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Two types of aggregation structure formed in a thermotropic aromatic polyester

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Abstract

The aggregation structures of the enantiotropic liquid crystalline polyester, K145N213 (°C), were investigated using polarizing optical microscope (POM), wide-angle X-ray diffraction (WAXD) and scanning electron microscope (SEM). Depending on annealing temperature, two types of aggregation structure (AS), I and II, were formed. AS I was grown directly from nematic melt, while AS II was formed from supercooled liquid crystalline state. By comparing AS I and AS II it was found that there was much difference between them, such as the morphology, the melting behaviour and the pattern of WAXD. The experimental results showed that the aggregation behaviour of AS II was more like that of the conventional crystalline polymers, while AS I made conspicuous difference. A sketch map of the formation mechanism of AS I was suggested, which showed that the particular AS I was composed of nematic domains.

Keywords: Aggregation; Enantiotropic; Liquid crystal

1. Introduction

Recently, the crystallization behaviour of liquid crystalline polymers (LCPs) has been extensively reported [1–4]. On the basis of the numerous reports [5–9], it can be concluded that the crystallization behaviour and crystal structure of LCPs depend strongly on the chemical structure and thermal history.

It is well known that the thermotropic LCPs may be monotropic or enantiotropic [10]. For the monotropic LCPs, crystallization may occur either from isotropic state or from liquid crystalline state. Cheng's research group has made great effort on the crystallization behaviour of different types of monotropic LCPs [5,11–14], such as polyether, poly(ester imide) et al. Their results show that the crystalline morphology is distinctly affected by the crystallization temperature. For example, for a monotropic polyether the crystal formed from isotropic melt appears spherulitic morphology, while the other one crystallized from nematic melt shows lamellar structure [14]. The similar conclusion has also been drawn by Heberer et al. [10]. In Heberer's work, a kind of spherulite with distinct Maltese crosses and concentric banding pattern under polarizing optical microscope (POM) is found to grow from the isotropic melt of a monotropic polyether, while when the annealing temperature is decreased to below the isotropic transition temperature (T_i), the nematic-spherulite void of Maltese crosses and banding pattern is observed to exhibit a mottle texture. In general, most of the reports on monotropic LCPs are focused on the crystallization behavior occurred from the isotropic state and from the liquid crystalline state. While for enantiotropic LCPs, because the liquid crystalline phase is thermodynamically stable, the crystal can usually be grown from the supercooled liquid crystalline states. Polyesters, especially copolyesters have been extensively investigated. Cheng et al. have showed the presence of two transition processes for different molar ratios of hydroxybenzoic(HBA)/hydroxy-naphthoic acid(HNA) copolyesters from nematic to solid state [15,16] and concluded that the

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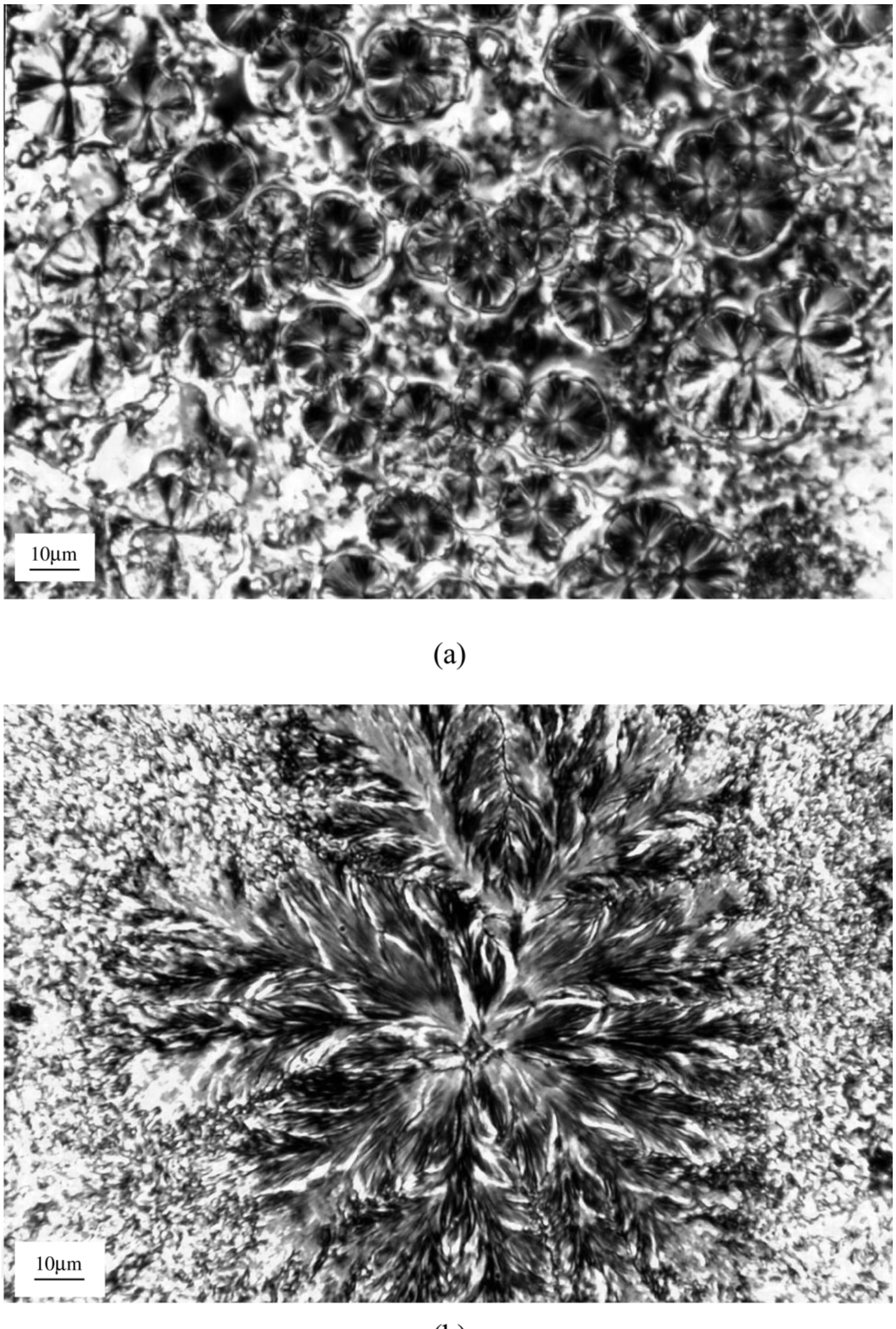


Fig. 1. The POM micrographs of AS I, (a) spherulite-like grown at 170 °C and (b) snowflake-like grown at 185 °C.

two transition processes result in two different crystalline structures that is the hexagonal packing with cylindrical symmetry along the chain direction and the orthorhombic packing. Recently, Lettieri, Liu, and Hu et al. have also reported the effect of the crystallization temperature on the crystalline morphology of enantiotropic LCPs [6,8,9].

The main objective of this work is also to investigate the effect of annealing temperature on the aggregation structure of a kind of enantiotropic aromatic polyesters. Particularly, the present work provides a specific illustrative example that is a kind of aggregation structure (AS) is grown directly from nematic melt.

