Polymer 42 (2001) 5543–5547

polymer

www.elsevier.nl/locate/polymer

# Crystal transitions of Nylon 11 under drawing and annealing

Qingxin Zhang[a], Zhishen Mo[a,*], Hongfang Zhang[a], Siyang Liu[a], S.Z.D. Cheng[b]

[a]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China*

[b]*Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA*

Received 21 July 2000; received in revised form 16 October 2000; accepted 29 December 2000

**Abstract**

The crystal transitions of Nylon 11 annealed and drawn at different temperatures ($T_d$) with different drawing ratios ($n$) were investigated by wide-angle X-ray diffraction (WAXD). The α-form of Nylon 11 could be transformed from the δ′-form by annealing at high temperature. The results showed that the crystal transitions of Nylon 11 strongly depended on the thermal history and the conditions of drawing. The δ′-form Nylon 11 could be gradually transformed into the α-form when it was drawn at high temperature and the α-form was only partly transformed into the δ′-form when it was drawn at low temperature. This should be due to the effect of the competition between thermal inducement and drawing inducement. The thermal inducement was favorable to producing the α-form, while the drawing inducement was favorable to producing the δ′-form. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Nylon 11; Crystal transition; WAXD

## 1. Introduction

Nylon 11 is a high-performance semicrystalline polymer. In recent years, the curious piezoelectric and ferroelectric properties of Nylon 11 have been studied [1–5]. It is well known that its piezoelectricity is related to the crystal forms of Nylon 11. In order to find out the relationship between its piezoelectric properties and crystal structure, the polymorphism of Nylon 11 has been demonstrated by several researchers [6–14]. Nylon 11 has been found to have at least five crystal forms: the triclinic α-form, the monoclinic β-form and three hexagonal or pseudo-hexagonal forms (γ, δ and δ′-forms) with different crystal lattices. Isothermal crystallization of Nylon 11 from the melt [6] and solvent cast films [8] (from a phenol/formic acid solution) give the polar α-form which reflects two strong X-ray reflections (100) and (010) with $d$ spacings at 0.44 and 0.37 nm, respectively. Slichter [7] studied the crystal structures of Nylon 11 and reported the lattice of the triclinic unit cell (α-form): $a = 0.49$ nm, $b = 0.54$ nm, $c = 1.49$ nm, $\alpha = 49°$, $\beta = 77°$ and $\gamma = 63°$. Kawaguchi [10] obtained the triclinic α-form and the other two forms of Nylon 11 from different solutions sealed in glass tubes and their unit cell dimensions: the monoclinic β-form ($a = 0.98$ nm, $b = 1.5$ nm, $c = 0.80$ nm, $\beta = 65°$) and the pseudo-hexagonal γ-form ($a = 0.95$ nm, $b = 2.94$ nm, $c = 0.45$ nm, $\beta = 118.5°$). The δ-form [11] appears to be somewhat similar to the "smectic" pseudo-hexagonal δ′-form obtained by quenching the melt into an ice bath [3], but the reflection at 0.42 nm appears much sharper than that of the δ′-form.

The ferroelectric and piezoelectricity of Nylon 11 films with different drawing ratios shows more obvious piezoelectricity [15,16]. However, little attention has been paid until now to the crystal form transitions of Nylon 11 at different drawing temperatures with different drawing ratios. The purpose of this work is to examine the crystal transitions of the δ′-form and the α-form Nylon 11 during hot drawing by wide-angle X-ray diffraction (WAXD).

## 2. Experimental section

### 2.1. Materials and preparation of the samples

Semitransparent granules of Nylon 11 were synthesized by Changchun Institute of Applied Chemistry ($M_n = 16,000$), the glass transition temperature $T_g$ is 42°C and the melting temperature $T_m$ is 184°C.

The granules of Nylon 11, dried in a vacuum oven at 90°C for 1 week, were sandwiched between aluminum foils, hot

* Corresponding author. Tel.: +86-431-568-2801; fax: +86-431-568-5653.

