TEM Studies on Thin Films of Natural Rubber and Polychloroprene Crystallized under Molecular Orientation II. Highly Prestretched Thin Films

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ABSTRACT: Thin films of natural rubber (NR) or polychloroprene (CR) were made by casting a 1.0–2.0 wt% solution in *n*-hexane or benzene onto the water surface, and were prestretched up to a fairly large amount of strain (500–800%) at an ambient temperature in wintertime. Each of the specimens thus prepared was introduced into a transmission electron microscope (TEM) column with a cryo-transfer specimen-holder and examined by TEM observation without any electron staining. Most of the specimens were isothermally crystallized for 1–2 h inside the TEM column by using the holder before TEM observation: at -25°C for NR and at -5°C for CR. On the basis of the morphological observations in bright- and dark-field imaging modes and the selected-area electron diffraction analysis, the identity of the “ γ -filaments”, which were named by Andrews (*Proc. Roy. Soc. A.*, **277**, 562 (1964)), and the crystallization mechanism in highly prestretched NR and CR were discussed.

KEY WORDS Orientation-Induced Crystallization / Oriented Crystallization / Morphology / Transmission Electron Microscopy / Electron Diffraction / Dark-Field Image / Defocus Contrast /

Crystallization behaviors of flexible linear-chain polymers have been extensively studied so far by various methods such as X-ray diffraction (including the small-angle scattering technique), light scattering, dilatometry, optical microscopy, electron microscopy, etc.¹ Crystallization under molecular orientation, namely oriented crystallization (or orientation-induced crystallization)² or strain-induced crystallization,³ of the polymers is much faster than that from the unoriented amorphous state. Oriented crystallization is a phenomenon which occurs in the industrial processing steps such as spinning, film production, molding and so on and determines physical properties of the resulting products. The oriented crystallization, however, has not fully been clarified up to now, though it is one of the important subjects from an academic and also industrial point of view.

On the basis of the investigations by transmission electron microscopy of thin films of natural rubber (NR) which were prestretched up to respective given amounts of strain (ϵ), isothermally crystallized and then fixed/stained with osmic acid (OsO_4), the resulting crystalline morphologies of NR were classified into five groups by Andrews⁴: The morphology observed for $\epsilon=0\%$ (no strain) is characterized by the spherulitic structure where the α -filaments (named by Andrews⁵) are arranged radially. The morphology for $\epsilon \approx 50\%$ is well expressed by the sheaf-like (or flattened-spherulitic) structure where the α -filaments tend to grow in the direction perpendicular to the stretching direction, and accordingly the long axis of a sheaf (or a flattened spherulite) will be oriented perpendicular to the stretching direction. In the case of $\epsilon \approx 100\%$, the morphology corresponds to the structure in which α -filaments are mostly grown perpendicular to the prestretching direction and stacked in that direction due to, for example row nucleation.^{4,6} Though the morphology for $\epsilon \approx 200\%$ is similar to that for $\epsilon \approx 100\%$, the α -filaments become shorter and

shorter with increasing ϵ and the number of rows, each of which consists of the stacked α -filaments, increases with increasing ϵ . The morphologies for $\epsilon = 100\text{--}200\%$ are the same as that expressed as the row (or shish-kebab) structure. The morphology for $\epsilon > 300\%$ is, however, expressed by different structure in which filaments of another type (termed “ γ -filaments” by Andrews^{5,7}) can be observed to orient parallel to the stretching direction: the γ -filaments and row nuclei were speculated to be the same species.⁸ An almost similar classification into five groups was given later by Reed,⁹ in which slightly different correlation was, however, proposed between ϵ and morphologies. Similar morphological results as above were also reported for crystallized thin films of polychloroprene (CR).^{10,11} In particular, we successfully confirmed that the α -filament in NR^{12,13} and the corresponding filamentous entity (we may call it an α -filament) in CR^{11,13} are both an edge-on lamella, by transmission electron microscope (TEM) observations of their thin films which had been moderately prestretched ($\epsilon \approx 200\%$) and then isothermally crystallized but not stained.

Andrews⁷ reported that the crystalline nuclei (γ -filaments) were organized in strings under molecular orientation in NR, which were running in the stretching direction but were not continuous crystalline entities. Andrews then proposed the following two formation mechanisms of the γ -filaments, on the basis of the result observed in an NR film which was prestretched by 200% and crystallized at -26°C for 1 h: i) Nuclei form along lines of high strain existing in the film before isothermal crystallization. ii) The strings of nuclei are self-propagating, *i.e.*, the formation of one nucleus yields a second one close by, in a way that the line joining the nuclei lies in the stretching direction.

