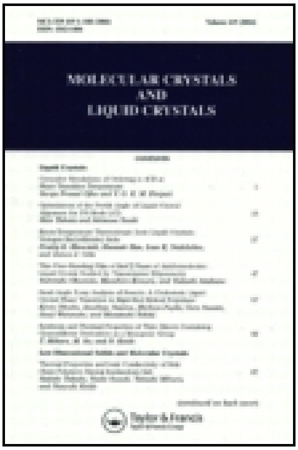

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Molecular Alignment of n-Alkanes and Head-to-Tail-Type Poly(3-Alkylthiophene) on Substrates: Study with Films Prepared by Casting and Vacuum Deposition

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Molecular Alignment of *n*-Alkanes and Head-to-Tail-Type Poly(3-Alkylthiophene) on Substrates: Study with Films Prepared by Casting and Vacuum Deposition

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Cast and vacuum-deposited films of several kinds of n-alkanes with different crystal systems were made on a glass substrate. X-ray diffraction (XRD) data showed that n-alkane molecules in both the cast and the vacuum-deposited films were essentially aligned perpendicularly on the substrate. When the vacuum-deposited film of n-alkane became thicker, the XRD pattern indicated that n-alkane molecules in the upper layer lay on the perpendicularly aligned n-alkane layer. Molecular alignment of the film of head-to-tail-type poly(3-hexylthiophene-2,5-diyl), HT-P3HexTh, also depended on the thickness of the film.

Keywords: casting; molecular alignment; *n*-alkane; poly(3-hexylthiophene-2,5-diyl); vacuum deposition

INTRODUCTION

Investigations of π-conjugated polymers have actively been carried out for their interesting optical and electric properties [1–3]. For application of the π-conjugated polymers to optical and electronic devices, obtaining their films with good quality and controlling of molecular alignment of the polymer molecules in the film are essential [4–11]. For example, improvement of carrier-transporting properties of the π-conjugated polymer in electronic devices such as

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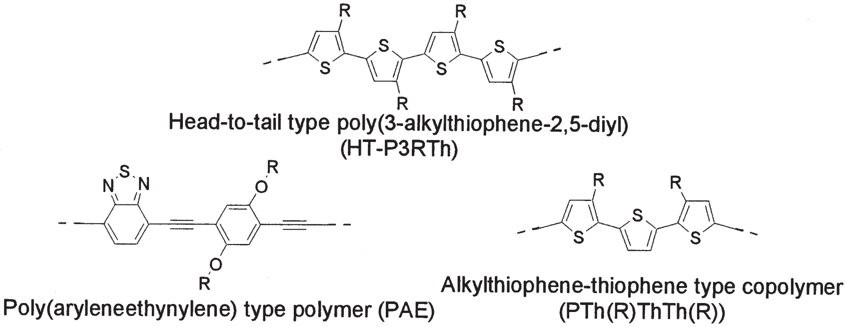

SCHEME 1 Example of π-conjugated polymers, which show parallel alignment of the main chain with the side R chains oriented toward the substrate.

field-effect transistors (FET) can be achieved by control of molecular alignment of the π-conjugated film on the substrate [4,12,13]. Head-to-tail-type poly(3-alkylthiophene-2,5-diyl) [14–16], HT-P3RTh (cf. Scheme 1), and its p-doped (or oxidized) molecule show a strong tendency to be aligned in cast films formed on the substrate [4,17,18], with the side alkyl chains oriented toward the surface of the substrate. In this film, the π-conjugated main chain is ordered in parallel to the surface of the substrate.

Such alignment can take place with other (π-conjugated polymers and various substrates, and the following poly(aryleneethynylene)-type polymer, PAE [17,19], and alkylthiophene-thiophene-type copolymer, PTh(R)ThTh(R) (cf. Scheme 1) [20], also form similar aligned structures on substrates. On the other hand, poly(thiophene-2,5-diyl) without the alkyl side chain stands upright on the substrates to show a perpendicular alignment of the main chain [21–23], The parallel alignment of the polymers with the alkyl side chains toward the surface of the substrate may originate from a strong tendency for the alkyl group to be aligned perpendicularly on the substrates.

Previously, we found, based on X-ray diffraction (XRD) analysis, that n-alkanes (n-C_nH_{2n+2}, $n = 29$ or 30) in cast films were aligned essentially perpendicularly on various substrates [17,18]. To obtain more detailed information about the alignment of n-alkanes, we have investigated the molecular alignment by expanding the kind of n-alkanes and by using films obtained by a vacuum-deposition technique, and herein report the results.

It is known that (n-C_nH_{2n+2}) assume the following three types of crystal systems, depending on n, in a single crystal [24,25]:

1. Orthorhombic: for $n =$ even numbers ($n \geq 36$) and all odd numbers.
2. Triclinic: for $n =$ even numbers ($6 \leq n \leq 26$).
3. Monoclinic: for $n =$ even numbers ($26 \leq n \leq 38$).

Based on the results obtained with *n*-alkanes, molecular alignment of HT-P3HexTh (R = hexyl) will also be discussed. Molecular alignment of *n*-alkanes has been the subject of many papers [26–34]. Vacuum-deposited *n*-alkanes usually stand up on substrates; however, long *n*-alkanes sometimes lie on the surface of substrate [33,34].