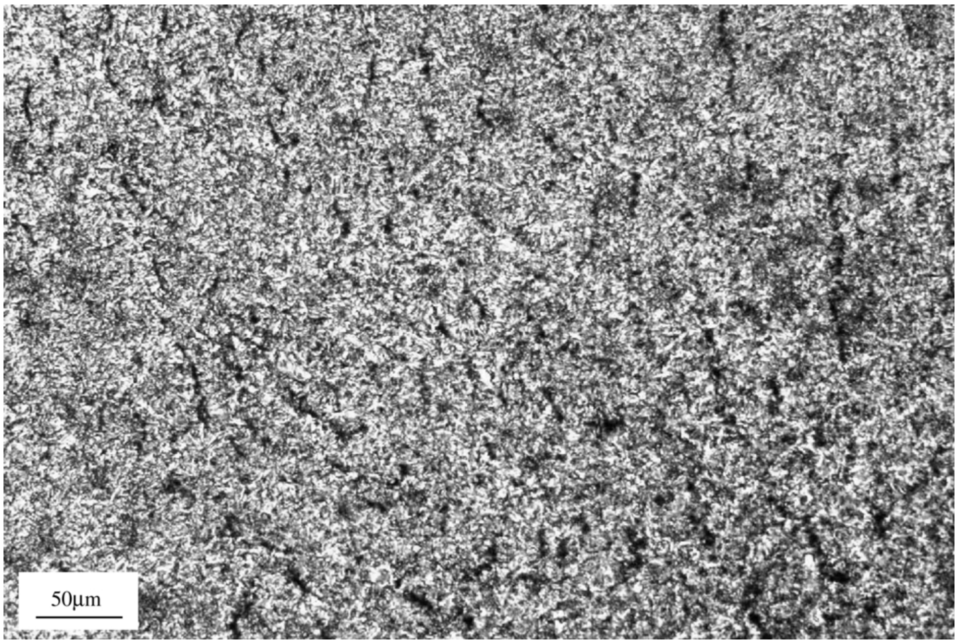
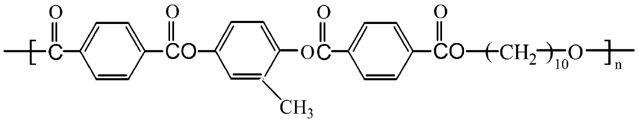


Fig. 2. The POM micrograph of AS II grown at 130 °C.

2. Experimental section

The studied aromatic polyester contains an aromatic ester triad as the mesogen group and a methylenic segment as the flexible spacer, which is referred to in the abbreviated form Pd-10. The chemical structure of it is shown by the formula below.



Its inherent viscosity [η] was 0.29 dL/g, which was measured at 30 °C in phenol-1,1,2,2-tetrachloroethane mixed solvent (1:1 according to weight ratio). The transition temperatures of it were $T_{K-N} = 145$ °C and $T_{N-I} = 213$ °C determined by Perkin-Elmer DSC-7 Differential Scanning Calorimeter (DSC).

A small amount of specimen powder was compressed into a thin layer film between two glass slides at 205 °C and held at the same temperature for 2 min to eliminate the effect of thermal history. Then the specimen was cooled down to a predetermined temperature as soon as possible to carry out isothermal treatment.

The phase and crystalline morphology were examined using a POM (Olympus BH-2, Japan) with a Mettler hot stage (FP-52) and an automatic camera. The melting behaviour of different types of aggregation structure was observed under POM with a heating rate of 3 °C/min.

For the wide-angle X-ray diffraction (WAXD) measurements, the polymer sample was sandwiched between one slide glass and one PTFE film, and then was compressed into a thin layer film on a hot stage. After quenching the thin layer film to room temperature, the PTFE film was removed. The sample film with a free surface was kept at 205 °C for 2 min to eliminate the effect of thermal history. Finally the film was quenched from 205 °C to the designed solidification temperature to carry out isothermal treatment. According to the different isothermal temperature, the samples of two types of aggregation structure can be obtained. One dimensional (1D) WAXD was carried out on a WAXD spectrometer (Rigaku D/max-2400). The point-focused beam was monochromatized with a graphite crystal to assure the Cu K_α radiation (corresponding to a wavelength of 1.5418 Å). The film samples with glass slide as substrate were used to perform WAXD measurements. The background scattering of amorphous glass was not subtracted from the sample diffraction pattern.

The scanning electron microscope (SEM) images were detected by a HITACHI S-570 SEM, which was operated at a voltage of 25 kV. The specimen with AS I sandwiched between two microscopic slides was divided into two parts by uncovering one of the slides from the specimen. One of the two parts was coated with Aurum using Eiko IB-3 Ion coater for SEM observation.

3. Results and discussion

3.1. The POM observation

3.1.1. The morphology of AS I and AS II

Depending on annealing temperature, two types of aggregation structure, AS I and AS II, are observed under POM, as shown in Figs. 1 and 2. AS I is formed in the temperature range of 140–190 °C, while the normal melting