In 1964, Andrews⁵ defined and reported the nucleation index (N) of α -filaments as a function of crystalliza-

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tion time and pre-strain (ϵ) for NR thin films crystallized at -28°C or -14°C : Andrews claimed that N represents approximately the length of γ -filament and reported that N increased with increasing time for greater ϵ . This result suggests that the γ -filaments on which α -filaments are overgrown might be formed by the Mechanism-(ii). On the other hand, Andrews and Reeve¹⁰ cited the following result obtained by Owen¹⁴: It was demonstrated by TEM observation that there was a central thread on which folded-chain lamellae (α -filaments) were nucleated and that the lamellae could be melted off, leaving only the central thread of about 3 nm in diameter. This result seems to support the Mechanism-(i). Because these experimental results are conflicting with each other, it is difficult to determine which mechanism is more plausible, (i) or (ii). Consequently, there still remain some morphological subjects to be solved, such as a) establishing the identity of the γ -filament in NR and that of the corresponding filament in CR (because the filament in question is highly elongated in the direction parallel to the c -axis of CR crystal, we here call it also a γ -filament) and b) elucidating the mechanism of oriented crystallization of NR and CR.

In this article, morphological studies on the NR and CR thin films, which are highly prestretched ($\epsilon=500$ – 800%) outside and then crystallized inside a TEM column, will be presented mainly to establish the identity of the “ γ -filaments” in NR and CR and partly to discuss the crystallization mechanism in highly prestretched NR and CR.

EXPERIMENTAL

Materials and Sample Preparation

Materials used here are NR (Ribbed smoked sheet: RSS#1) and CR (Neoprene-W, which is a “normal” CR¹⁵ containing *trans*-1,4 (84%) and *cis*-1,4 (ca. 10%) structural units¹⁰). The procedure for preparing thin films of NR and CR was essentially the same as that reported by Andrews^{5,10,16} for NR and that by Andrews and Reeve¹⁰ for CR. Thin films of NR and CR were made by casting each solution (1.0–1.5 wt% for NR and 2.0 wt% for CR) in *n*-hexane (for NR) or benzene (for NR and CR) onto the water surface. (In our experiment, the kind of solvent (*n*-hexane or benzene) gave no significant difference in morphology for NR.) The thickness of each film was judged from the interference color, and gold-colored portions (about 80 nm in thickness¹⁷) for CR¹¹ and light-gold-colored through violet-colored portions for NR¹⁸ were selected for subsequent steps. The appropriate portion of the thin film was prestretched up to a desired amount of strain ($\epsilon=500$ – 800%) on the water surface by hand or by using our homemade film-stretching device^{18,19} (the device was operated at a constant stretching-rate (1 cm s^{-1})). The prestretched portion of the film was mounted onto a carbon-coated copper (Cu) grid for TEM observation (namely, onto a Cu grid on which a vapor-deposited carbon support-film had been mounted in advance), and then air-dried at room temperature. The NR specimens were frozen/stored at -196°C in a cryobiological storage vessel until TEM observation. (All these procedures were carried out at an ambient temperature in wintertime.) The specimens thus

prepared, without any electron staining, were introduced one by one into a TEM column.

Transmission Electron Microscopy

A TEM (JEM-200 CS, JEOL Ltd.) equipped with a TV system (Model 622SC and 663, Gatan Ltd.) was operated at an accelerating voltage of 160 kV or 200 kV, and this TV system was utilized to search a suitably crystallized region in the specimen film. A cryo-transfer specimen-holder (EM-CTH 11, JEOL Ltd.) was used to cool and crystallize the specimen in the TEM column. The specimen temperature was controlled to be -25°C for NR, at which the growing rate of the α -filaments in an NR thin film was reported to be approximately the maximum even in the process of its oriented crystallization,²⁰ or to be -5°C for CR, at which the crystallization rate of CR was reported to be approximately the maximum.²¹ Crystallization time in the TEM column was mostly 1–2 h for both of the NR and CR films. Selected-area electron diffraction (ED) patterns from a specimen area of ca. 8 μm in diameter, and bright- and dark-field images were recorded onto photographic films (Kodak SO-163 or Mitsubishi MEM), and the exposed films were developed at 20°C for 5 min with Mitsubishi Gekkol (full strength). The diffraction camera-length was calibrated with the help of reflection rings from the vapor-deposited gold particles. Though TEM observation of CR was all performed at -5°C , that of NR was carried out at -80°C ¹⁸ to minimize electron irradiation damage. (This temperature, -80°C , is slightly lower than the glass transition temperature of NR.)

