Polymer 40 (1999) 5939–5945

Structure and liquid crystallinity of the comb-like complexes made of poly(ethylene imine) and some aliphatic carboxylic acids

T. Takahashi*, T. Kimura, K. Sakurai

Faculty of Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910-8507, Japan

Received 5 September 1996; received in revised form 9 September 1998; accepted 9 November 1998

Abstract

The present investigation deals with the comb-like complexes made of poly(ethylene imine) (PEI) and stearic acid (SA) or oleic acid (OA). On cooling the mixture of dimethylformamide solutions of PEI and carboxylic acid to room temperature, the corresponding complexes were phase-separated and precipitated. Structures and liquid crystallinity of the PEI–OA and PEI–SA complexes were studied by means of various techniques. It was confirmed by infrared spectroscopy studies that the carboxylic acid molecules are linked by ionic bonds to form the comb-like complexes. The complexes give a narrow peak at $2\theta = 2°–3°$ in their wide-angle X-ray diffractograms, indicating that the side aliphatic chains are packed in layer structure with a spacing of 3.2–4.4 nm. In spite of the rather weak secondary valence force between an imine group of PEI and a carboxylic end group, the layer structures of the complexes are maintained even at the temperatures above the melting point of the side chains. Both of the comb-like complexes form optically positive spherulitic textures from the melt, indicating that the layer structures are oriented concentrically and consequently side aliphatic chains are oriented in a radial direction. Concentric arrangement of the layer structure is characteristic of the smectic-type liquid crystal. These results suggest the liquid crystallinity of the comb-like complexes are made of PEI and carboxylic acid. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Comb-like complexes; Poly(ethylene imine) based complex; Smectic-type liquid crystal

1. Introduction

The family of comb-like polymers carrying only alkyl side-chains, such as poly(α-olefins), poly(*n*-alkyl acrylates), poly(vinyl-*n*-alkyl esters), and poly(vinyl-*n*-alkyl ethers) were studied in earlier works [1]. It was shown that these polymers are usually not liquid crystalline. In recent years, another family of comb-like polymers carrying a mesogenic side group attached to the backbone chain via a flexible spacer has aroused interest because of its liquid-crystalline behaviour. The structures, properties and applications of a great number of the comb-like liquid crystalline polymers were investigated by many worker [2–5].

We reported in the previous paper that the comb-like complexes could be obtained by mixing the dimethylformamide (DMF) solutions of poly(ethylene imine) (PEI) and octyloxybenzoic acid (OOBA) or cholesterol hydrogen succinate (CHS) [6]. We proposed that the interaction between an imine group of PEI and a carboxylic end group of OOBA and CLIA contribute to the formation of the comb-like complexes. X-ray diffraction studies showed that the OOBA or CHA groups are packed in the layer structure, where side groups are arranged in parallel at right angle to a PEI-containing plane.

Recently, the liquid-crystalline comb-like complexes built by noncovalent interaction were studied by some workers. Antonietti synthesized some polyelectrolyte–surfactant complexes made of poly(styrenesulfonate) and different alkyltrimethyl-ammonium derivatives by precipitation in water [7]. It was confirmed by X-ray diffraction studies that the cast films of these complexes exhibit highly ordered mesomorphous phases. Kato et al. and Bazuin et al. have obtained the supramolecular hydrogen-bonded or ionic-bonded liquid crystalline comb-like complexes [8–11].

The present investigation deals with the comb-like complexes made of PEI and some aliphatic carboxylic acids formed by precipitation in DMF. The structure and liquid crystallinity of the comb-like complexes were studied by infrared absorption spectroscopy (IR), wide-angle X-ray diffractometry (WAXD), DSC and polarized optical microscopy (POM). It was found that these complexes exhibit mesomorphous phases. In spite of the rather weak secondary valence force between an imine group of PEI and a

---

* Corresponding author. Tel.: + 81776-27-8616; fax: + 81776-27-8767.