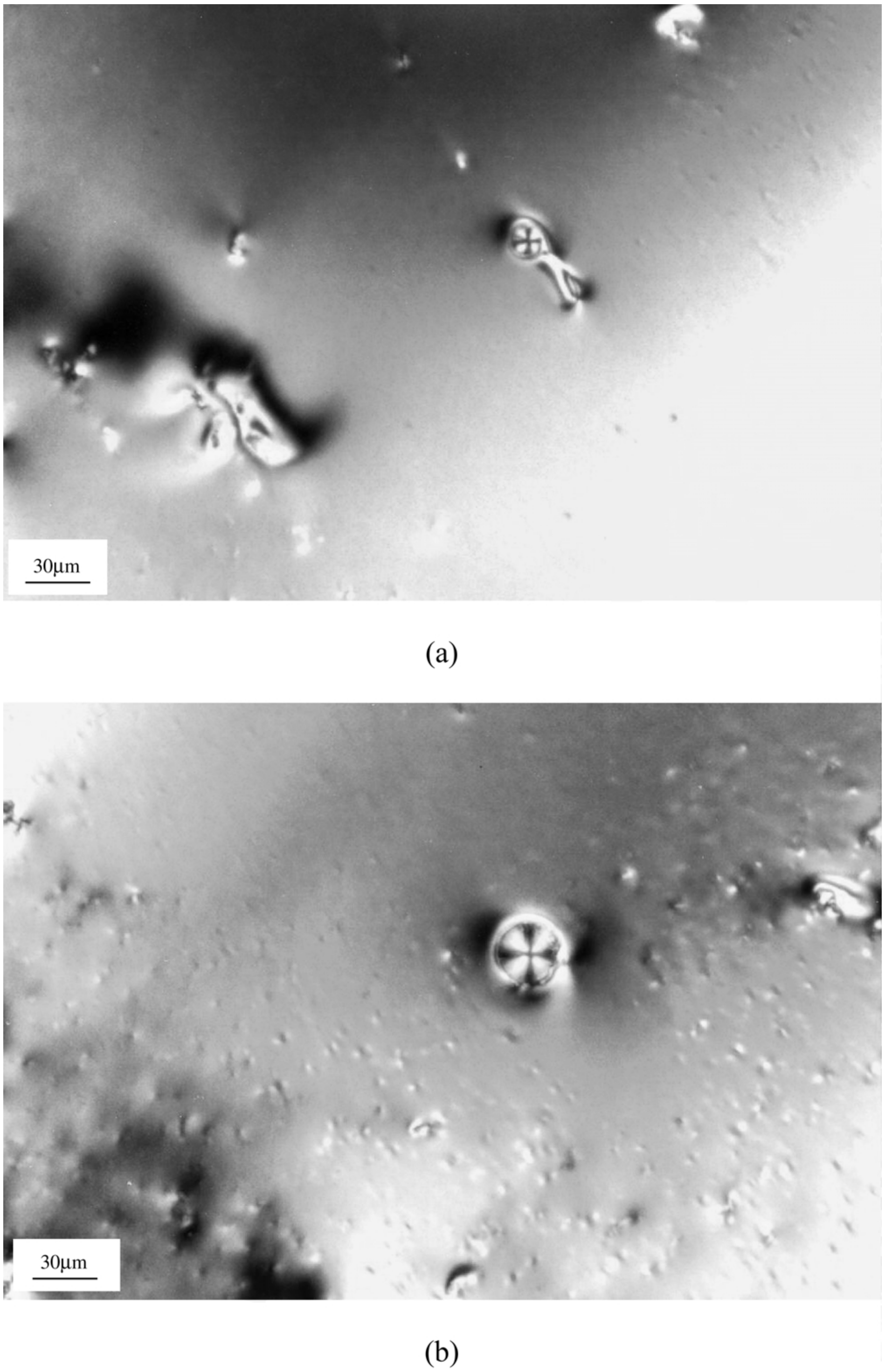


Fig. 3. The POM micrographs of the growth process of AS I at 180 °C, (a) 0 min, (b) 10 min, (c) 20 min and (d) 30 min.

temperature (T_m) of Pd-10 is 145 °C, which means that AS I can be grown directly from nematic melt. On the contrary, just like the conventional crystalline polymers, AS II can only be grown at a temperature below T_m.

According to the morphology exposed by POM, AS I can be divided into two types i.e. spherulite-like (Fig. 1(a)) and snowflake-like (Fig. 1(b)). The spherulite-like one is grown with a radial fibrillar structure and exhibits clear Maltese-crossed extinction pattern. Studying using the full-wave retardation plate shows that the spherulites are negative and thus the chains are arranged perpendicular to the spherulite radius [10]. Contrast to the spherulite-like one, the snowflake-like AS I is usually grown at a higher annealing temperature and the size of it is much larger than that of the

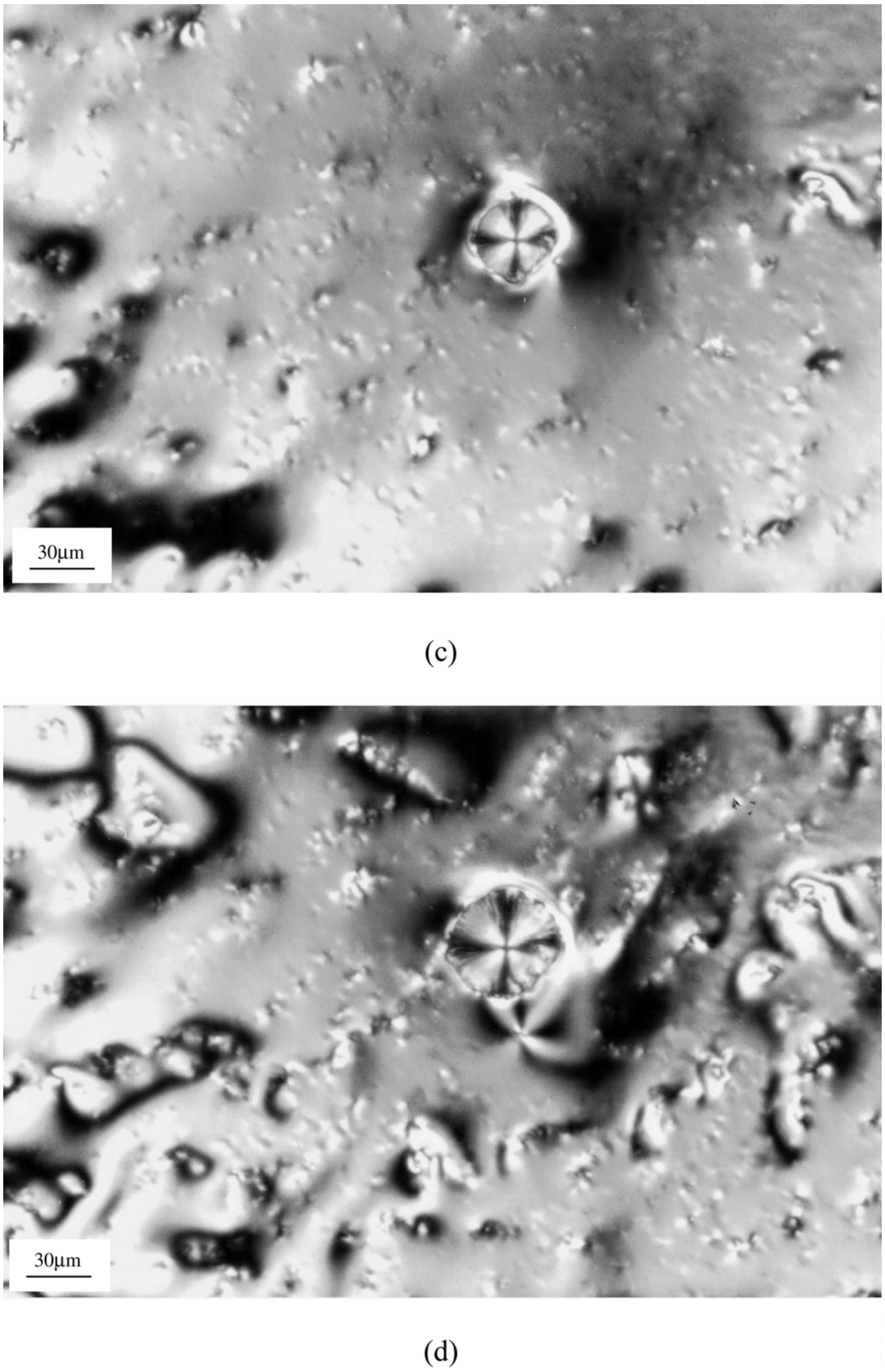
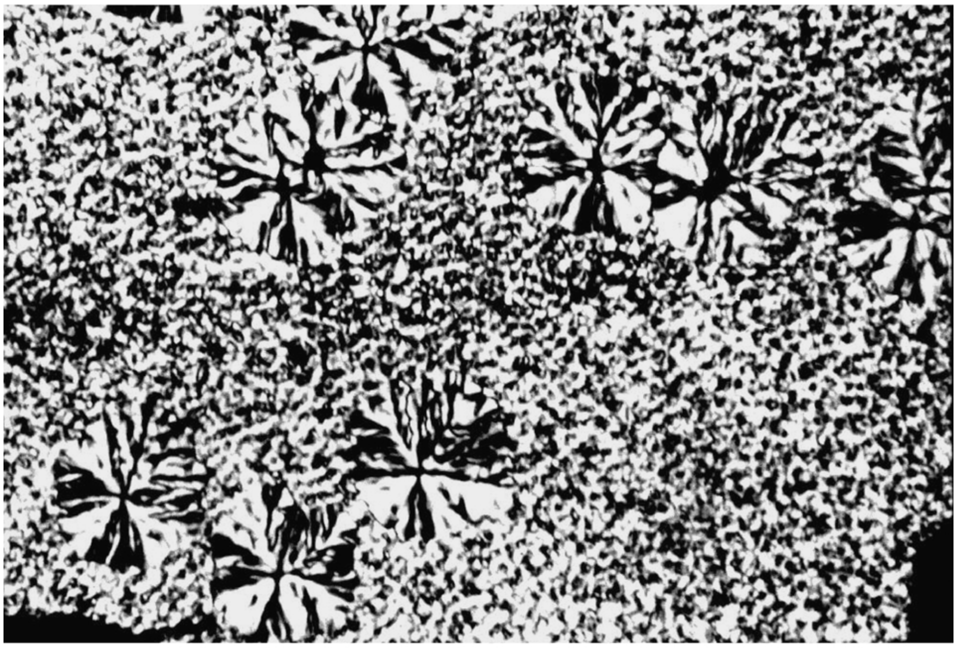
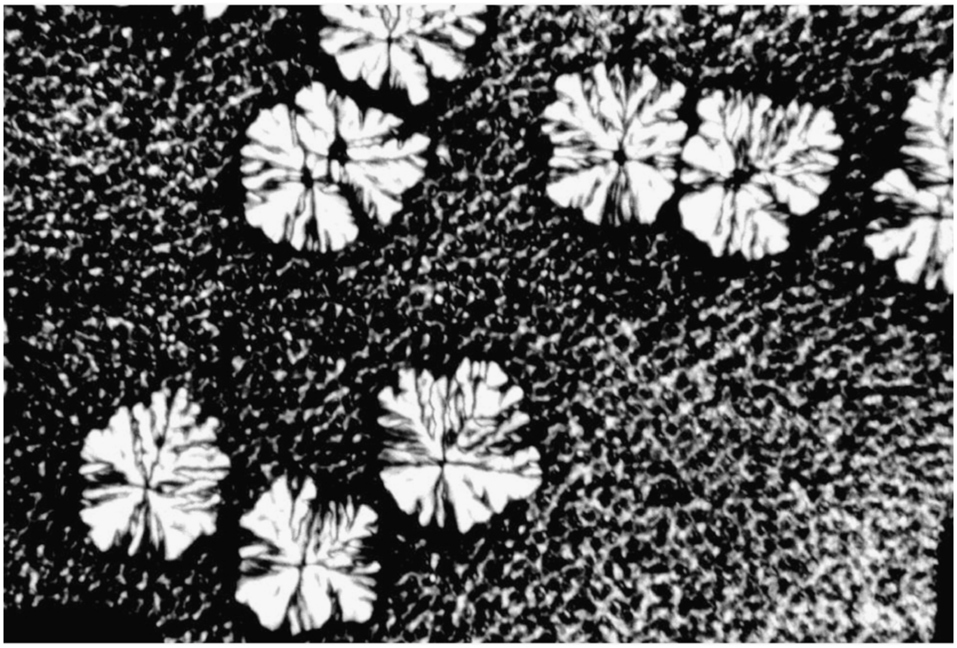