RESULTS AND DISCUSSION

Polychloroprene (CR) Thin Films Which Were Prestretched up to $\epsilon=500$ – 600% and Then Isothermally Crystallized

The crystal structure of CR, namely of *trans*-1,4-polychloroprene, was determined by Bunn,²² and its crystal system is orthorhombic (space group= $P2_12_12_1$): $a=0.884\text{ nm}$, $b=1.024\text{ nm}$, c (chain axis)= 0.479 nm . All the ED patterns obtained from CR thin films in this study were indexed by using these unit cell dimensions. Four molecular chains pass through the unit cell, and there is no planar chain conformation nor special chain packing which may cause, for example, a double orientation. In the projection of the CR crystal lattice onto the ab -plane, the chain stems are located approximately on a two-dimensional hexagonal lattice.

TEM observation revealed coexistence of non-oriented and oriented regions in the film prestretched up to $\epsilon\approx 600\%$, as in the case of the moderately prestretched thin films of CR (for example, $\epsilon\approx 200\%$ ¹¹). Figure 1a demonstrates a representative ED pattern from an oriented region in the CR thin film which was prestretched by hand up to $\epsilon\approx 600\%$ and then crystallized at -5°C for about 1 h. In this figure, only one arc-shaped reflection, which is determined as 120 and/or 200, is clearly recognized on the equator. Faint 210 and 220 reflections are, however, also recognized undoubtedly on the equator in the original negative of this ED pattern. The chain axis (c -axis) is found to be oriented in the stretching direction (vertical direction of all the figures in this report), because the

Figure 1. CR thin film which was cast from a benzene solution, prestretched up to $\epsilon \approx 600\%$ and then crystallized at -5°C for *ca.* 1 h. The stretching direction is vertical. (a) ED pattern from an oriented region in the film (reversed contrast). The oblique bright rod is a beam stop. (b) Bright-field (BF) defocus-contrast image of the same region used for (a).

weak 002 reflection appears on the meridian and in addition, the $120(+200)$ reflection is concentrated rather sharply on the equator, of course much more sharply than that from the specimen prestretched by $\epsilon \approx 200\%$ ^{11,13} and slightly better than that from the one prestretched quickly by $\epsilon \approx 250\%$.¹¹

Figure 1b is the bright-field image taken by the defocus contrast method,²³ namely the image taken at a rather large amount of defocus (usually, underfocus) in the bright-field imaging mode, of the same region in the film used to obtain Figure 1a. With this method, for example, a sheaf-like structure, namely an immature spherulite, is clearly visualized as an assembly of dark striations in the CR thin films crystallized under no strain, even if the films are prepared with no electron staining, and each of such dark striations corresponds to the α -filament in NR^{11,13} (Accordingly hereafter, the striation in CR is also called an α -filament in this article). Therefore, as in our previous results^{11,13} for CR thin films which were prestretched up to $\epsilon \approx 200\%$ and then isothermally crystallized, each of the dark striations (10–20 nm in width) observed in Figure 1b can be assigned to an edge-on lamella. That is to say, Figure 1b reveals that the α -filaments, namely the edge-on lamellae are oriented perpendicular to the stretching direction. The length of such dark striations reaches *ca.* $0.5\ \mu\text{m}$. They are stacked in the stretching direction to make a row (or shish-kebab) structure, for example as indicated with the arrow and a letter A. The texture of Figure 1b resembles the Japanese mat, "Tatami", in appearance and is fairly similar to the morphology observed in the TEM photograph of surface replica showing the stacked-lamellar structure in polyethylene.²⁴ The whole appearance of this figure, however, resembles the structure model for $\epsilon = 100$ – 200% proposed by Andrews⁴, in spite of the fact that the specimen film was prestretched up to $\epsilon \approx 600\%$. This morphological difference seems to be

Figure 2. CR thin film which was cast from a benzene solution, prestretched quickly up to $\epsilon \approx 500\%$ and then crystallized at -5°C for *ca.* 1 h. The stretching direction is vertical. (a) ED pattern from an oriented region in the film (reversed contrast). The oblique bright rod is a beam stop. (b) $120(+200)$ dark-field (DF) image of another region in the same film used for (a).

caused probably by considerable relaxation before isothermal crystallization at -5°C because of the lower degree of polymerization of CR than of NR.

In Figure 1b, dark areas of 0.5 – $1\ \mu\text{m}$ in width and bright ones of *ca.* $0.2\ \mu\text{m}$ are also recognized, both of which are elongated in the vertical direction (stretching direction). This uneven darkness in the image means that the thickness of the specimen film is not constant, and the darker the thicker. (The black spots in the figure are dust particles.)