EXPERIMENTAL

n-$C_{30}H_{62}$ (triacontane, monoclinic) and *n*-$C_{29}H_{60}$ (nonacosane, orthorhombic) were purchased from Tokyo Kasei Kogyo Co., Ltd. *n*-$C_{24}H_{50}$ (tetracosane, triclinic) and *n*-$C_{23}H_{48}$ (tricosane, orthorhombic) were purchased from Aldrich Chemical Company, Inc. HT-P3HexTh [15] (R = hexyl) was purchased from Rieke Metals, Inc. A chloroform-soluble part of HT-P3HexTh was used for preparation of the cast films. Substrates were used without special cleaning and polishing. Cast films were prepared by dropping chloroform solutions of *n*-alkane and HT-P3HexTh on a glass substrate and on a Pt substrate, respectively. Chloroform was removed by natural evaporation. XRD patterns were recorded on a RINT 2100 Ultima+/PC X-ray diffractometer. The X-ray was irradiated from the out-of-plane direction, and the XRD pattern was measured under the symmetrical reflection mode. Vacuum deposition of *n*-alkanes was carried out by using ULVAC EBV-6DA under 10^{-6} Torr. Thicknesses of vacuum-deposited films were monitored with a quartz microbalance (ULVAC CRTM-1A). Vacuum deposition was carried out at a rate of 60 Å min^{-1}. Thickness of the cast film was measured by using a DEKTAK3ST surface-profile measuring system.

RESULTS AND DISCUSSION

Cast Film of *n*-Alkane

Figure 1 compares XRD patterns of a powder (Figure la), cast film (Figure lb), and vacuum-deposited films (Figure 1c and 1d) of *n*-$C_{30}H_{62}$. Although the powder XRD pattern of *n*-$C_{30}H_{62}$ shows strong peaks assigned to (00*l*), (111), (110), and (020) planes, the XRD pattern of the cast film gave only one set of peaks assigned to (00*l*) planes at $d = 35.2/n$ Å ($n = 1{-}8$) as depicted in Figure lb. The (111), (110), and (020) peaks disappeared. This indicates that the *n*-$C_{30}H_{62}$ molecules in

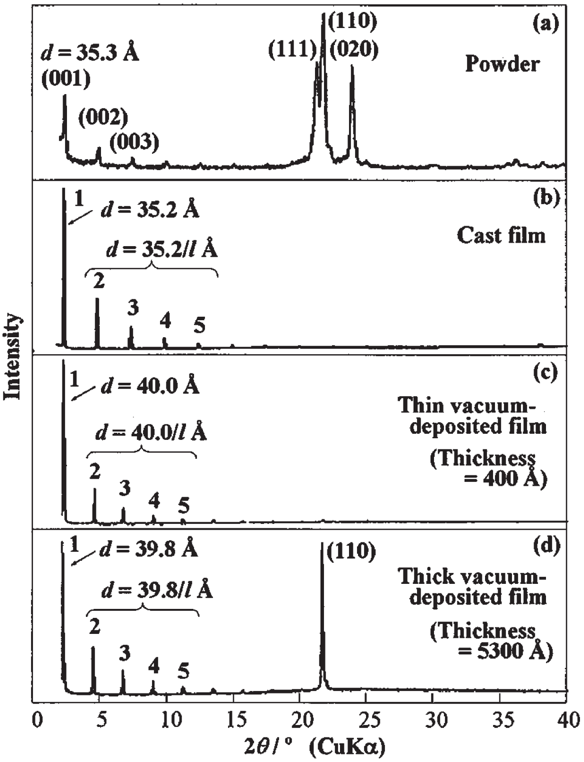

FIGURE 1 XRD patterns of triacontane (n-$C_{30}H_{62}$): (a) powder, (b) cast film, (c) thin vacuum-deposited film (thickness = 400 Å), and (d) thick vacuum-deposited film (thickness = 5300 Å) on a glass substrate.

the cast film are essentially perpendicularly aligned on the glass substrate. n-$C_{30}H_{62}$ has a repeting length of 40.71 Å [24]; however, XRD pattern of the cast film gave the peaks at 35.2 Å/l (l = 1, 2, 3, ...), indicating that the cast n-$C_{30}H_{62}$ molecules lean at an angle of 120° [$=\sin^{-1}$ (35.2/40.7)] on the substrate. The angle essentially agrees with the β value in a single crystal of n-$C_{30}H_{62}$ (cf. Figure 2a), suggesting that n-$C_{30}H_{62}$ molecules in the cast film are packed in a manner similar to that in the single crystal. Cast films of n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, and n-$C_{29}H_{60}$ gave analogous results, and examples of the obtained XRD patterns are shown in part (b) of Figures 3–5. In Figures 3b and 4b, small [(110) and (010)] peaks are obtained, respectively, and these peaks are considered to be due to partly formed microcrystals of the n-alkanes. The obtained results are summarized in the second row in Figure 2 and the third column of Table I.