E-mail address: d930753@icpc00.icpc.fukui-u.ac.jp (T. Takahashi)

PII: S0032-3861(98)00797-6

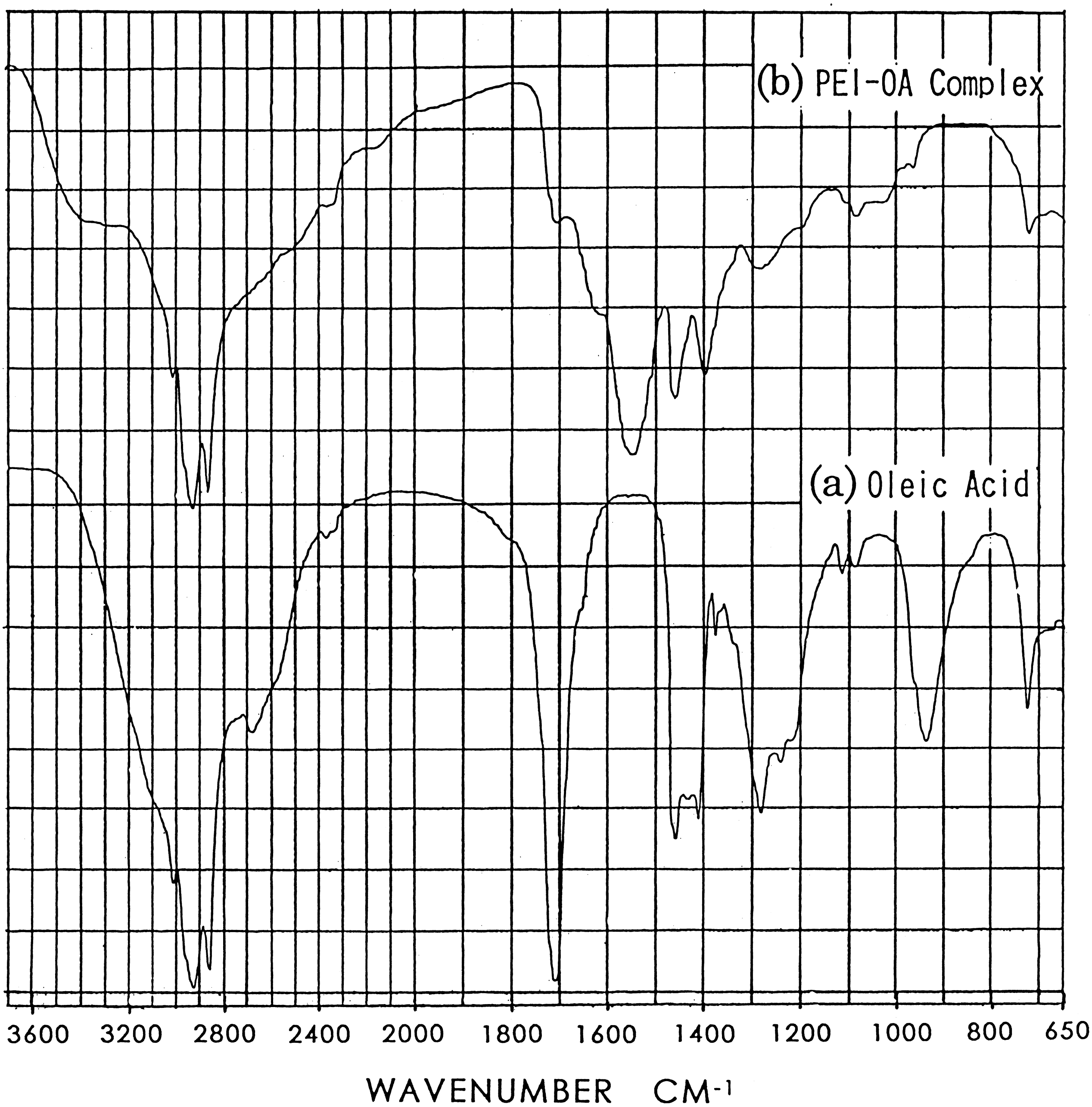


Fig. 1. Infrared absorption spectra of oleic acid and the corresponding poly(ethylene imine)-oleic acid complex (PEI-OA complex).

carboxylic acid, the layer structures of the complexes with a spacing of 3.2–4.4 nm are maintained even at temperatures above the melting point of the side chains.

2. Experimental

2.1. Materials

An aqueous 30% solution of branched PEI (Mw 40 000–50 000, mole ratio of primary/secondary/tertiary amines ≈ 1/2/1) was obtained from Tokyo Kasei Co. Ltd. Commercially available stearic acid (SA), oleic acid (OA) and DMF were used without further purification.