Figure 2a demonstrates a representative ED pattern from the CR thin film which was prestretched quickly by hand up to $\epsilon \approx 500\%$ and then crystallized at -5°C for about 1 h. The 002 reflection on the meridian reveals that the *c*-axis is highly oriented in the stretching direction. On the equator, the strong $120(+200)$ and fairly strong 210 reflections are observable. The appearance of this fairly strong 210 reflection seems to mean that the specimen film has so-called fiber structure. The degree of arcing of these reflections is much smaller than that in Figure 1a, indicating that the degree of chain orientation is much higher than that for $\epsilon \approx 600\%$. It is deduced that by quick stretching, the structure induced by pre-stretching was preserved in the resulting film. In Figure 2a, accordingly, the 002 reflection is streaked in the direction parallel to the equator. The off-meridional 011 reflection is also streaked parallel to the equator. The $120(+200)$ and 210 reflections on the equator exhibit slight broadening along the equatorial direction, but not seriously. The fairly sharp reflections on the equator and other streaked reflections seem to indicate the existence of paracrystalline nature.²⁵ That is to say, it is presumed that the film under consideration has fiber structure accompanied by lattice distortion due to the axial shift of chain stems relative to one another along the chain axis (*c*-axis).²⁵ The $120(+200)$ and 210 reflections are slightly broadened along the equator in comparison with the ones in Figure 1a, and this fact seems to indicate that the corresponding crystallite size decreased by fibrillation due to the faster prestretching for sample preparation.

Figure 2b is the dark-field image taken by using the $120(+200)$ reflection, which was obtained from another region in the same film that was used to obtain Figure 2a. In such a dark-field image, crystallites which have given the reflection in question in the ED pattern are ex-

pected to be much brighter than their amorphous surroundings and also the rest of crystallites.¹³ Therefore, bright narrow striations (or rods) of *ca.* 100 nm in length, which are observed to orient almost perpendicularly to the stretching direction in Figure 2b, are crystalline entities. As in our previous reports,^{11,13} it can be concluded that each of the narrow bright striations (or rods) in Figure 2b is an edge-on crystalline lamella or a part of it, and these striations are shorter than those in the moderately prestretched films: The length (*ca.* 100 nm) of the striations (or rods) in Figure 2b is smaller than that (*ca.* 200 nm) in the specimen prestretched by $\epsilon \doteq 200\%$ ^{11,13} and also smaller than that (*ca.* 200 nm) in the one prestretched quickly by $\epsilon \doteq 250\%$.¹¹

Unfortunately for the moment, we have neither dark-field image corresponding to Figure 1b nor bright-field image corresponding to Figure 2b. As mentioned above, one bright striation (or rod) in the dark-field image does not always correspond to one whole edge-on lamella but corresponds to a part of it. It can, however, be postulated that the length of edge-on lamellae, namely that of the dark striations (α -filaments) in the bright-field image (for example, Figure 1b) decreases with increasing amount of pre-strain (ϵ), taking account of the morphological similarity and difference between Figure 1b for $\epsilon \doteq 600\%$ and the bright-field images of moderately prestretched specimens¹¹. It is, accordingly, assumed that the population density of "nucleating threads" (*viz.*, γ -filaments) increases with increasing ϵ and the length of the edge-on lamellae (α -filaments) is limited owing to collision with their neighbors. This morphological change that the length of α -filament, namely the length of the edge-on lamellae, decreases with increasing ϵ is also in accord with the results reported so far for OsO₄-stained CR¹⁰ and NR.^{2,4} In Figure 2b, we do not recognize any regions in which striations (or rods) are closely stacked in the prestretching direction. Crystallographic orientation of the α -filaments seems to be not coherent even in a localized region, probably due to quick prestretching and the resultant rotational fluctuation of them around the stretching direction. This rotational fluctuation might come from the twisting of the nucleating thread (γ -filament) which worked as a substrate for homo-epitaxy of folded-chain lamellae onto it. As described on moderately prestretched CR in our previous paper,¹¹ the stretching rate is another factor responsible for some morphological difference similar to that discussed in this article. Taking account of the results of Figures 1 and 2 and those from ref 11, it is postulated that the higher stretching rate works so as to increase the effectiveness of a given amount of pre-strain (ϵ) on the resulting morphology in CR.