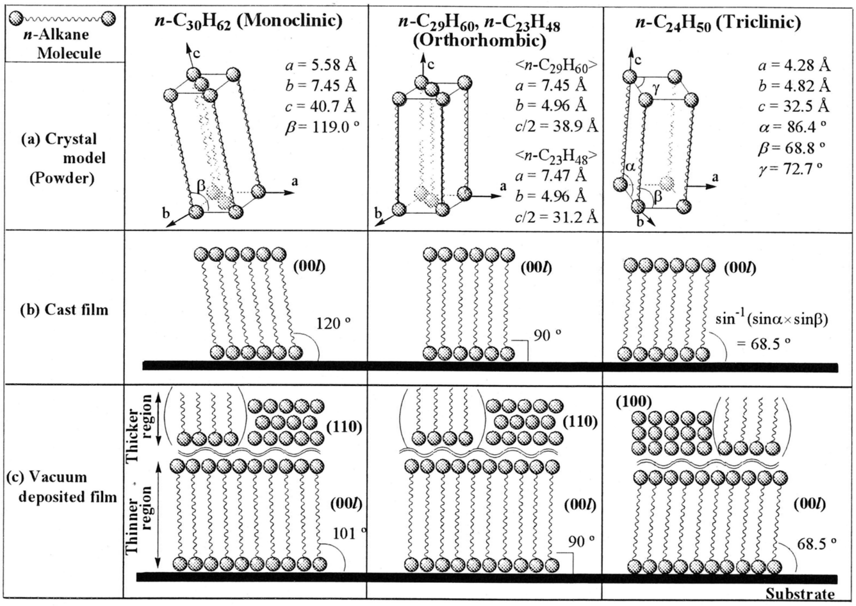

FIGURE 2 Plausible structural models of n-alkanes on the substrate: (a) crystal (powder), (b) cast film, and (c) vacuum-deposited film. Crystal data were referred to ref. [24].

n-$C_{23}H_{48}$ and n-$C_{29}H_{60}$ molecules stood upright on a glass substrate, and n-$C_{24}H_{50}$ molecules tilted, in agreement with their single crystal structures.

Vacuum-Deposited Films of *n*-Alkane

Figures 1c and 1d exhibit XRD patterns of vacuum-deposited films of n-$C_{30}H_{62}$. When the thickness of the film was thin (ca. 400 Å), the XRD pattern shows only peaks assigned to the (00l) planes. The observed d value of vacuum-deposited n-$C_{30}H_{62}$ film, 40.0 Å/l (l = 1, 2, 3, …) was longer than that observed with the cast film ($d = 35.2$ Å), indicating that n-$C_{30}H_{62}$ molecules are inclined at 101° [$=\sin^{-1}$ (40.0/40.7)] and the vacuum-deposited n-$C_{30}H_{62}$ molecules were packed in a way different from that in the single crystal.

On the contrary, vacuum-deposited n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, and n-$C_{29}H_{60}$ molecules in thin film were aligned on the glass substrate without changing their crystal systems from those of single crystals; examples of the XRD patterns are given in parts (c) and (d) in Figures

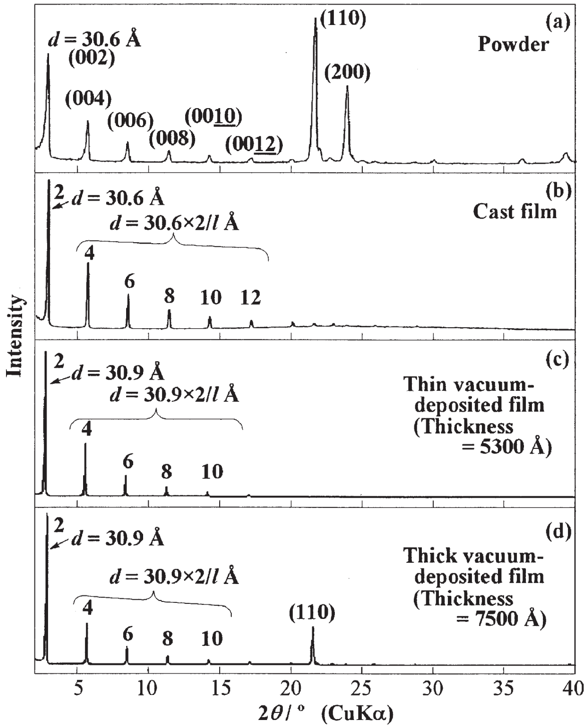

FIGURE 3 XRD patterns of tricosane (n-$C_{23}H_{48}$): (a) powder, (b) cast film, (c) thin vacuum-deposited film (thickness = 5300 Å), and (d) thick vacuum-deposited film (thickness = 7500 Å) on a glass substrate.

3–5. These results are summarized in the third row in Figure 2 and the third column in Table I.

Use of other substrates, such as Pt plate, Au plate, various crystalline Al_2O_3 plates, stainless steel plate, mica plate, and Si zero-background sample plate, gave essentially the same results for the vacuum-deposited thin films of n-$C_{23}H_{48}$, n-$C_{24}H_{50}$, n-$C_{29}H_{60}$ and n-$C_{30}H_{62}$.

XRD patterns of thicker (ca. 5300 Å) vacuum-deposited films of n-$C_{30}H_{62}$ exhibited peaks not only from the (00l) planes but also from the (110) plane, as exemplified in Figure 1d. These data suggest that the n-alkane molecules in the upper layer of the vacuum-deposited film are stacked in parallel to the surface of the substrate as depicted in the part (c) of Figure 2. Thicker vacuum-deposited films of n-$C_{23}H_{48}$ and n-$C_{29}H_{60}$ also showed a (110) XRD peak in addition to the (00l) peaks. However, a thicker vacuum-deposited film of n-$C_{24}H_{50}$