2.2. Preparation of the complexes [6]

An aqueous 30% solution of PEI was diluted with DMF to obtain a 1 wt.% solution. The resultant DMF solution of PEI containing 2% water was added to a 9% solution of carboxylic acid (SA or OA) in DMF at 60°C with stirring. Upon cooling the mixture of DMF solutions of PEI and carboxylic acid to room temperature, the corresponding complexes precipitated. The complexes were filtered,

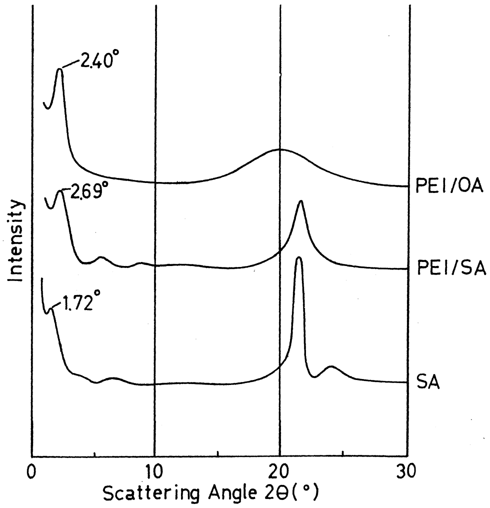


Fig. 2. Wide-angle X-ray diffraction (WAXD) intensity curves of stearic and poly(ethylene imine) (PEI) based complexes. WAXD measurements were carried out at room temperature. SA: stearic: acid, PEI/SA: PEI–SA complex, PEI/OA: PEI–oleic acid (OA) complex.

washed with cold DMF, and dried in vacuo. The present paper deals only with the complexes obtained from the starting mixture of a ethylene imine unit (EI)/SA (or OA) mole ratio of 1.0/1.0.

2.3. Measurements

IR absorption spectra of OA the corresponding PEI-OA complex were obtained with a Shimadzu spectrometer, IR-400, interposing the sample between two NaCl single-crystal plates. WAXD studies were carried out with a Rigaku–Denki diffractometer and a Toshiba model X4-40H generator equipped with a flat-plate camera. The X-ray source was nickel-filtered CuK$_\alpha$ radiation. A Rigaku–Denki DSC apparatus (Type 8001) was used for differential thermal analysis. Observations by a polarized microscope were performed using an Olympus POM microscope.

3. Results and discussion

3.1. Interaction between PEI and carboxylic acid (IR studies)

Upon cooling the mixture of DMF solutions of PEI and a carboxylic acid to room temperature, the corresponding complex precipitated at the bottom of the flask. The complexes made of PEI and SA or OA will hereafter be abbreviated as PEI–SA or PEI–OA complex, respectively. The PEI–SA complex is a crystalline solid, while the PEI–OA complex is an opaque paste-like substance.

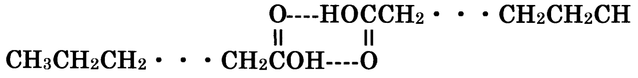
The EI/carboxylic acid mole ratio of the complex can be evaluated from the weight of the reaction products by assuming that all PEI molecules are incorporated in the resulting complex. The starting mixture of the EI/SA mole ratio of 1.0/1.0 gave the PEI–SA complex with a EI/SA mole ratio of 1.00/0.8, suggesting that all of the primary and secondary amines of PEI take part in the formation of the complex. The exact EI/OA mole ratio of the PEI-OA complex obtained from the starting mixture with the EI/OA mole ratio of 1.0/1.0 could not be evaluated, because the PEI–OA complex is a paste-like substance. However, it seems reasonable to assume that the similar interaction occurs between PEI and OA during complexation.

The IR absorption spectra of OA and the corresponding PEI–OA complex were obtained to elucidate the interaction between the carboxylic end group and the imine group of PEI. The results are shown in Fig. 1. The IR absorption spectrum of pure PEI could not be obtained, because PEI was unstable when allowed to stand in contact with the atmosphere. Fig. 1 reveals that the characteristic absorption bands of OA substantially change upon complexation with PEI.

The IR spectrum of PEI–OA complex is characterized as follows:

1. The strong C=O stretching vibration ($\nu_{C=O}$) of the associated two COOH groups at 1710 cm^{-1} becomes very weak.
2. The out-of-plane bending vibration of the OH group (δ_{OH}) at 935 cm^{-1} disappears and the in-plane-bending vibration of the OH group (δ_{OH}) at 1280 cm^{-1} becomes weak.
3. The broad absorption originating from the NH bending vibration (δ_{NH}) of $> NH_2^+$, $-NH_3^+$, $>$ NH and the C=O stretching vibration ($\nu_{C=O}$) of COO$^-$ appears at 1552 cm^{-1}.

It is well known that two carboxylic acids associate to form the following molecular aggregate:



$$\begin{array}{rl} & \mathrm{O\text{----}HOCCH_2\cdots CH_2CH_2CH} \\ & \;\|\qquad\quad\;\; \| \\ \mathrm{CH_3CH_2CH_2\cdots CH_2COH\text{----}O} & \end{array}$$

Results (1) and (2) indicate that the molecular aggregation of OA is destroyed upon complexation with PEI. Result (3) strongly supports the suggestion that each OA is linked by an ionic bond to an imine group of the backbone PEI.