From the experimental results shown in Figures 1 and 2, the following can be proposed: In the highly prestretched and then crystallized thin films of CR, well-defined parts (*viz.*, edge-on lamellae), which give the 120 (+200) reflection on the equator in the ED pattern, ought to give also the less-streaked 002 reflection on the meridian, because these lamellae should have overgrown onto the γ -filaments and accordingly the chain axes (*c*-axes) of both lamellae and γ -filaments should have been all oriented parallel to the stretching direction. On the other hand, ill-defined parts containing a lot

Figure 3. NR thin film which was cast from a benzene solution, prestretched up to $\epsilon = 500\%$ and then isothermally crystallized at -25°C for 2 h. The stretching direction is vertical. (a) Typical ED pattern (reversed contrast). (b) 200 dark-field (DF) image of another region in the same film used for (a). (c) Bright-field (BF) defocus-contrast image from the same region used for (b). The areas indicated with the arrows in (c) show respectively the same areas in (b).

of γ -filaments, in which the chains are highly prestretched/oriented in the stretching direction and are parallel to one another but poor-packed laterally in a crystallographical sense, are to have contributed to the 002 reflection as well as to 120(+200). The γ -filaments are to be very thin (probably, not greater than several nanometers in diameter) and to have a low degree of crystalline ordering because they have never been observed up to now in our dark-field images of CR. Consequently, it might be reasonably assumed that the streaked 002 and 011 reflections in Figure 2b are attributed mainly to such ill-defined parts containing a lot of thin γ -filaments (in other words, to the regions each of which is in a paracrystalline state caused by axial shift, as described above).

Natural Rubber (NR) Thin Films Which Were Prestretched up to $\epsilon = 500$ –800%

The crystal structure of NR, namely of *cis*-1,4-polyisoprene, was first determined by Bunn.²² Four molecular chains pass through the monoclinic unit cell (space group = $P2_1/a$). The chains take an approximately planar conformation in the unit cell, and their approximated molecular planes are all parallel to the crystallographic *ac*-plane. This chain conformation is similar to that in the other crystal structure, which was proposed by Nyburg²⁶ and subsequently improved by Natta and Corradini²⁷ and in which the *pseudo*-planar chain-stems are packed in a statistical manner with their approximated molecular planes being parallel to the crystallographic *ac*-plane of the orthorhombic unit cell (space group = $P2_12_12_1$; $a = 1.246$ nm, $b = 0.889$ nm, c (chain axis) = 0.810 nm). All the ED patterns in the present study were indexed by using these unit cell dimen-

sions of orthorhombic system.

$$\varepsilon = 500\%.$$

Figure 3a shows an example of frequently observed ED patterns from the NR thin film which was cast from a benzene solution, prestretched up to $\varepsilon = 500\%$ by using the film-stretching device, and then isothermally crystallized at -25°C for 2 h. The chain axis (*c*-axis) is oriented rather highly in the stretching direction, because the 002 and 004 reflections appear in this direction, namely on the meridian and the 200 and 400 reflections are concentrated sharply on the equator. The weak 120 reflection, however, is observed between the 200 and 400 ones though the absolute value of its structure factor has been calculated to be greater than that of 200^{22,26} (In Figure 3a, the intensity of 120 is smaller than that of 400). Hence the ED pattern shown in Figure 3a might be called the $h0\ell$ net-pattern. This fact well evidences a so-called double orientation (the uniplanar axial orientation) which is believed to be caused by the *pseudo*-planar conformation of NR chain-stems in the crystal lattice.¹³ It is concluded, therefore, that the (010) lattice plane is oriented preferentially parallel to the film surface and accordingly the electron beams are incident onto the specimen film in the direction parallel to the *b*-axis. This tendency of double orientation is similar to that for the NR film prestretched by $\varepsilon \approx 200\%$ in our previous study^{12,13} and also to that for the NR film prestretched up to $\varepsilon \approx 900\%$ in the study by Fisher.²⁸ (Fisher reported a preferred orientation, *i.e.*, the *a*- and *c*-axes tended to lie in the plane of the film, taking into consideration the ED patterns obtained from the film set perpendicular to the direction of the incident electron beams and from the same film inclined at an angle of 45° to the incident-beam direction.)