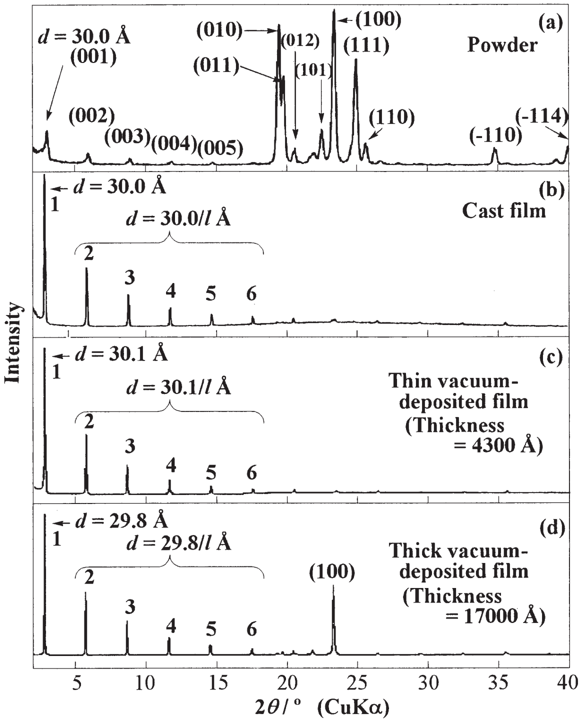

FIGURE 4 XRD patterns of tetracosane (n-$C_{24}H_{50}$): (a) powder, (b) cast film, (c) thin vacuum-deposited film (thickness = 4300 Å), and (d) thick vacuum-deposited film (thickness = 17,000 Å) on a glass substrate.

exhibited an XRD peak assigned to a (100) peak (Figure 4), revealing that the direction of the orientation of the n-alkane molecules in the upper layer was controlled by a delicate difference in the structure of n-alkane. XRD data of the thick vacuum-deposited films are also given in Table I (cf. the footnote b).

As described, the vacuum-deposited n-alkane molecules have a tendency to be aligned perpendicularly on the surface of the substrates. The driving force for the alignment is not clear; however, it has been reported, based on molecular dynamics, that n-alkane have a trend to gather together with their terminal CH_3 groups located outside of the molecular assembly [35–37], In addition, it is known that parallel and perpendicular alignment of long molecules on substrates are controlled by delicate conditions on the substrate [38]. These results indicate that the parallel alignment of HT-P3RTh main chain toward the surface of the substrate is, at least partly, impelled by the

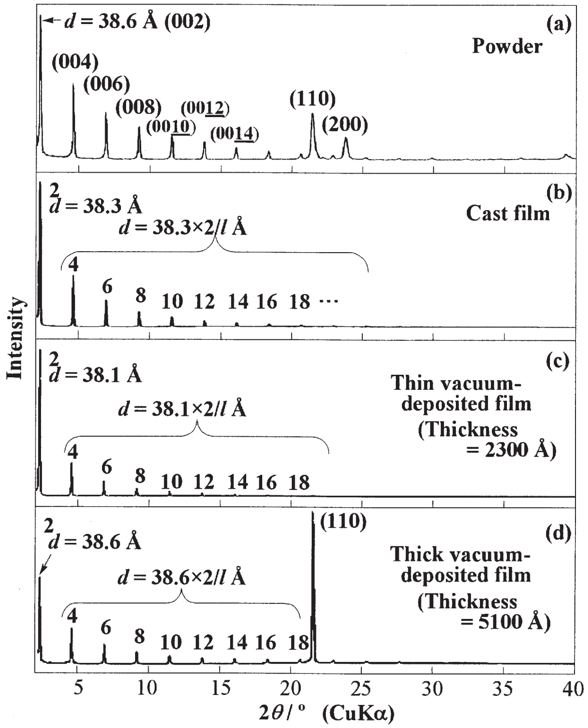

FIGURE 5 XRD patterns of nonacosane (n-$C_{29}H_{60}$): (a) powder, (b) cast film, (c) thin vacuum-deposited film (thickness = 2300 Å), and (d) thick vacuum-deposited film (thickness = 5100 Å) on a glass substrate.

tendency for the alkyl side chains to align on the surface of the substrate.

Mixed *n*-Alkane System

Casting of a chloroform solution containing two kinds of n-alkanes (in 9:1, 7:3, 5:5, 3:7, and 1:9 molar ratios) on the glass substrate also gave a film. All the XRD patterns of the "binary" n-alkane films gave peaks assigned to the ($00l$) planes, and the peaks assigned to the (hkl) planes were not detected in the region of $2\theta = 20$–$25°$. These results indicate that the n-alkane molecules in the film also stood on the substrate. Examples of the XRD pattern are exhibited in Figures 6–8, and XRD data are summarized in Tables II–IV. In the low-angle region, three kinds of peaks were observed: namely (i) peaks from the ($00l$) planes of the n-alkane (n-C_xH_{2x+2}) with a longer molecular length, (ii) peaks from ($00l$) planes of the n-alkane (n-C_yH_{2y+2}) with a shorter

TABLE I Crystal and Obtained XRD Data of n-alkanes (n-C_nH_{2n+2}; $n = 30, 29, 24,$ and 23) at room temperature