3.2. Layer structure (X-ray studies)

Fig. 2 shows the WAXD intensity curves of SA, PEI–SA and PEI–OA complexes; measurements were carried out at room temperature. The WAXD intensity curves in Fig. 2 are characterized by a narrow diffraction peak at 2θ = 2°–3° with higher orders and a sharp diffraction peak or halo at

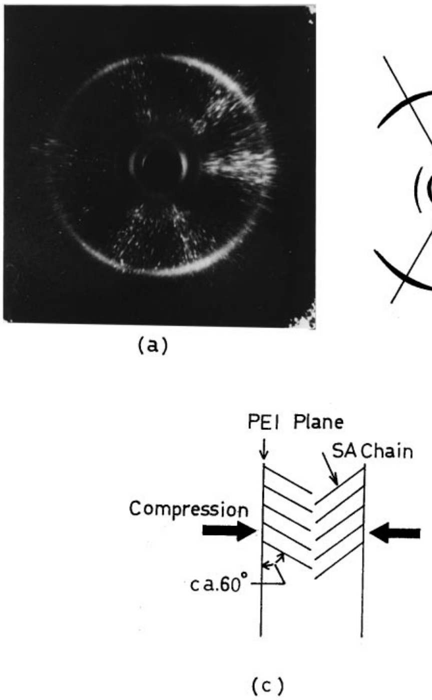


Fig. 3. Wide-angle X-ray diffraction pattern (Edge View) and a schematic representation of the layer structure of the rolled poly(ethylene imine) (PEI)–stearic acid (SA) complex.

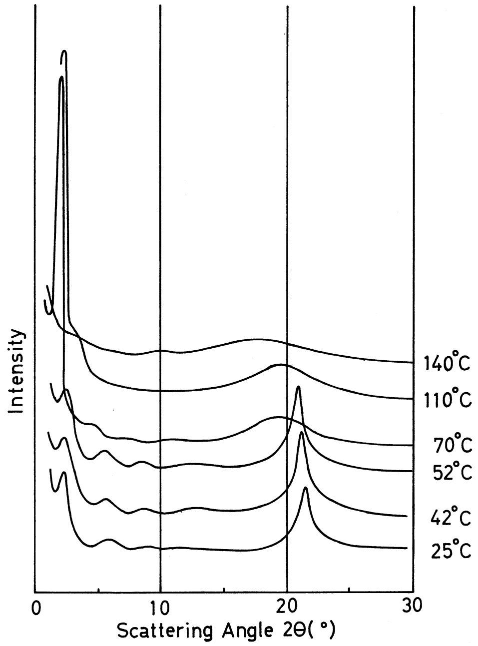


Fig. 4. Wide-angle X-ray diffraction (WAXD) intensity curves of the poly(ethylene imine)-stearic acid complex at the various temperatures. WAXD measurements were carried out over the temperature range of 25°C ~ 140°C.

$2\theta = 15°–25°$. Results are summarized as follows:

$[2\theta = 15°–27°]$	
PEI–SA complex	single peak at $2\theta = 21.7°$
PEI-OA complex	amorphous halo at $2\theta = \sim 20°$
SA	two peaks at $2\theta = 21.40$ and 24. 1°
Poly(vinyl stearate) [12]	single peak at $2\theta = \sim 21.6°$

$[2\theta = 1°–3°]$	
PEI–SA complex	narrow peak at $2\theta = 2.60°$ ($d = 3.38$ nm)
PEI-OA complex	narrow peak at $2\theta = 2.40°$ ($d = 3.68$ nm)
SA	narrow peak at $2\theta = 1.72°$ ($d = 5.11$ nm)
Poly(vinyl stearate) [12]	narrow peak at $2\theta = 1.68–1.78°$

($d = 4.96–5.25$ nm)

The above results indicate that the side SA chains of the PEI–SA complex and poly(vinyl stearate) (PVSt) are hexagonally packed in the layer structure giving a sharp diffraction peak at $2\theta = 21.7°$, while pure SA crystallizes in the orthorhombic form. On the other hand, the PEP OA complex gave a halo at $2\theta = -21.7°$. It is reasonable to assume that the side OA chains of the PEI-OA complex already melt at room temperature, because the melting temperature of OA crystal is 14°C.

