl_3$. GPC data *vs* polystyrene are given. [b] Radium of gyration. [c] Degree of depolarization. [d] At 30 °C. [e] Not measured. [f] GPC curve shows two peaks.

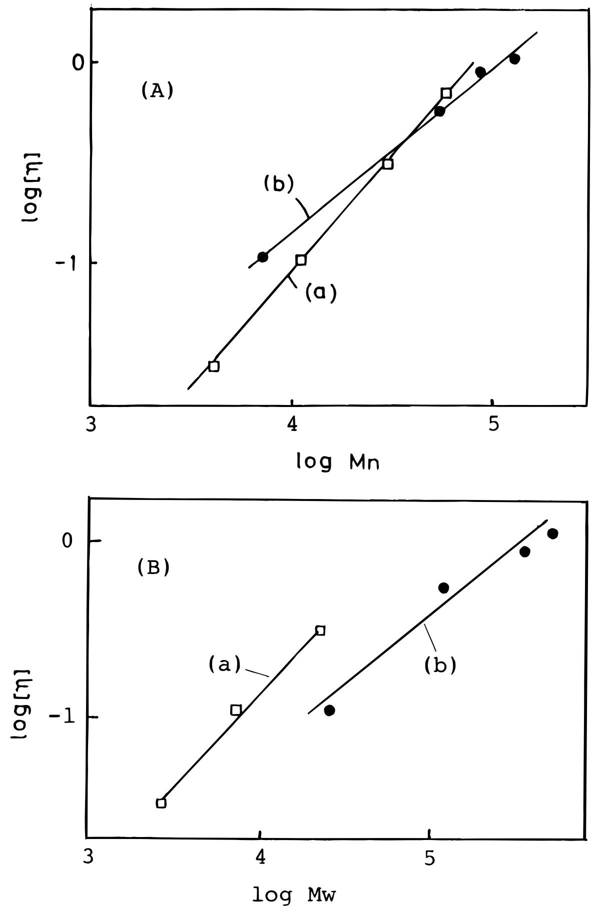
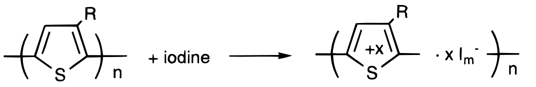


Figure 1. (A) Plot of log [η] *vs* log M_n(GPC) and (B) that of log [η] *vs* log M_w(LS) for (a) P3HexTh(Ni) and (b) P3DodTh(Fe). [η] is obtained in $CHCl_3$ at 30 °C.

minor change in the viscosity of the solution; P3HexTh(Ni)-V (Table 1) shows the same [η] value in both (i) $CHCl_3$ and (ii) $CHCl_3$ containing 0.61 mol of I_2 (or 0.24 mol of I_5^-)[2f] per 1 mol of the 3-hexylthiophene monomer unit. The addition of iodine to P3RTh will lead to idodine doping,[2f,3d,e] thus forming polymeric ion pair(s).



(6)

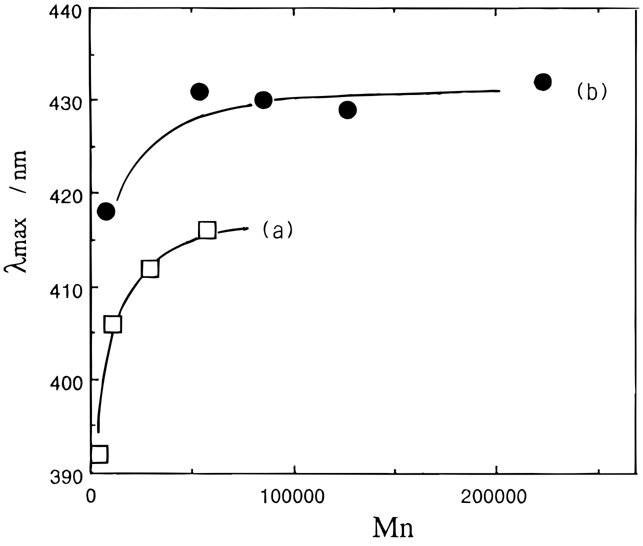


Figure 2. λ_{max} *vs* M_n for (a) P3HexTh(Ni) (□) and (b) P3DodTh(Fe) (●). In $CHCl_3$.

However, the doping essentially gives no obvious change in the viscosity of the solution. The plot of η_{sp}/c *vs c* is also normal without showing an increase of the η_{sp}/c values at a low *c* region.

The viscosity of the P3HexTh(Ni)/iodine system in $CHCl_3$ showed no time dependence for several hours, indicating iodine does not induce cross-linking between the polymer chains, in consistent with previously reported results.[2f] Addition of $FeCl_3$ (1 mol/1 mol of monomer unit of P3HexTh(Ni)) to the $CHCl_3$ solution of P3HexTh(Ni)-V leads to rapid precipitation of almost all polymeric materials. The formation of the precipitate is ascribed to the p-doping (or oxidation) by $FeCl_3$[1] and/or cross-linking between the polymer molecules. Undoping of the black precipitate by a successive treatment with HCl-acidic methanol and a mixture of NH_4OH and methanol gives an orange (color of original P3HexTh(Ni)-V) solid. About half of the solid is unextractable with $CHCl_3$, indicating occurrence of the cross-linking.