Fig. 3 (*continued*)

spherulite-like one, as shown in Fig. 1. In general, the aggregation structure grown from nematic melt always results in a well-formed morphology. The similar result has ever been observed lyotropic nematic solutions of aromatic polyamide [17]. On the contrary, the morphology of AS II displays no clear outline and no Maltese-crossed extinction pattern (see Fig. 2). Many cracks and microcracks can be formed in such aggregation structure when the specimen with AS II is quenched from the annealing temperature to room temperature. The similar phenomenon has ever been found in the spherulites of poly(hydroxybutyrate) by Barham [18]. It is believed that the appearance of the cracks and microcracks for spherulites is the result of a large coefficient of thermal expansion along the radial direction



(a)



(b)

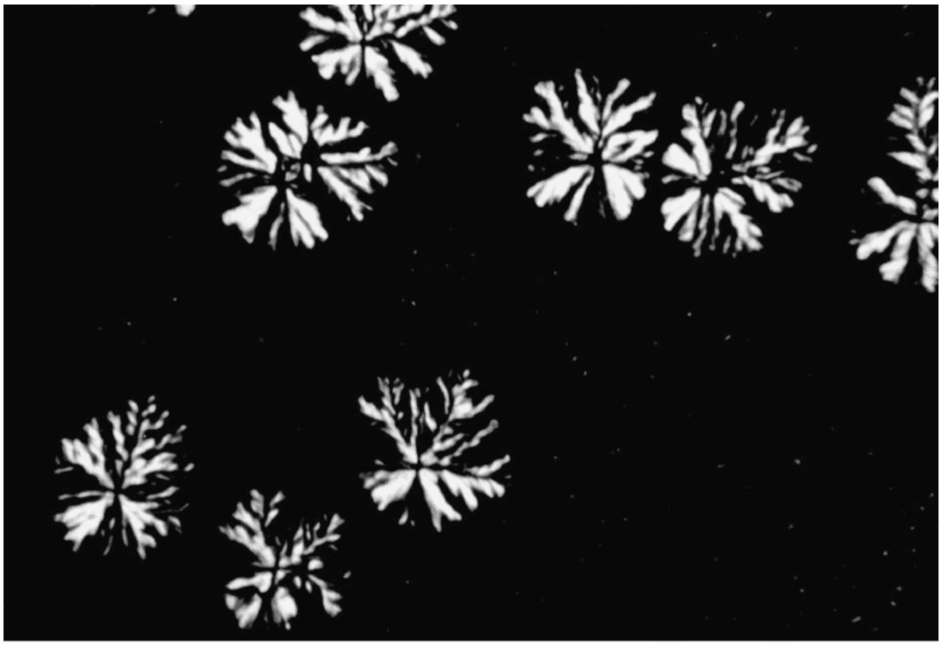
Fig. 4. The POM micrographs of AS I during heating and cooling, (a) 170 °C, (b) 200 °C, (c) 210 °C and (d) 195 °C.

for rigid chain polymers and they will disappear when the specimen is heated again to a certain temperature. For AS II the cracks and microcracks disappear when the sample is heated to 90 °C.

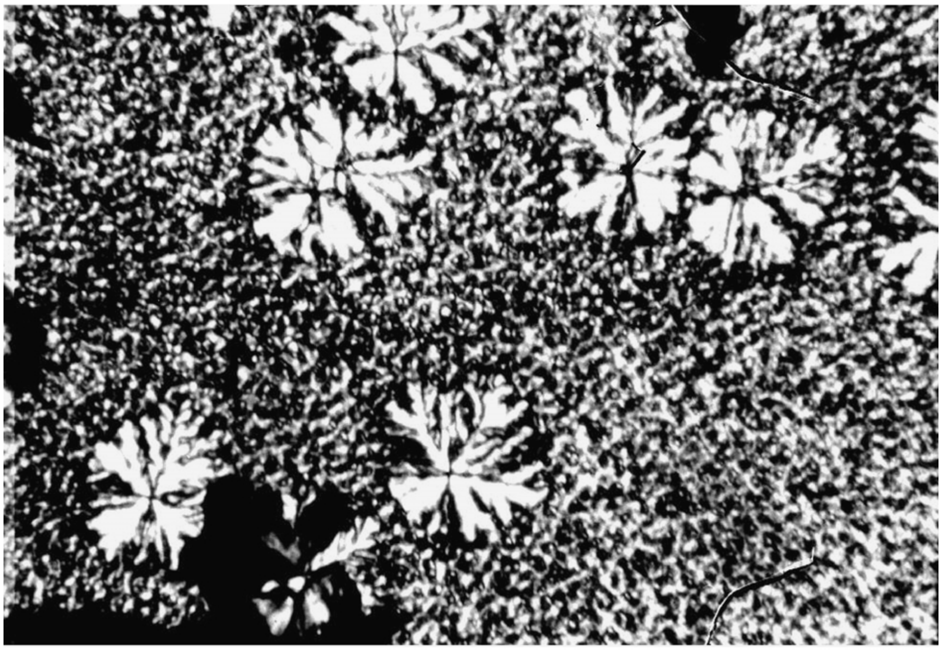
The similar phenomenon discussed above has also been reported by Hu et al. for another member of the same family, which is marked as Pd-8 with eight methylene groups as spacer [9]. But it should be noted that the aggregation structure grown directly from nematic melt is not involved in their research.