A narrow peak of the comb-like complexes and the PVSt at $2\theta = 2°–3°$ arises from a layer structure of alternating alkane and backbone layers, whereas a narrow peak of SA at $2\theta = 1.72°$ arises from a double layer structure. It is interesting to note that the layer structure of the PEI-OA complex is still maintained even at temperatures above the melting point of the side OA chains [Tm^{OA}]. The complexes made of PEI and octyloxybenzoic acid or cholesterol succinate gave WAXD intensity curves similar to that of the PEI-OA complex [6].

We will discuss in detail the layer structure of the PEI–SA complex comparing it with that of SA and PVSt. The thickness of the layer structure will hereafter be abbreviated as T_{LS}. Both the melt-grown SA and PVSt have a layer structure with a T_{LS} of 5.1 nm, indicating that the extended

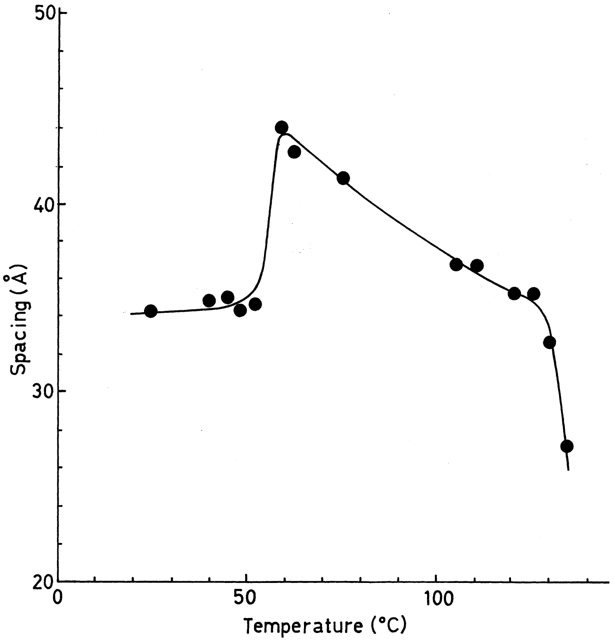


Fig. 5. Thickness of the layer structure of the poly(ethylene imine) stearic acid complex plotted versus temperature.

SA chains are oriented perpendicular to a layer plane. In contrast, the T_{LS} of the PEI–SA complex is moderately smaller than that of the SA and PVSt crystals. These observations support the suggestion that the side SA chains of the PEI–SA complex are not arranged at right angle to a layer plane.

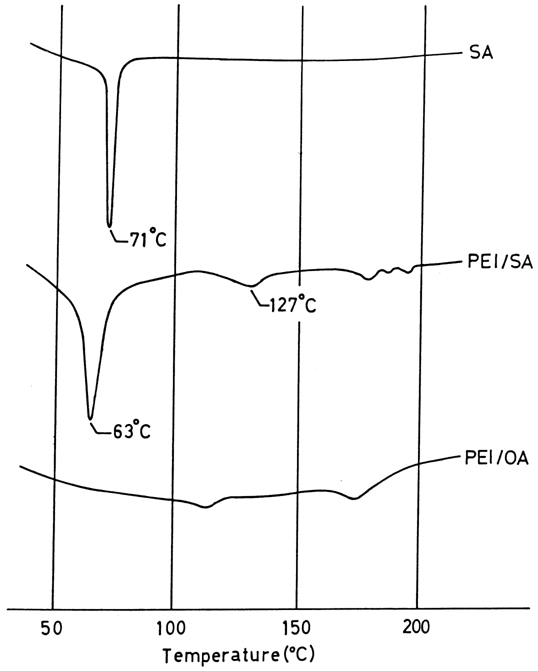


Fig. 6. DSC curves of stearic acid and poly(ethylene imine) (PEI) based complexes. SA: stearic acid, PEI/SA: PEI–SA complex, PEI/OA: PEI–oleic acid (OA) complex.

The WAXD pattern of the rolled PEI–SA complex was obtained in order to estimate the tilt angle of the side chains to a layer plane. For this study, the PEI–SA complex was rolled with a hand roller. Fig. 3 shows the edge-view WAXD pattern and a corresponding scheme of the rolled PEI–SA complex. Arcs derived from the layer structure of the PEI–SA complex appear on the equator, indicating that the layer plane is oriented parallel to the roll plane. On the other hand, the reflection at $2\theta = 21.7°$ is split into four arcs located at azimuthal angles of about 30° as shown in Fig. 3(a). This result seems to be in accord with the suggestion that the side SA chains are arranged in the layer structure at an angle of about 60° from a layer plane, as schematically shown in Fig. 3.