λ_{max} and Molar Absorption Coefficient. Figure 2 exhibits a plot of the λ_{max} value of P3RTh's *vs* M_n. The leveled off λ_{max} values in Figure 2 agree with the reported values, 415 and 430 nm, for P3HexTh(Ni)[3d] and P3DodTh(Fe),[3g] respectively, and the leveled off λ_{max} of

Table 2. Molar Absorption Coefficient ϵ' per the Thiophene Unit[a]

run	compd[b]	$\epsilon'/10^3$ M^{-1} cm^{-1}	λ_{max}	ref
1	P3HexTh(Ni)	8.1		
2	P3DodTh(Fe)	7.8		
3	Th	5.4 (i-C_8H_{18})[a]	232	9
4	Th_2	6.1 (C_6H_6)[a]	300	10
5	Th_3	7.5[c]	354[c]	
6	Th_4	8.0 (C_6H_6)[a]	391	10
		8.6 (C_6H_{14})[a]	385	10
7	Th_5	7.6 (C_6H_6)[a]	418	10

[a] In $CHCl_3$ unless otherwise noted in parentheses. [b] Th = thiophene; Th_n = oligo(thiophene-2,5-diyl)H$(C_4H_2S)_n$H. [c] Almost the same data (7.3×10^3 M^{-1} cm^{-1} and 355 nm) are reported for Th_3 in C_6H_6.[9]

P3HexTh(Ni) appears at a shorter wavelength than that of P3HexTh[4] prepared by the oxidation polymerization with $FeCl_3$ due to the higher proportion of head-to-head units contained in P3HexTh(Ni).[3d,h]

Both P3HexTh(Ni) and P3DodTh(Fe) with M_n(GPC) of larger than 1×10^4 give molar absorption coefficients ϵ' of about 8.0×10^3 M^{-1} cm^{-1} per thiophene unit, respectively (Table 2).[8] The ϵ' values of P3RTh are comparable to those of oligothiophenes, as shown in Table 2. The data shown in Table 2 indicate that the various oligo- and polythiophenes give a similar molar absorption coefficient, ϵ', allocated to each thiophene unit.

Experimental Section

Materials. P3RTh(Ni)[2f,3d] and P3RTh(Fe)[3g,h] were prepared as reported in the literature. They were fractionated as follows.

P3HexTh(Ni):P3HexTh(Ni) (1.9 g) dispersed in hexane (500 mL) was stirred at room temperature (2 days). After the hexane-extract was condensed to 100 mL, acetone (400 mL) was added to obtain an orange suspension of P3HexTh(Ni)-III. Acetone (300 mL) was further added to the recovered solution to obtain a precipitate of P3HexTh(Ni)-II. The 1:7 mixture of hexane and acetone was evaporated to dryness to obtain P3HexTh(Ni)-I. On the other hand, the hexane-unextractable powder was extracted by hot hexane with a Soxhlet extractor to yield P3HexTh(Ni)-IV. The polymer powder was further extracted by hot CH_2Cl_2 with the Soxhlet extractor. Almost all of the polymer was extracted by CH_2Cl_2, and hexane (400 mL) was added to the CH_2Cl_2 (100 mL) solution to obtain a trace amount of a precipitate. The 1:4 mixture of CH_2Cl_2 and hexane was evaporated to dryness to yield P3HexTh(Ni)-V.

P3DodTh(Fe):P3DodTh(Fe) (4.2 g) dispersed in hexane (500 mL) was stirred at room temperature (ca. 20 °C; twice, 1 day for each). A red hexane solution and a black precipitate were obtained. The combined extracts were cooled to 0 °C to obtain a precipitate of P3DodTh(Fe)-II. The filtrate was evaporated to dryness to yield P3DodTh(Fe)-I.

On the other hand, the black precipitate was extracted by hot hexane with the Soxhlet extractor; reprecipitation in CH_3OH yielded P3DodTh(Fe)-III. The unextractable solid was extracted with CH_2Cl_2 (500 mL) at room temperature for 1 day with stirring and by hot CH_2Cl_2 with the Soxhlet extractor. From the combined extracts, P3DodTh(Fe)-IV was obtained by reprecipitation in CH_3OH. The unextractable part in hot CH_2Cl_2 was extracted by a 1:1 mixture (600 mL) of CH_2Cl_2 and THF at room temperature for 6 h (once) and 1 day (once), and P3DodTh(Fe)-V was obtained by reprecipitation in CH_3OH. The unextractable part was further extracted in a similar way by a 1:4 mixture (500 mL) of CH_2Cl_2 and THF, and P3DodTh(Fe)-VI was obtained by precipitation in CH_3OH. The remaining unextractable fraction was assigned to P3DodTh(Fe)-VII, which was soluble in $CHCl_3$ and THF. These results indicate that the solubility of P3RTh increases in the following order: acetone < hexane < CH_2Cl_2 < THF, $CHCl_3$.

Measurement. $[\eta]$ was measured with an Ubbelohde viscometer. Light scattering data were obtained as previously reported[5] (laser: He–Ne laser, 632.8 nm) or by using an Otsuka DLS-700 (laser: He–Ne laser, 632.8 nm) dynamic light scattering spectrophotometer.

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(8) P3RTh's with M_n(GPC) lower than 1×10^4 (P3HexTh(Ni)-I and P3DodTh(Fe)-I) give the ϵ' value of about 6×10^3 M^{-1} cm^{-1}.

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