3.1.2. The growth process of AS I

The POM micrographs of the growth process of AS I during annealing at 180 °C are shown in Fig. 3. It can be



(c)

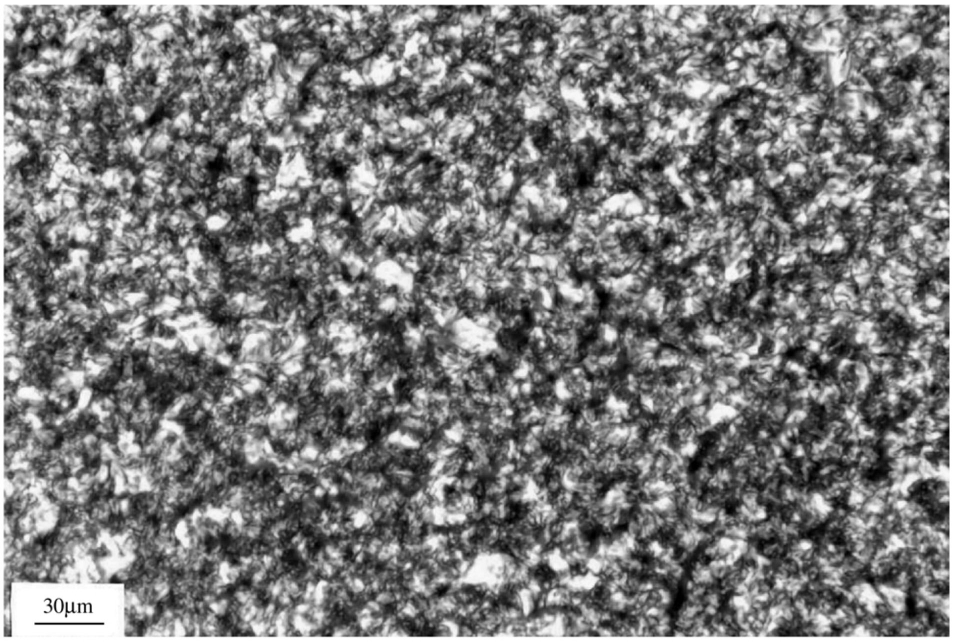


(d)

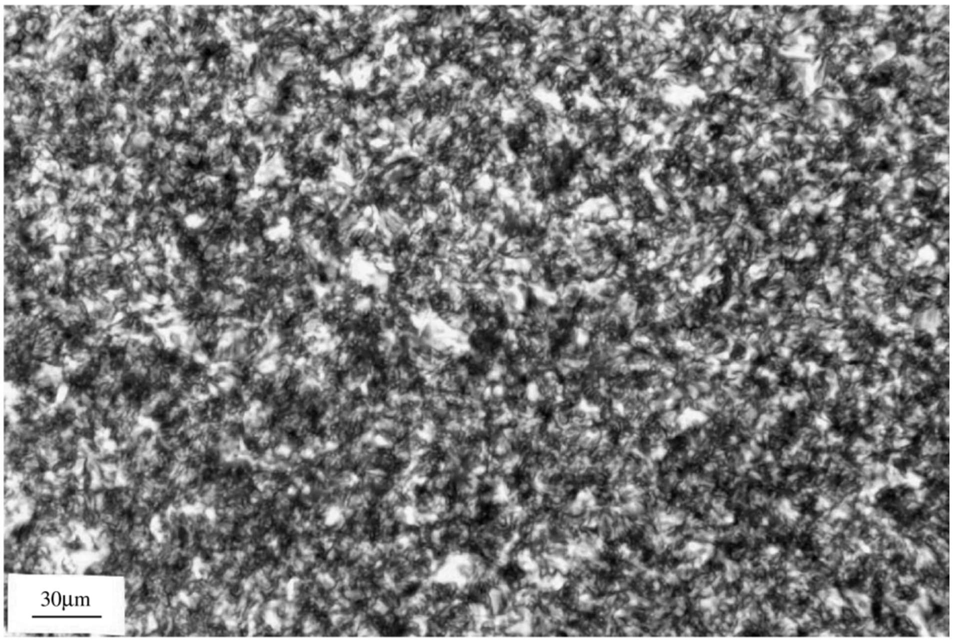
Fig. 4 (*continued*)

seen that AS I grows in radial direction in the background with nematic phase. The radius growth rate (G_r) is approximately 0.45 μm/min. In addition, the G_r of AS I is no more than 1 μm/min in the whole annealing temperature range of 140–190 °C.

It can also be seen from Fig. 3 that along with the growth of AS I some nematic schlieren textures disappear and the others appear. The total number of the schlieren is increased, which indicates that there exists a fluidity in the specimen during the formation of the AS I. Such a phenomenon shows that the specimen is still in the nematic state although the spherulitic AS I is formed. Then an interesting question should be asked, is the AS I a real crystalline spherulite or just a spherulite-aggregation of



(a)



(b)

Fig. 5. The POM micrographs of heating and cooling process of AS II, (a) room temperature, (b) 90 °C, (c) 205 °C and (d) 120 °C.

nematic domains? The following experiments will support further information to answer this question.

The growth process of AS II cannot be directly recorded by POM observation because there is no obvious outline of it and so, the radius growth rate of AS II cannot be obtained by this means.

3.1.3. The melting behaviour of AS I and AS II

Fig. 4 shows the POM micrographs revealing the melting behaviour of AS I. It can be seen that the birefringence of both the AS I and the nematic background decreases with the increasing temperature. At 210 °C, close to the isotropic temperature of 213 °C, the nematic phase is transformed