Figure 3b shows the dark-field image taken, by using mainly the 200 reflection on the equator, from the NR thin film used in taking Figure 3a. The short bright striations (or rods) are oriented perpendicular to the stretching direction and some of them are stacked in the direction (two examples of stacked striations are indicated with the arrows). Each of these short bright striations in Figure 3b is an edge-on lamella (α -filament) or a part of it. The length of the striations in Figure 3b is about 100 nm and is normally smaller than that (*ca.* 300 nm) in the case of $\varepsilon \approx 200\%$.^{12,13}

Figure 3c is the bright-field defocus-contrast image of the same region that was used for obtaining Figure 3b. The morphology in Figure 3c is representative of the NR specimens prestretched up to $\varepsilon = 500\%$. In the darker areas, α -filaments of *ca.* 30 nm wide and *ca.* 300 nm long look to be stacked in the stretching direction, as indicated with arrows in Figure 3c, though the image contrast of this figure is rather weak. The arrows in Figure 3c also indicate respectively the same areas that are indicated with the arrows in Figure 3b, and each of these areas corresponds to a part of a row (or shish-kebab) structure. The darker areas in Figure 3c are crystalline regions in which α -filaments, namely edge-on lamellae, are stacked in the stretching direction. This is in accord with the result for highly prestretched CR (for example, Figure 1), though the edge-on lamellae in NR are much shorter than those in CR.

Figures 4a and 4b are bright-field defocus-contrast im-

Figure 4. Bright-field (BF) defocus-contrast images of different specimen portions from those used for Figure 3 (NR thin film which was cast from a benzene solution, prestretched up to $\varepsilon = 500\%$ and then isothermally crystallized at -25°C for 2 h). The stretching direction is vertical.

ages obtained from different regions in the NR thin film which was cast from a benzene solution, prestretched up to $\varepsilon = 500\%$ by using the film-stretching device, and then crystallized at -25°C for 2 h. In both figures, many α -filaments are observed as dark striations of *ca.* 25 nm in width. The crystalline textures in these figures are grouped into four different kinds of domains, namely A-, B-, C-, and D-domains which are indicated, respectively, with the arrows and letters A, B, C, and D. The A-domains are a typical example of the crystalline textures in NR thin films prestretched up to $\varepsilon = 500\%$ in the present study, and each of them shows the similar morphology to that of Figure 3c. That is to say, the morphologies of B-, C-, and D-domains are not typical for the specimen films prestretched up to $\varepsilon = 500\%$, and were occasionally observed.

Each of the A-domains can be assigned to a crystalline region in which short edge-on lamellae (α -filaments) are oriented perpendicular to the stretching direction and some of them are stacked in the direction. The length (*ca.* 300 nm) of the edge-on lamellae is fairly limited in such an A-domain. The reason for this limitation is thought to be that the population density of certain "crystalline entities" made only by prestretching was very high, in which the chain axis is oriented almost parallel to the stretching direction and which are considerably slender and work as a substrate for overgrowth of lamellae. (These "crystalline entities" correspond to the "nucleating threads" described above for CR. In the following section of this report (at the discussion about Figure 6), these "crystalline entities" will be confirmed to be really crystalline and assigned to the γ -filaments.)

Each of the B-domains has a thinner area at its own center and has relatively long edge-on lamellae (ca. 0.5 μm in length) connected to the area. The area is supposed to be crystalline, and a large number of "crystalline entities" made by prestretching are to orient in the stretching direction in the area. Only when the space is enough for lamellae to grow perpendicularly to the stretching direction, they are nucleated onto the "crystalline entities" in the area and grow outward in the direction perpendicular to the stretching direction.

The C-domain has a small sheaf-like structure, which was accidentally oriented with its long axis being roughly perpendicular to the stretching direction. The orientation of another sheaf, for example that of a sheaf neighboring to the right-hand side of the arrowed C-domain, however, is different by about 90° from the above-mentioned orientation, and therefore such a C-domain looks to have received no (or at least very weak) effect by prestretching. Probably no "crystalline entities" could be formed by prestretching in the C-domains.

Each of the D-domains is characterized by edge-on lamellae (0.3–0.5 μm long) grown radially along the edge of the hole. Because major strains are considered to have been induced tangentially along the edge of the hole by prestretching, it is understood that lamellae, in the subsequent isothermal crystallization, were overgrown onto "crystalline entities" which had been developed along the strained edge of the hole when prestretched, and that accordingly the lamellae could grow radially along the edge of the hole.

$\epsilon = 800\%$.

Figure 5a is an example of the ED patterns from the NR thin film which was cast from an *n*-hexane solution, prestretched with the film-stretching device up to $\epsilon = 800\%$ and then isothermally crystallized at -25°C for 1 h. The chain axis (*c*-axis) is highly oriented in the stretching direction. This figure also demonstrates the presence of so-called double orientation (the uniplanar axial orientation) in the film prestretched up to $\epsilon = 800\%$, as in the case of Figure 3a for 500%. The 120 reflection in this case is still weaker than 200, but is stronger than 400 though the intensity of 120 was smaller than that of 400 in Figure 3a. Anyway, the 120 reflection is definitely recognized in Figure 5a, probably because the specimen film was undulated or fibrillated due to high prestretching.