Single crystal data at 23°C [24]	Powder		Cast film		Vacuum-deposited film	
	d/Å	(hkl)	d/Å	(hkl)	d/Å	(hkl)
n-$C_{30}H_{62}$ (triacontane)						
Monoclinic, $P2_1/a$	$(35.49)^a$	(001)	$(35.38)^a$	(001)	$(40.04)^a$	(001)
$a = 5.58$ Å	4.08	(110)			$[4.13]^b$	(110)
$b = 7.45$ Å $\beta = 119°$	3.72	(020)				
$c = 40.7$ Å						
n-$C_{29}H_{60}$ (nonacosane)						
Orthorhombic, Pbcm	$(38.78)^a$	(002)	$(38.66)^a$	(002)	$(38.72)^a$	(002)
$a = 7.45$ Å	4.13	(110)			$[4.13]^b$	(110)
$b = 4.96$ Å	3.73	(200)				
$c = 77.7$ Å						
n-$C_{24}H_{50}$ (tetracosane)						
Triclinic, $P\bar{1}$	$(30.27)^a$	(001)	$(30.26)^a$	(001)	$(30.27)^a$	(001)
$a = 4.28$ Å $\alpha = 86.4°$	4.58	(010)				
$b = 4.82$ Å $\beta = 68.8°$	3.81	(100)			$[3.81]^b$	(100)
$c = 32.5$ Å $\gamma = 72.7°$						
n-$C_{23}H_{48}$ (tricosane)						
Orthorhombic, Pbcm	$(30.85)^a$	(002)	$(30.85)^a$	(002)	$(30.92)^a$	(001)
$a = 7.47$ Å	4.12	(110)			$[4.13]^b$	(110)
$b = 4.96$ Å	3.72	(200)				
$c = 62.4$Å						

[a] From the (00l) peaks with d_l the d spacing of the original peak ($d = d_l \times l$) was evaluated. The d spacings calculated from the (00l) peaks ($l = 1, 2, \ldots$) were averaged to give the value given in the parentheses.

[b] Data of additionally observed peak for the upper layer of the thicker film (cf. the text).

molecular length, and (iii) peaks from (00l) planes of a newly formed crystal system from the binary n-alkanes. Many articles have been published about crystalline phases formed with a binary mixture of n-alkanes [39–43]. In the reported studies, the binary system was gradually cooled after heating to melting point to yield new crystalline phases. However, to our knowledge, formation of such molecularly aligned crystalline film structures of n-alkane by casting the solution containing two kinds of n-alkanes has not been reported.

Effect of Thickness of Film on the Molecular Alignment of HT-P3HexTh

Figure 9a shows XRD patterns of powdery HT-P3HexTh. As shown in Figure 9a, the XRD pattern of HT-P3HexTh gives a sharp 100 peak at

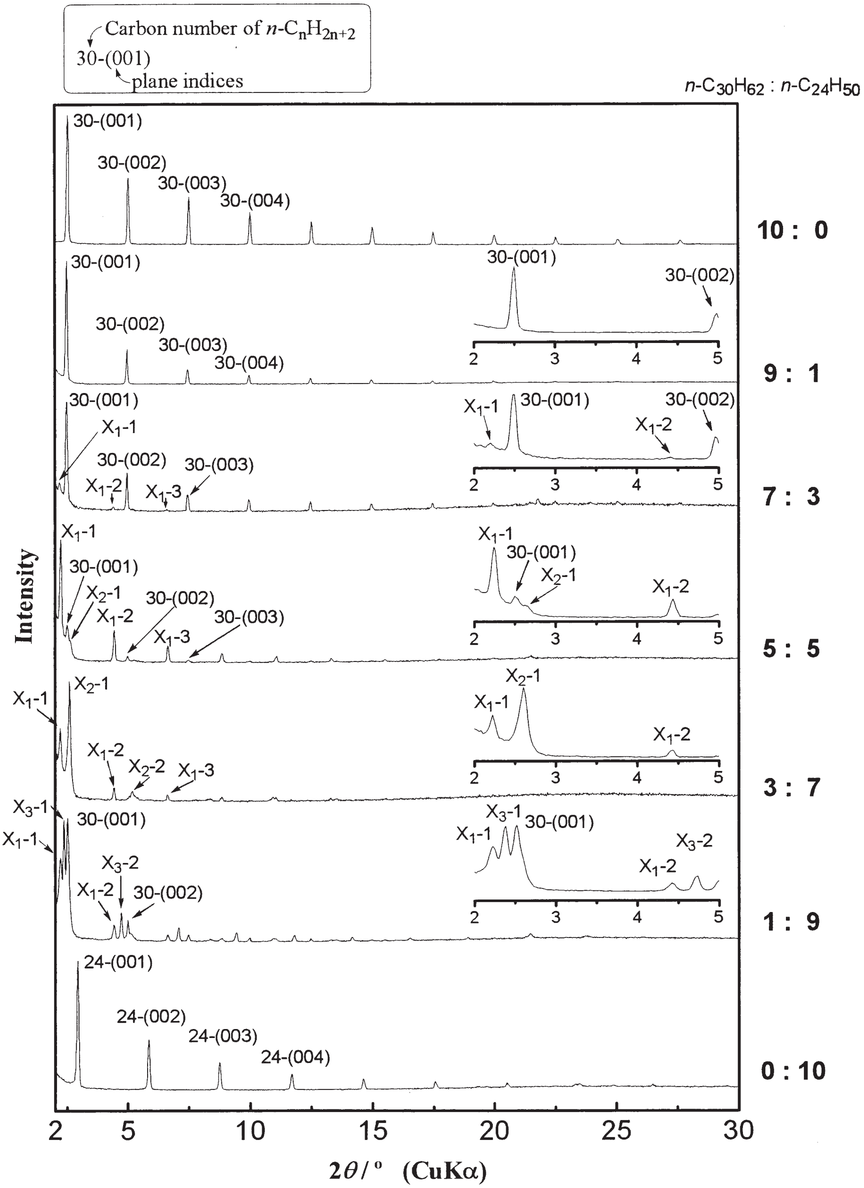

FIGURE 6 XRD patterns of film of binary mixed n-alkane system (n-$C_{30}H_{62}$) and (n-$C_{24}H_{50}$) on a glass plate. The inset shows the XRD pattern in the low-angle region. Mixed n-alkanes (n-$C_{30}H_{62}$ and n-$C_{24}H_{50}$) were dissolved in chloroform, and the mixed n-alkane solution was dropped on a glass plate. Chloroform was removed by natural evaporation. The peaks assigned to a new crystalline phase are described as X-l ($l = 1 - 4$).