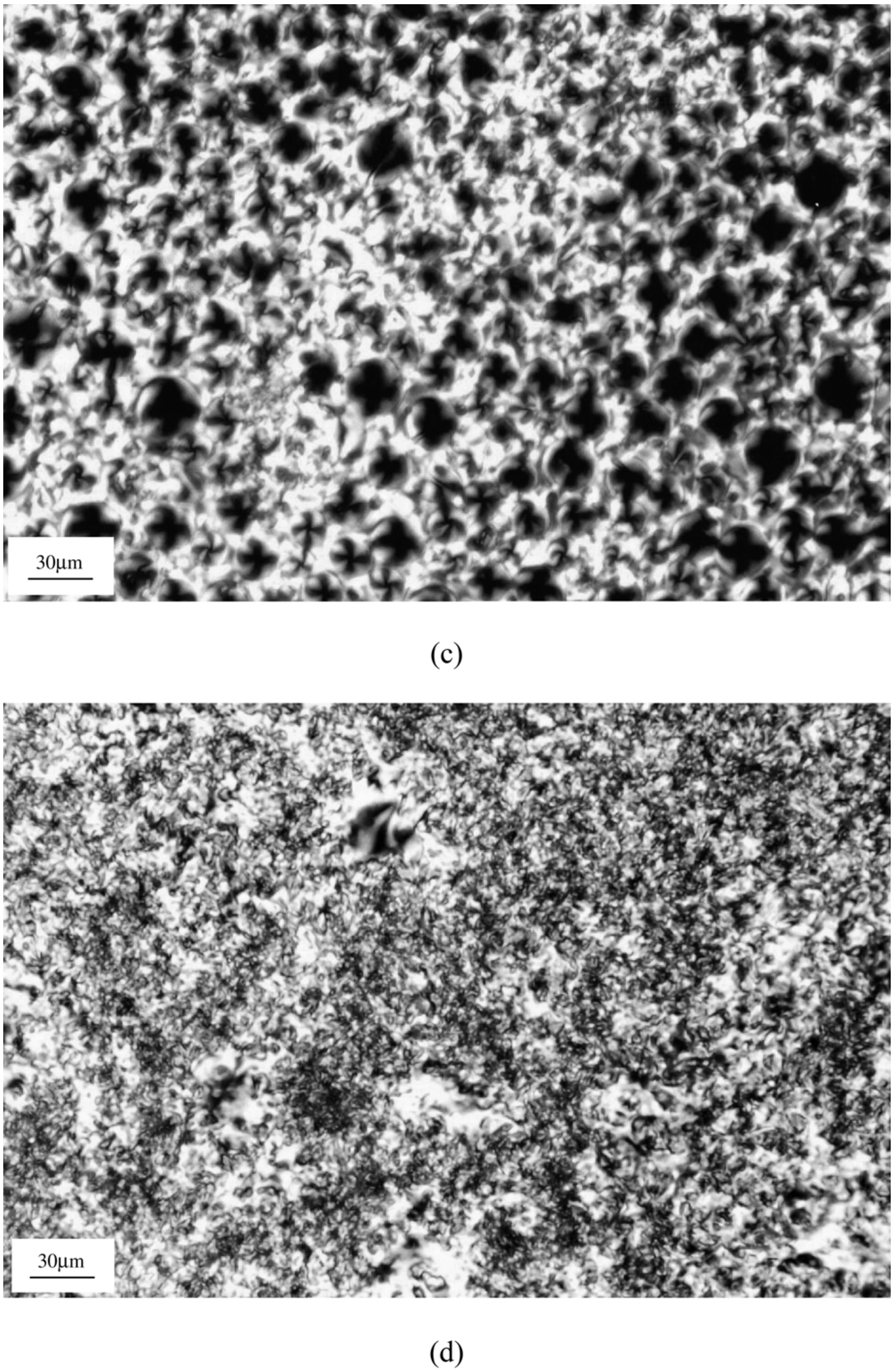


Fig. 5 (*continued*)

into isotropic phase, while the AS I still exists (see Fig. 4(c)). It is interesting that AS I never disappear completely even though the temperature is up to 230 °C. When the specimen is cooled again to a temperature below the isotropic temperature, here 195 °C, the nematic background is formed again (Fig. 4(d)).

Despite the difference in morphology, the melting behaviour of AS II is also different from that of AS I, as indicated in Fig. 5. The cracks and microcracks existing at room temperature (Fig. 5(a)) disappear when the specimen with AS II is heated up to 90 °C (Fig. 5(b)). After the ambient temperature is increased to 150 °C, the AS II shows

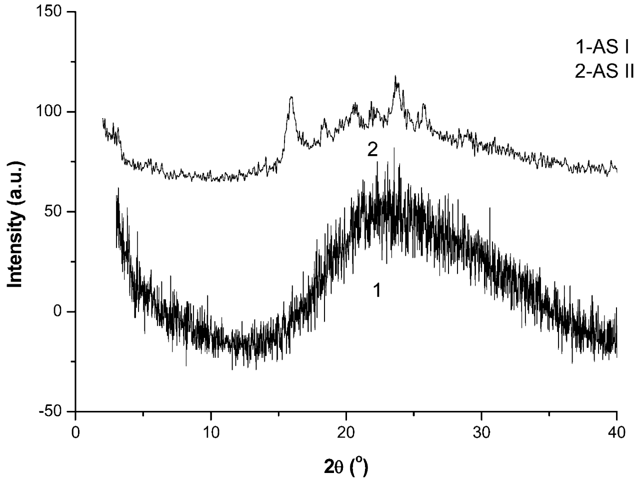


Fig. 6. The WAXD pattern of AS I and AS II.

the phase transition from the crystal to the nematic phase. Subsequently, the bi-phase texture i.e. nematic phase and isotropic phase, can be observed at about 205 °C (Fig. 5(c)). The isotropitization of the whole specimen occurs at 218 °C. During the cooling process, the nematic texture appears at 210 °C while the AS II is not formed until the temperature is lower than 140 °C (Fig. 5(d)).

The results of the POM observation indicate that the aggregation and melting behaviour of AS I and AS II are distinctly different from each other. For example, AS I is grown almost only at a temperature above the transition temperature of crystalline-to-nematic phases (145 °C), which means that AS I is formed only in nematic melt. In addition, along with the growth process of AS I, the fluidity phenomenon is also observed in the specimen, which results in the formation of more schlieren texture. While, the aggregation behavior of AS II occurs at a temperature below 140 °C, that is, AS II is formed from the supercooled liquid crystalline state. On the other hand, AS I does never disappear completely during the heating process even though the ambient temperature is up to 230 °C, while AS II is melted into nematic phase when it is heated to 150 °C. Therefore, there is an intrinsic difference between the two aggregation structures. Contrast to that of AS I, the aggregation and melting behavior of AS II is more similar to that of the conventional crystalline polymers.

3.2. The WAXD measurements

The WAXD spectra of the two aggregation structures are shown in Fig. 6. It can be seen from the diffraction pattern of AS I that only a diffuse peak at about $2\theta = 22.5°$ indicating an intermolecular spacing of 3.95 Å is detected. Such a phenomenon indicates that although the morphology of AS I observed by POM appears similar to the spherulite of conventional crystalline polymers, there is no sharp diffraction peak representing the crystalline lattice information in WAXD pattern. On the contrary, several sharp peaks representing the crystalline lattice information are illustrated in the WAXD spectrum of the specimen with AS II, as shown in Fig. 6. Therefore, the WAXD patterns of AS I and AS II are also distinctly different. The molecular packing pattern of AS I more resembles to that of nematic melt, while the diffraction pattern of AS II is more similar to that of conventional crystalline polymers.

3.3. The SEM observation for AS I

The specimen with AS I is formed between two microscopic slides for POM observation, as shown in Fig. 7(a). The surface of the specimen is exposed to perform SEM observation by uncovering one of the slides from the specimen and then, the specimen is correspondingly divided into two parts. The POM micrograph of one part is shown in Fig. 7(b). An interesting phenomenon is observed clearly from Fig. 7(b) that many homocentric loops appear after one slide is uncovered. The average spacing between two homocentric loops along the radial direction is approximately 10 μm.

Fig. 8 shows the POM micrographs of the specimen with uncovered surface, which contains many AS I spherulites. Fig. 8(b) is the same view region as Fig. 8(a) but removing the polarizer. It can be seen from Fig. 8(a) that except for the AS I spherulites with strong birefringence, some quasi-circular regions without birefringence are also observed under crossed polarizers. By removing the polarizer it can be found that the regions without birefringence under crossed polarizers show the same morphology as that of the spherulites with strong birefringence (Fig. 8(b)). The difference of the birefringence between them under crossed polarizing light may result from two factors, that is, the heterogeneous forces during the uncovering process and the difference of the original AS I thickness.