Figure 5b is the 200 dark-field image of another region in the same film that was used to obtain Figure 5a. This dark-field image indicates that edge-on lamellae (α -filaments) are grown perpendicularly to the stretching direction, and that some of them are stacked in the direction in rather limited regions, as encircled and indicated with arrows. The lamellae, in which the chain axis is oriented almost parallel to the stretching direction, are considered to be nucleated on the "crystalline entities" generated by prestretching, and to grow perpendicularly to the stretching direction in the subsequent isothermal crystallization.

Figure 5c is the bright-field defocus-contrast image of another new region in the same specimen film used for taking Figures 5a and 5b. In this figure, very short α -filaments, namely edge-on lamellae appear as dark rods of ca. 30 nm in width to be arranged almost perpendicu-

Figure 5. NR thin film which was cast from an *n*-hexane solution, prestretched up to $\epsilon = 800\%$ and then isothermally crystallized at -25°C for 1 h. The prestretching direction is vertical. (a) Typical ED pattern (reversed contrast). (b) 200 dark-field image (reversed contrast) of another region in the same film used for (a). (c) Bright-field (BF) defocus-contrast image of another new region in the same film used for (a) and (b).

Figure 6. Bright-field (BF) defocus-contrast image obtained from the NR thin film, which was cast from an *n*-hexane solution and then prestretched up to $\epsilon = 800\%$, but was not subjected to subsequent isothermal crystallization.

lar to the stretching direction and then stacked in the direction, though the image contrast is weak. The average length (ca. 250 nm) of the edge-on lamellae in this case, which could grow perpendicularly to the stretching direction, is slightly smaller than that (ca. 300 nm) in the case of $\epsilon = 500\%$ (compare this figure with Figure 3c and with the A-domains in Figure 4).

Figure 6 is the bright-field defocus-contrast image from the NR thin film which was cast from an *n*-hexane solution and then prestretched up to 800% but was not subjected to subsequent isothermal crystallization. In this figure, the thin "fibrils" of about 25 nm in width are observed to orient almost parallel to the stretching direc-

tion, but no α -filaments are recognized. This result implies that no lamellae can grow perpendicularly to the stretching direction without subsequent isothermal crystallization. It is supposed that each of the thin "fibrils" recognized in Figure 6, which are winding (not straight) but oriented almost parallel to the stretching direction, consists of a large number of "crystalline entities" generated only by prestretching because such a specimen film before isothermal crystallization has already been partly crystalline and undoubtedly given crystalline reflections in its ED pattern.^{18,19} Taking into account the result obtained by Andrews⁵ that the morphology for $\varepsilon > 300\%$ is characterized by "chains of nuclei" (γ -filaments) oriented parallel to the stretching direction, the "crystalline entities" (this terminology has frequently been used above for NR in this article) are to correspond to the γ -filaments. Later on, Yau and Stein,²⁹ on the basis of the low-angle light scattering from stretched NR films, proposed that a γ -filament was a row-like cluster consisting of a large number of short α -filaments: These α -filaments were oriented perpendicular to the stretching direction but the resulting γ -filament was slightly leaned against the stretching direction, making an angle of about $\pm 10^\circ$ to the stretching direction. As written above, Figure 5c was obtained from the NR thin film which had been prestretched up to 800% and then crystallized isothermally. In that figure, we can also recognize another texture in addition to the stacked-lamellar structure, that is to say, it is recognized that some fairly thick elongated domains (200–300 nm in width) are leaning to the left by 20–25° against the vertical (namely, stretching) direction. A typical example is indicated with the arrow in Figure 5c. In such a domain, the edge-on lamellae, *viz.* α -filaments, which have grown perpendicularly to the stretching direction, are organized in piles; the resulting elongated domain makes, accordingly, an angle of 20–25° to the stretching direction. Though the lean angle is different, the texture in Figure 5c resembles the structure model of γ -filaments proposed by Yau and Stein.²⁹ More detailed study is, however, needed to clarify this subject.

Yau and Stein³⁰ and Mitchell and Meier³¹ demonstrated that crystallization of NR at high ε occurred almost immediately. It is difficult, however, to imagine that lamellae, even if fairly short, grow perpendicularly to and stack themselves in the stretching direction on prestretching the NR. In connection to this discussion, we should refer here again to the important result by Owen¹⁴ which was cited by Andrews and Reeve¹⁰: There was a central thread on which folded-chain lamellae (α -filaments) were nucleated, and the lamellae could be melted off, leaving only the central thread of *ca.* 3 nm in diameter. It is deduced, therefore, that each of the thin fibrils (*ca.* 25 nm in width) observed in Figure 6 consists of some γ -filaments (probably, several nanometers in width or below) and that one γ -filament corresponds to a "shish" crystal which is made up of chains extended highly by prestretching. In a thin fibril, the γ -filaments, namely "shishes" seem to be bundled in an incoherent manner. The γ -filaments in NR are to be very thin and to have a low degree of crystalline ordering because we have never recognized them in our dark-field images of NR. In any event, the γ -filament is a chain of nuclei run-

ning in the stretching direction, not a cluster of short α -filaments.