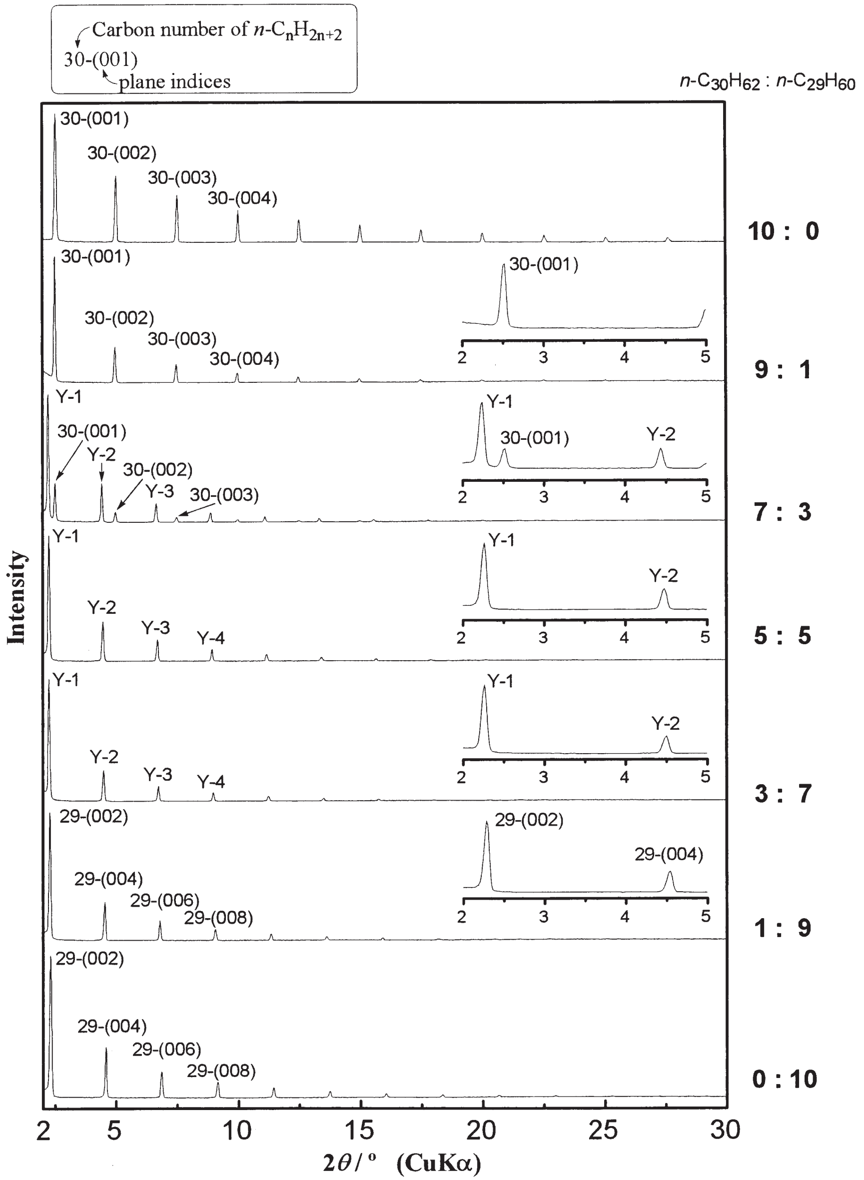

FIGURE 7 XRD patterns of film of binary mixed n-alkane system (n-$C_{30}H_{62}$ and n-$C_{29}H_{60}$) on a glass plate. The inset shows the XRD pattern in the low-angle region. The peaks assigned to a new crystalline phase are described as Y-l ($l = 1 - 4$).