The SEM micrograph of the specimen with uncovered surface is shown in Fig. 9. The average width of the broad zone is approximately 10 μm, which is in accordance with the average spacing between two homocentric loops along the radial direction observed by POM. The narrow zone under SEM observation corresponds to the homocentric loop in POM observation. Therefore, the homocentric loop observed by POM is generated by uncovering process and not the result of the extinction as shown by banded-spherulites of some crystalline polymers (e.g. polyethylene).

A SEM micrograph of AS I spherulites is shown in Fig. 10. It can be seen clearly from Fig. 10(a) that the SEM morphology of AS I exhibits the morphology of ripple-like concentric ring and the width of the ring along the radial direction is about 150 nm. Such morphology is different from that of the conventional crystalline polymers, such as polypropylene, which often shows the morphology of lamellar aggregates. It is interesting to find that the morphology of the background, the area around AS I, is

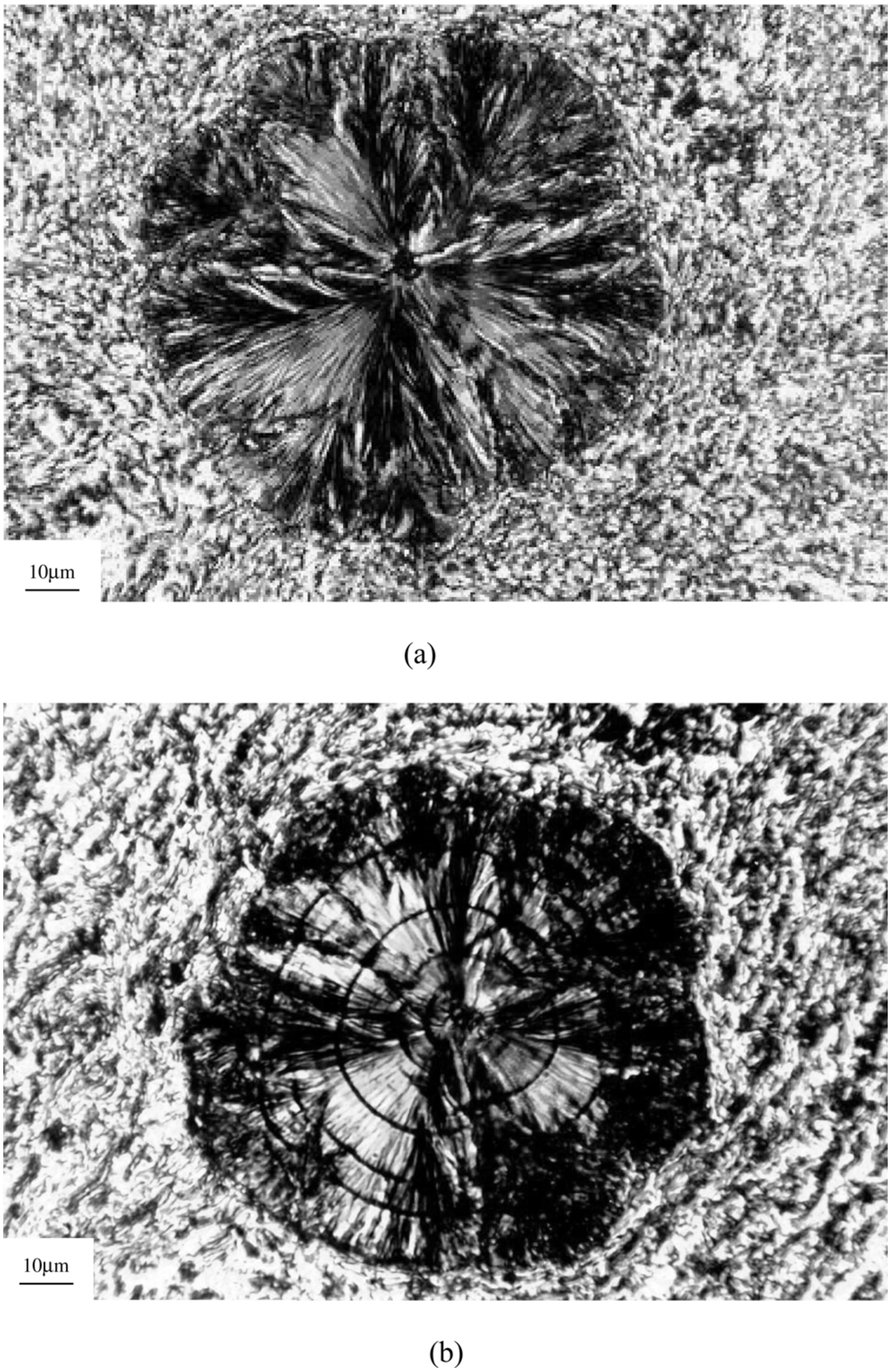
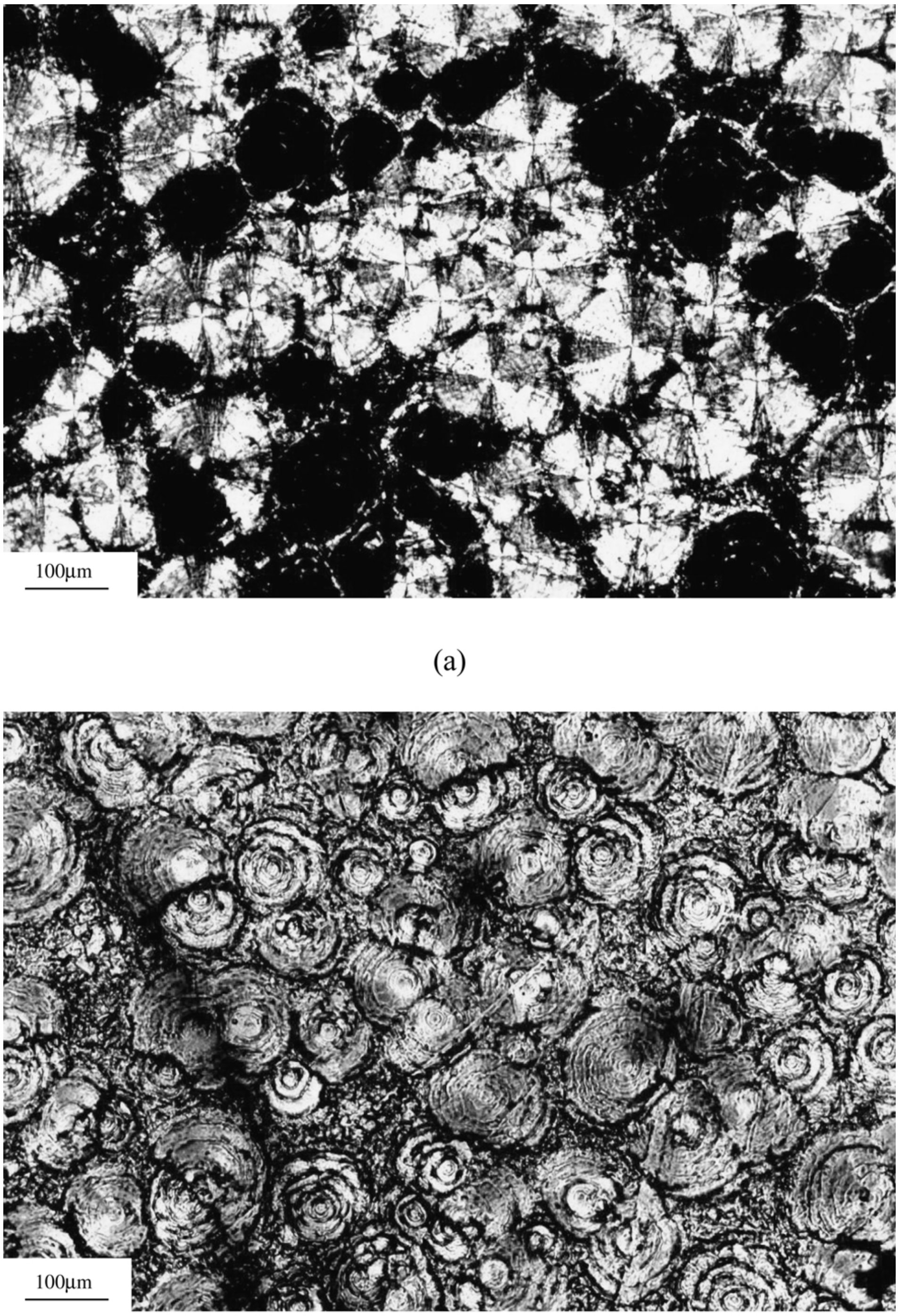