From the TEM observations of NR thin films which were prestretched up to $\varepsilon = 500\%$ or 800% ¹⁸ and $\varepsilon \approx 200\%$,^{12,13} it is concluded that the length of edge-on lamellae (α -filaments), which are oriented perpendicular to the stretching direction, decreases with increasing ε , because the population density of the γ -filaments generated by prestretching increases with increasing ε and the space for lamellae to grow laterally, namely perpendicularly to the stretching direction, in the subsequent isothermal crystallization decreases with increasing ε . Particularly in the case of $\varepsilon = 800\%$, lamellae are confined within much smaller space for lateral growth. These results are also in accord with that obtained for quickly prestretched CR (Figure 2), taking into consideration the effect of the stretching rate on the resultant morphology. As in the case of CR, our TEM images obtained for NR, which was prestretched up to $\varepsilon = 500\%$ or 800% and then crystallized isothermally at -25°C , showed undoubtedly the α -filaments, though Andrews⁴ proposed that no α -filaments were observed in the case for $\varepsilon > 300\%$. This might be due to partial relaxation before isothermal crystallization.

CONCLUDING REMARKS

In this article, morphological studies on NR thin films prestretched up to $\varepsilon = 500\%$ or 800% and on CR ones prestretched by $\varepsilon = 500$ – 600% were carried out to shed light on the entity of the γ -filament and on the crystallization mechanism under high molecular-orientation. Every morphology observed in the prestretched and then isothermally crystallized NR and CR in this article and also in our previous reports^{11–13} corresponds to Andrews' structure model for smaller ε than for the really given ε . Such morphological difference is deduced to be due to partial relaxation of polymer chains in the waiting period between sample preparation outside and isothermal crystallization inside the TEM column. The following results, however, have been obtained:

- 1) The γ -filaments, where the chain axis is oriented in the stretching direction and which are fairly slender, are speculated to correspond to "shish" crystals formed immediately by prestretching. The lamellae (α -filaments) are nucleated onto these γ -filaments, namely onto the "shish" crystals and grow perpendicularly to the stretching direction in the subsequent isothermal crystallization.
- 2) From the morphological studies on NR thin films which had been prestretched up to $\varepsilon = 500\%$ or 800% and then crystallized at -25°C , it was concluded that the average length of the lamellae, which were grown perpendicular to the stretching direction, decreases with increasing ε , because the length is dependent greatly on the population density of γ -filaments generated by prestretching, that is to say, because the space for the lamellae to grow laterally in subsequent isothermal crystallization decreases with increasing ε .
- 3) The thin "fibrils" were oriented parallel to the stretching direction in the NR thin film prestretched up to $\varepsilon = 800\%$ without the subsequent isothermal crystallization, and each of them was judged to consist of some γ -

filaments running in the stretching direction.

4) The thin film of CR, which had been quickly pre-stretched up to $\varepsilon \doteq 500\%$, gave a characteristic ED pattern in which off-equatorial reflections were streaked in the direction parallel to the equator, and therefore the film has so-called fiber structure accompanied by paracrystalline nature, namely by lattice distortion due to the axial shift of chain stems. These streaked reflections in the ED pattern seem to come mostly from the γ -filaments in the system.

5) From the above considerations (1)–(4), it is speculated that the γ -filament in CR and NR is a very slender “continuous crystalline entity” (namely, a shish crystal) of several nanometers in diameter or below but is not a row-like cluster of short α -filaments. In some case, the γ -filament might have a low degree of crystalline ordering (For example, it might be in a paracrystalline state caused by the axial shift of chain stems relative to one another along the chain axis). These seem to be major reasons for that they have never been observed up to now in our dark-field images of CR nor NR: CR and NR, of course, exhibit rubberlike elasticity, but for example, isotactic polystyrene (i-PS), in which shish crystals have already been visualized so far by dark-field imaging³² and also by high-resolution imaging,³³ is not a so-called rubberlike polymer. By the way, the CR and NR crystals are much more vulnerable to electron irradiation than the i-PS one,^{19,34} and this might be another reason.

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