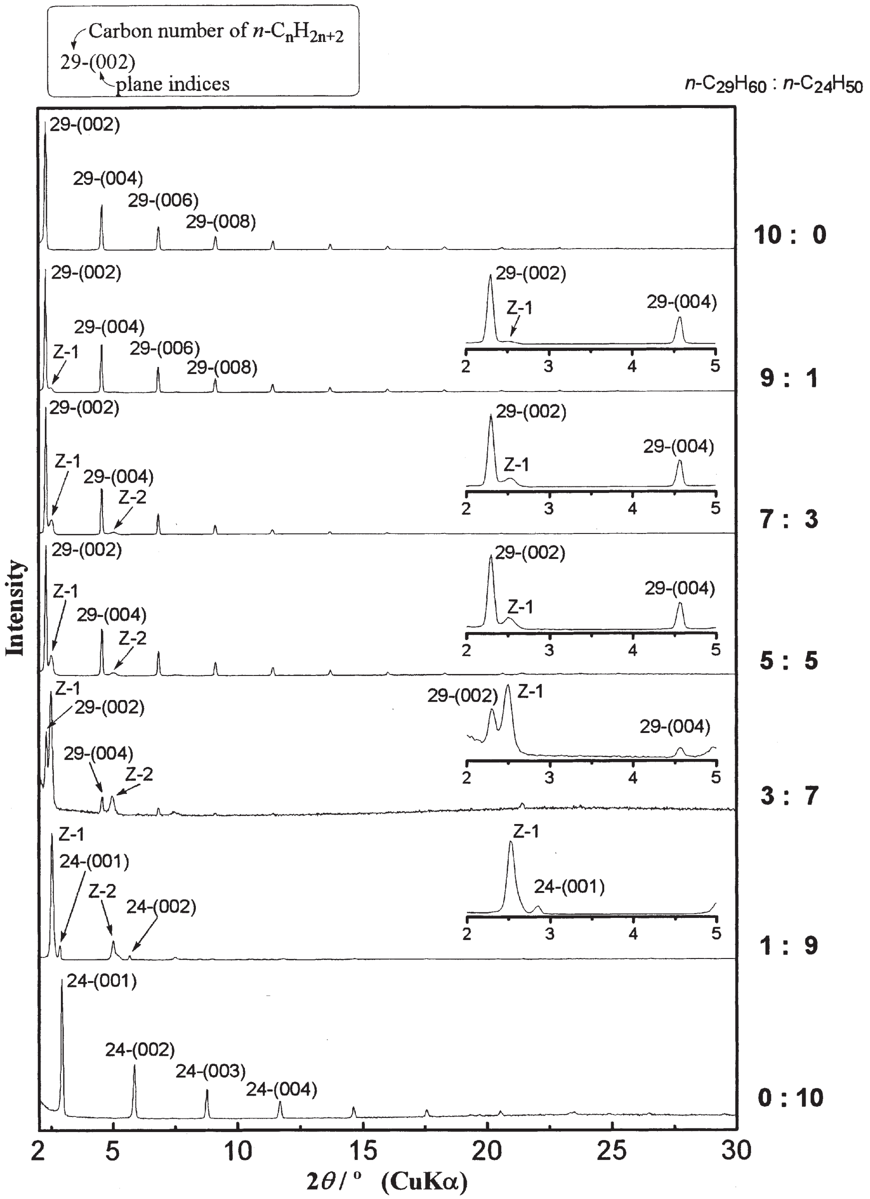

FIGURE 8 XRD patterns of film of binary mixed n-alkane system (n-$C_{29}H_{60}$ and n-$C_{24}H_{50}$) on a glass plate. The inset shows the XRD pattern in the low-angle region. The peaks assigned to a new crystalline phase are described as Z-l ($l = 1 - 4$).

TABLE II XRD Data for Films Obtained by Casting Chloroform Solutions Containing *n*-$C_{30}H_{62}$ and *n*-$C_{24}H_{50}$ ($2^\circ \leq 2\theta \leq 10^\circ$)

$C_{30}H_{62}/C_{24}H_{50}^{a}$	$2\theta/^\circ$(CuKα)	d/Å	Assignment[b]
9/1	2.50	35.4	30-(001)
	4.98	17.7	30-(002)
	7.47	11.8	30-(003)
	9.96	8.88	30-(004)
7/3	2.22	39.8	X_1-1
	2.50	35.3	30-(001)
	4.42	20.0	X_1-2
	4.98	17.7	30-(002)
	6.64	13.3	X_1-3
	7.48	11.8	30-(003)
	9.96	8.87	30-(004)
5/5	2.24	39.4	X_1-1
	2.50	35.3	30-(001)
	4.44	19.9	X_1-2
	4.98	17.7	30-(002)
	6.64	13.3	X_1-3
	7.48	11.8	30-(003)
	8.86	9.98	X_1-4
	9.98	8.86	30-(004)
3/7	2.22	39.8	X_1-1
	2.60	33.9	X_2-1
	4.43	19.9	X_1-1
	5.18	17.1	X_2-2
	6.62	13.3	X_1-3
	8.36	10.6	X_2-3
	8.84	9.99	X_1-4
1/9	2.21	39.7	X_1-1
	2.38	37.1	X_3-1
	2.52	35.0	30-(001)
	4.42	20.0	X_1-2
	4.73	18.7	X_3-2
	5.00	17.7	30-(002)
	6.64	13.3	X_1-3
	7.07	12.5	X_3-3
	7.45	11.8	30-(003)
	8.85	9.98	X_1-4
	9.44	9.36	X_3-4
	9.97	8.86	30-(004)

[a] The molar ratio of *n*-alkane in the solution used for film preparation. Cast from chloroform.

[b] The peak assigned for (001) plane of *n*-$C_{30}H_{62}$ is described as 30-(001). (00*l*) diffraction peak of new crystal phase are described as X-*l*. Three new crystalline phases were observed in this study.

TABLE III XRD Data for Films Obtained by Casting Chloroform Solutions Containing n-$C_{30}H_{62}$ and n-$C_{29}H_{60}$ ($2^\circ \leq 2\theta \leq 10^\circ$)

$C_{30}H_{62}/C_{29}H_{60}$[a]	$2\theta/^\circ$ (CuKα)	d/Å	Assignment[b]
9/1	2.51	35.1	30-(001)
	4.99	17.7	30-(002)
	7.48	11.8	30-(003)
	9.97	8.86	30-(004)
7/3	2.23	39.5	Y-1
	2.51	35.1	30-(001)
	4.44	19.9	Y-2
	5.00	17.7	30-(002)
	6.66	13.3	Y-3
	7.48	11.8	30-(003)
	8.87	9.97	Y-4
	9.98	8.86	30-(004)
3/7	2.26	39.1	Y-1
	4.48	19.7	Y-2
	6.70	13.2	Y-3
	8.93	9.89	Y-4
5/5	2.26	39.1	Y-1
	4.50	19.6	Y-2
	6.74	13.1	Y-3
	8.98	9.84	Y-4
1/9	2.28	38.7	29-(002)
	4.53	19.5	29-(004)
	6.80	13.0	29-(006)
	9.06	9.75	29-(008)

[a] The molar ratio of n-alkane in the solution used for film preparation. Cast from chloroform.