Fig. 7. The POM micrographs of AS I spherulites, (a) before separation and (b) after separation.

much different from that in AS I (Fig. 10(b)). The POM observations (Figs. 5 and 7) indicate that the morphology in the area round AS I is similar to that of AS II. The most distinct difference between the areas around AS I and in AS I is the ordering. The packing of the domains in AS I has a higher ordering than that in the area around AS I. Such an experimental results also support the conclusion that AS I spherulites are composed of nematic domains. A sketch map of the formation mechanism of AS I is suggested in order to explain the reason why AS I exhibits the morphology of ripple-like concentric ring. According to Fig. 11, the molecular chains in AS I are oriented perpendicular to the radial direction [10], which shows the negative birefringence nature and these oriented chains are packed into



(a)

(b)

Fig. 8. The POM micrographs of AS I after removing one slide, (a) with polarizer and (b) without polarizer.

nematic domains, which then assemble to the periodical domain aggregations with the ring diameter of about 150 nm along the radial direction. Therefore, the ripple-like concentric morphology is observed. The domain aggregations are packed together into the spherulitic form and finally the spherulite-like aggregation structure is observed by POM.

4. Conclusion

For the enantiotropic aromatic polyester Pd-10, two types of aggregation structure, AS I and AS II, are observed in different temperature range. The two types of aggregation structure are different from each other in many aspects, such as the morphology, the melting behaviour, the pattern of

Fig. 9. SEM micrograph of AS I spherulite.

WAXD, and so on. The results showed that AS II is more like the conventional crystallizable polymer, while it is not the same case for AS I. A sketch map of the formation mechanism of AS I is suggested on the basis of the experimental results of POM, WAXD and SEM. The sketch map indicates that AS I spherulites are composed of nematic domains which is well-assembled into the sphericity. Such a suggestion can explain some of the special properties of AS I, for example, AS I can almost only be grown from nematic melt; during the growth of AS I the fluidity can be observed in the specimen; the WAXD pattern of AS I shows only a diffuse peak as that of the nematic state; the ripple-like homocentric morphology is observed under SEM, and so on.

Acknowledgements

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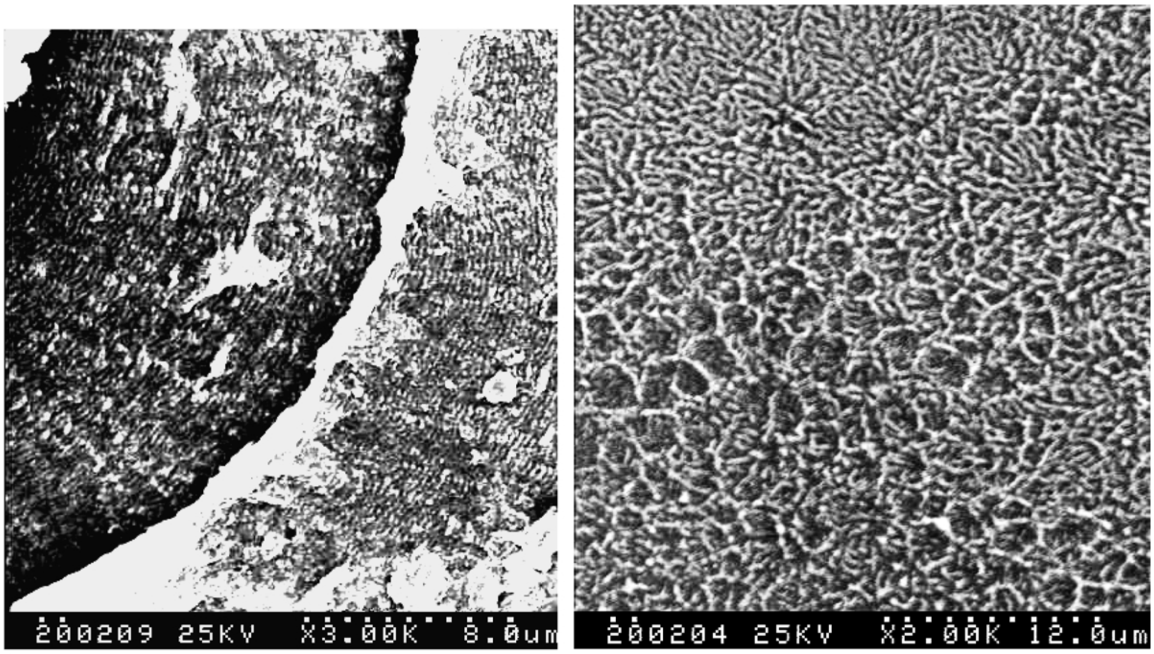

(a) (b)

Fig. 10. SEM micrographs of (a) in the AS I spherulites and (b) area around AS I spherulite.

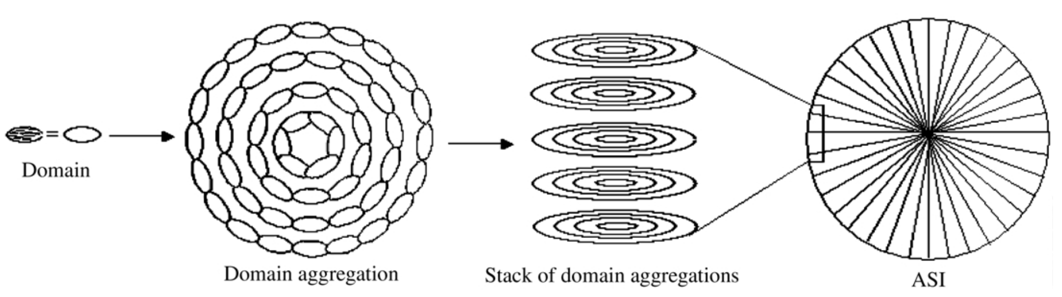

Fig. 11. The sketch map of the formation mechanism of AS I spherulite.

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