The layer structure of the PEI–SA complex was studied as a function of temperature. Fig. 4 shows the WAXD intensity curves of the PEI–SA complex obtained over the temperature range of 25°C–140°C, revealing that a sharp diffraction peak at $2\theta = 21.7°$ becomes a diffuse halo at temperatures above 70°C, while a narrow diffraction peak at $2\theta = 1°–3°$ becomes very sharp. This result indicates that the side SA chains lose their crystallinity at temperatures above 70°C. Despite the melting of the side SA chains, the layer structure of the PEI–SA complex is still maintained, as is the case of the PEI-OA complex. A narrow diffraction peak at $2\theta = 2°–3°$ derived from the layer structure disappears at 140°C. The T_{LS} calculated from a narrow peak at the lowest diffraction angle is plotted as a function of temperature in Fig. 5. The T_{LS} of the PEI–SA complex changed in four stages with increasing temperature. A gradual increase in T_{LS} over the temperature range of 20°C–50°C (first stage) is attributed to the gradual increase in the tilt angle between the side SA chains and a PEI-containing plane. A steep rise in T_{LS} over the temperature range of 50°C–60°C (second stage) arises from the melting of the side SA chains. In fact, as shown later, the PEI–SA complex gives a sharp melting peak at 63°C and also a sharp diffraction peak at $2\theta = 22°$ becomes a halo at temperatures above Tm^{SA}. Finally, the T_{LS} Of the PEI–SA complex increases to about 5 nm, twice the extended chain length of SA, indicating that the side SA chains of the PEI–SA complex are arranged almost at a right angle to a PEI-containing plane near Tm^{SA}.

The gradual fall of the T_{LS} of the PEI–SA complex over the temperature range of 60°C–125°C (third stage) may be attributed to chain distortion. It seems likely that chain distortions, such as kinking or bending, bring about the shortening of the T_{LS}. An abrupt fall of T_{LS} above 125°C (fourth stage) may be attributed to the destruction of the layer structure of the PEI–SA complex. In fact, a narrow diffraction maximum at $2\theta = 2°–3°$ was no longer detectable at 140°C.

The T_{LS} of the PEI–OA complex, 3.68 nm, is somewhat smaller than the *c*-axis of the OA crystal, 4.06 nm. It is possible that the conformation of the OA side chains appreciably deviates from the planar zigzag conformation.

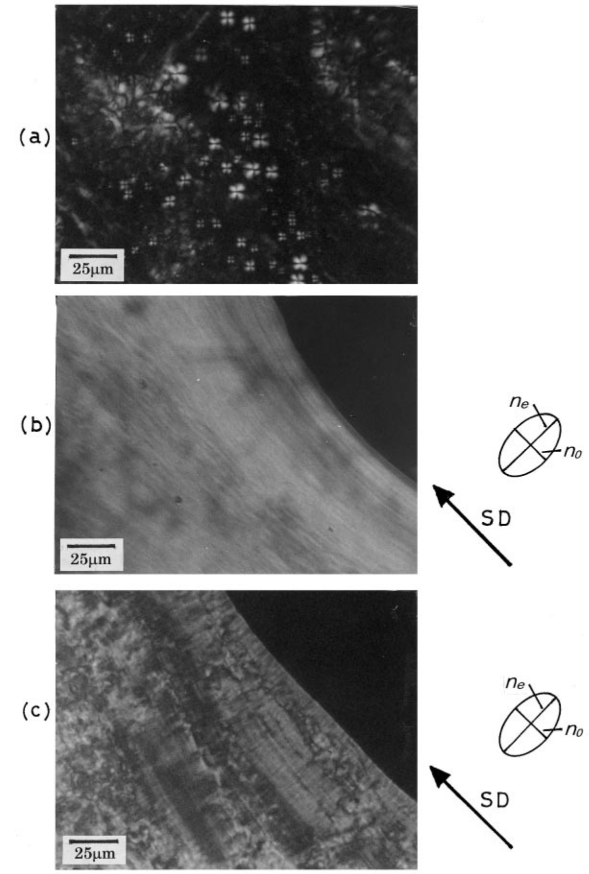


Fig. 7. Polarized optical micrographs of the poly(ethylene imine) (PEI)–oleic acid (OA) complex. formed under quiescent condition (a) and under shear [(b) and (c)]. (a): PEI–OA complex formed under quiescent condition. Sample was annealed overnight; (b) and (c): PEI-OA complex formed under shear. Photographs (b) and (c) were taken immediately after applying shear stress and being annealed overnight at room temperature, respectively.