[b] The peak assigned for (001) plane of n-$C_{30}H_{62}$ is described as 30-(001).(00l) diffraction peak of new crystalline phase is described as Y-l.

$d_1 = 16.1$ Å in a low-angle region and a 010 broad peak at about $d_2 = 3.8$ Å. The former peak is assigned to a distance between polythiophene main chains separated by the hexyl groups, and the latter to a face-to-face stacking distance between the P3HexTh planes [4,14,16].

The XRD pattern of a thin cast film of HT-P3HexTh (thickness ≈ 0.1 μm) showed only the (100), (200), and (300) peaks, and the (010) peak disappeared as exhibited in Figure 9b. This has been taken as an indication that HT-P3HexTh molecules are well aligned on the Pt substrate with the hexyl group oriented toward the surface of the Pt plate [4,14,17,18].

The XRD pattern of a thick cast film of HT-P3HexTh (thickness ≈ 1 μm), on the contrary, gave both the (100) and (010)

TABLE IV XRD Data for Films Obtained by Casting Chloroform Solutions Containing n-$C_{29}H_{60}$ and n-$C_{24}H_{50}$ ($2^\circ \leq 2\theta \leq 10^\circ$)

$C_{29}H_{60}/C_{24}H_{50}$[a]	$2\theta/^\circ$(CuKα)	d/Å	Assignment[b]
9/1	2.30	38.4	29-(002)
	2.51	35.2	Z-l
	4.56	19.4	29-(004)
	4.98	17.7	Z-2
	6.84	12.9	29-(006)
	9.13	9.68	29-(008)
7/3	2.30	38.4	29-(002)
	2.52	35.0	Z-1
	4.56	19.4	29-(004)
	5.04	17.5	Z-2
	6.84	12.9	29-(009)
	9.12	9.69	29-(008)
5/5	2.30	38.4	29-(002)
	2.50	35.3	Z-1
5/5	4.57	19.3	29-(004)
	5.02	17.6	Z-2
	6.84	12.9	29-(006)
	9.12	9.68	29-(008)
3/7	2.29	38.5	29-(002)
	2.49	35.5	Z-1
	4.56	19.4	29-(004)
	4.96	17.8	Z-2
1/9	2.53	34.9	Z-1
	2.84	31.1	24-(001)
	5.00	17.7	Z-2
	5.67	15.6	24-(002)
	7.50	11.8	Z-3

[a] The molar ratio of n-alkane in the solution used for film preparation. Cast from chloroform.

[b] The peak assigned for (002) plane of n-$C_{29}H_{60}$ is described as 29-(002). (00l) diffraction peak of a new crystalline phase is described as Z-l.

peaks as exhibited in Figure 9c. In the upper layer of the thick film of HT-P3HexTh, the polymer molecules do not seem to assume the highly aligned structure. Similar to the case of thick vacuum-deposited film of n-alkanes, HT-P3HexTh molecules in the upper layer may lie on the lower aligned layer. This behavior of HT-P3RTh has not been reported to our knowledge.

As described, cast and vacuum-deposited films of n-alkanes assume crystalline and oriented film on various substrates. The n-alkane molecules in the cast film were perpendicularly aligned on the

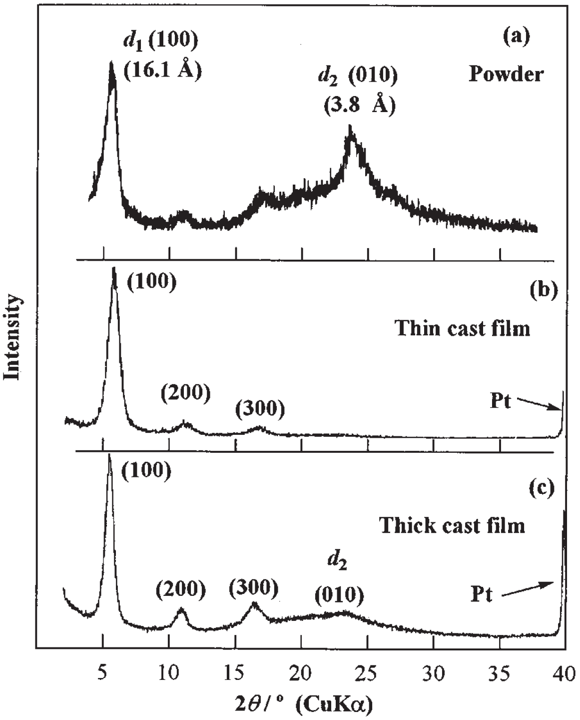

FIGURE 9 XRD patterns of HT-P3HexTh: (a) powder, (b) thin cast film on a Pt substrate (thickness ≈ 0.1 μm), and (c) thick cast film on a Pt substrate (thickness ≈ 1 μm).

substrate. These results suggest that the alignment of HT-P3RTh on the substrate is impelled by the inclination for the alkyl side chains to align perpendicularly on the substrate. XRD patterns of thick vacuum-deposited film of *n*-alkanes exhibited that *n*-alkane molecules had a tendency to lie on the perpendicularly aligned molecules. Similar phenomena were also observed for HT-P3HexTh.

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