3.3. Thermal behaviour (DSC studies)

The thermal properties of SA, PEI–SA and PEI-OA complexes were examined using DSC. The DSC scans for the heating of these samples are shown in Fig. 6. The SA gave only one sharp melting peak at 71°C, while the PEI–SA complex exhibited three thermal events over the temperature range from 30 to 220°C. The first endothermal peak at 63°C is obviously attributed to the melting of the side SA chains. The melting peak of the side SA chains of the PEI–SA complex is lower than that of pure SA, because as discussed in the previous section, the side SA chains crystallize in a hexagonal form. The PEI–SA complex becomes a viscous and cloudy liquid at temperatures above Tm^{SA}. The second broad endothermic peak at 127°C can be attributed to the destruction of the layer structure of the PEI–SA complex, judging from the fact that a narrow diffraction peak at $2\theta = 2^\circ$–3° disappears at temperatures above 135°C (Fig. 4). Some endothermic peaks at 170°C–210°C may probably be attributed to chemical decomposition. In fact, the PEI–SA complex became black after the DSC measurement.

The PEI–OA complex gave two endothermic peaks over the temperature range of 20°C–230°C. Considering the earlier discussion of the thermal behaviour of the PEI–SA complex, it seems reasonable to conclude that these peaks at 115°C and 175°C may be attributed to the destruction of a layer structure and chemical decomposition, respectively. An endothermic peak resulting from the melting of side OA chains is not detectable, because the side OA chains are already in the molten state at the starting temperature of the DSC scan, 25°C.

3.4. Liquid crystallinity and textures (polarizing optical microscopic studies)

The PEI–OA complex is an opaque paste-like substance. As revealed by WAXD studies, the layer structure is maintained at room temperature, suggesting the thermotropic smectic liquid crystallinity of the complex. The PEI-0A complex interposed between slide and cover glasses was annealed overnight at room temperature before microscopic observation. Fig. 7(a) shows a polarized optical micrograph of the PEI-OA complex obtained at room temperature. Many spherulitic textures with typical Maltese extinction crosse are dispersed in the birefringent matrix. By inserting a gypsum plate in the light path of the polarized optical microscope, it was confirmed that the spherulitic textures are optically positive, that is, the refractive index along the radial direction is greater than that in the tangential direction.

The PEI–SA complex becomes an opaque paste-like substance at temperatures above Tm^{SA}. The melt-grown PEI–SA complex also forms the optically positive spherulitic textures. As discussed in the previous section, the layer structure of the PEI–SA complex, characteristic of the smectic-type liquid crystal, is maintained even in the molten state. It was confirmed by POM equipped with the heating stage that the PEI–SA complex is still birefringent even at the temperatures above the melting point of the side SA chains. Thus, it can be concluded that the optically positive spherulitic textures of PEI–SA complex grow from the thermotropic smectic-type liquid crystalline state.

The optical properties of the textures of the PEI–OA and PEI–SA complexes can be explained as follows. The optical properties of these comb-like complexes are apparently governed by the orientation of side aliphatic chains, because these complexes contain more than 80 wt.% of side aliphatic chains. The optically positive spherulitic textures of these complexes, therefore, provide a proof that the layer structure is concentricity oriented and, consequently, the aliphatic side chains are radially oriented in the spherulitic textures. The concentric arrangement of the layer structure is characteristic of the smectic-type liquid crystal. In fact, we observed a spherulitic texture composed of concentric arrangement of the lamellar crystals in the thin film of poly(hexamethylene p, p'-bibenzoate) (BB-6) grown from a smectic liquid crystal [13]. As we discussed, the spherulitic texture can be regarded as Dupan cyclides [13]. On the other hand, pure SA forms very large optically negative spherulites from the melt, indicating that because of the radially growing lamellae, the SA chains are tangentially oriented in the spherulites.

It is interesting to note that the PEI–OA and PEI–SA complexes reveal thermotropic liquid crystallinity, whereas most of the comb-like polymers containing aliphatic side chains, such as poly(α-olefins) and poly(*n*-alkyl acrylates), are usually not liquid crystalline. These comb-like polymers lose their layer structure at temperatures above the melting point of the side chains, because the cohesive forces between the aliphatic side chains are weak. We do not have an exact reason why the PEI-SA and PEI-OA complexes are able to maintain their layer structure at temperatures above the melting point of the side chains. However, if the T_g of PEI backbone chains is as high as 120°C–130°C, it seems reasonable to assume that the non-mobile PEI backbone chains keep the side chains together even at temperatures above the melting point of the side chains, and consequently, they exhibit thermotropic liquid crystallinity. Once the PEI backbone chains begin to move, the layer structures of these complexes are decomposed at temperatures of 120°C–130°C, as Fig. 6 shows.

The development of the textures of these complexes under shear was also studied. Shear stress was applied by sliding a glass plate over the molten complexes. Fig. 7(b) is a polarizing optical micrograph of the PEI-OA complex, which is taken immediately after applying the shear stress. As can be seen, elongated fibrillar textures develop along the shear direction. A thin layer of the PEI-OA complex formed under shear is annealed overnight at room temperature prior to observation. Fig. 7(c) shows a POM micrograph of the annealed PEI-OA complex. The stripe-type textures grow at almost a right angle to the shear direction, indicating that the original fibrillar textures are obviously transformed to the stripe-type textures during annealing. By using a gypsum plate, it was confirmed that the direction of the highest refractive index in the fibrillar and stripe-type textures was perpendicular to the shear direction. The PEI–SA complex gave similar results.

According to our previous studies of the smectic liquid crystalline BB-6, shear flow causes the smectic layers to orient parallel to the shear direction, leading to preferred molecular orientation, perpendicular to the shear direction [13]. As the WAXD pattern of the rolled PEI–SA complex (Fig. 3) indicates, the layer structure is oriented parallel to the shear direction. Further, by obtaining the WAXD pattern of the PEI-OA complex formed under shear, it was confirmed that the layer structure was also oriented parallel to the shear direction, although its orientation was distorted to some extent resulting from the orientation relaxation during the measurement. It is reasonable to conclude, therefore, that the layer structure of these complexes is oriented parallel to the shear direction, and consequently, the side aliphatic chains orient almost perpendicular to the shear direction. The results presented here are in agreement with the polarized optical microscopic observation. These results provide another proof that the comb-like complexes reveal a thermotropic, smectic-type liquid crystallinity.

Comb-like complexes made of polyarylamine and aliphatic carboxylic acid (SA or OA) were also studied. Their thermal behaviour, layer structure, and liquid crystallinity are very similar to those of PEI based comb-like complexes. The results will be reported and discussed elsewhere.

4. Conclusions

The comb-like complexes were prepared on cooling the mixture of DMF solutions of PEI and SA or OA to room temperature. The structure and liquid crystallinity of the complexes were studied using various techniques.

IR studies of the PEI-OA complex show that the carboxylic acid molecules are linked by ionic bond to imine groups of the back bone PEI to form the comb-like complex. The complexes give a narrow peak at $2\theta = 2°–3°$ in their wide-angle X-ray diffractograms, indicating that the side aliphatic chains are packed in a layer structure with a spacing of 3.2–4.4 nm. In spite of the rather weak secondary valence force between an imine group of PEI and a carboxylic end group, the layer structures of the complexes are maintained even at temperatures above the melting point of the side chains. The comb-like complexes form optically positive spherulitic textures from the melt, indicating that the layer structures are concentrically oriented and as a result, the side aliphatic chains are radially oriented in the spherulitic textures. The concentric arrangement of the layer structure is characteristic of the smectic-type liquid crystal, suggesting the smectic liquid crystallinity of these comb-like complexes.

References

[1] Plate NA, Shibaev VP. J Polym Sci: Macromolecular Reviews 1974;8:117.
[2] Finkelman H, Rehage G. Adv Polym Sci 1984;60/61:100.
[3] Shibaev VP, Plate NA. Adv Polym Sci 1984;60/61:175.
[4] McArdle CB. Side chain liquid crystal polymers. New York: Chapman and Hall, 1989.
[5] Koide N. Kohunshi 1987;36:98.
[6] Takahashi T, Yamane T, Nishio Y. Kobunshi-Ronbunshu 1984;41:159.
[7] Antonietti M, Conrad J, Thunemann A. Macromolecules 1994;27:6007.
[8] Kato T, Fréchet JMJ. Macromolecules 1989;22:3818.
[9] Kato T, Hirota N, Fiujishima A, Fréchet JMJ. J Polym Sci, Part A: Polym Chem 1996;34:57.
[10] Kato T, Nakano M, Koteki T, Uryu T, Ujiie S. Macromolecules 1995;28:8875.
[11] Bazuin CG, Tork A. Macromolecules 1995;28:8877.
[12] Takahashi T, Kobayashi T. Kobunshi-Ronbunshu 1988;45:839.
[13] Takahashi T, Nagata F. J Macromol Sci-Phys 1989;B28:349.