*E-mail address:* mozs@ns.ciac.jl.cn (Z. Mo).


PII: S0032-3861(01)00050-7

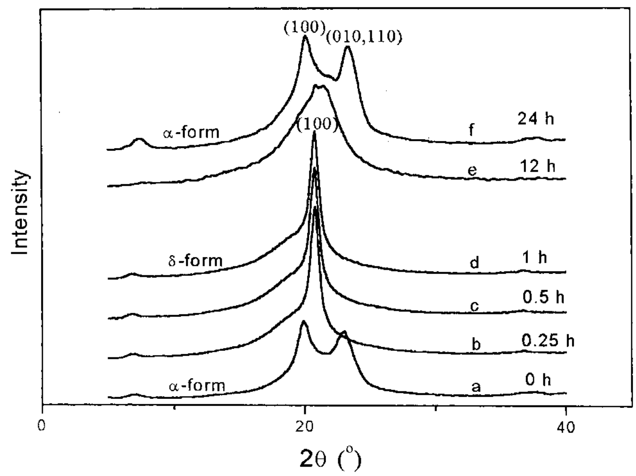


Fig. 1. WAXD patterns of α-form Nylon 11 annealed at 165°C for different times: (a) original sample, (b) 0.25 h, (c) 0.5 h, (d) 1 h, (e) 12 h, and (f) 24 h.

pressed to the melt and then quenched into an ice bath to form δ′-form [3] films with thicknesses of about 0.1 mm. The α-form Nylon 11[6] was produced by isothermal crystallization at 165°C for 1 h from the melt.

### 2.2. Instrument and experiments

The films were drawn (drawing speed = 1 cm/min) by an INSTRON-1211 tensile tester at different drawing temperatures ($T_d$) with different drawing ratios ($n$) ($T_d$ and $n$ were shown in the corresponding figures).

WAXD was performed at room temperature using a Rigaku D/max II B diffractometer operated at 40 kV and 20 mA with curved graphite crystal filtered, CuK$\alpha_1$ radiation ($\lambda = 0.15406$ nm). The specimens were fixed on the equipment with a rotating sample-stage and the data were collected with a step interval of 0.02°.

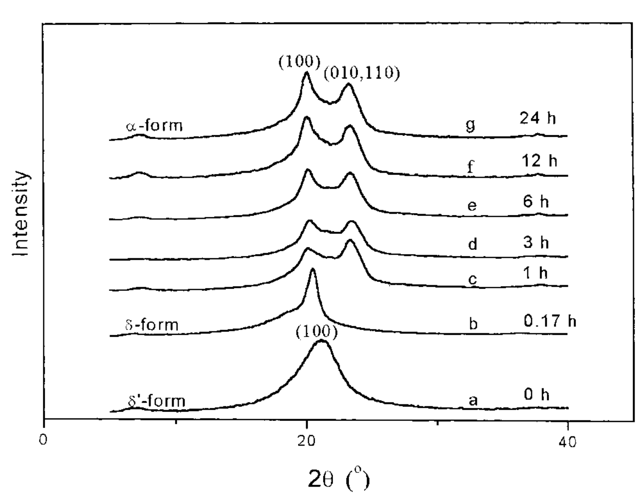


Fig. 2. WAXD patterns of δ′-form Nylon 11 annealed at 165°C for different times: (a) original sample, (b) 0.17 h, (c) 1 h, (d) 3 h, (e) 6 h, (f) 12 h, and (g) 24 h.

## 3. Results

### 3.1. Crystal transitions at high temperature

Fig. 1 presented the WAXD patterns of the α-form of Nylon 11 annealed at 165°C for different times. It can be seen that the original sample (sample a) exhibited two strong reflections (100) and (010,110) at the diffraction angle 2$\theta$ of 20.02 and 23.01°, which were characteristic of the triclinic α-form. The α-form transformed into the δ-form which showed only one strong (100) reflection (samples b–d) when they were heated to 165°C. However, with the increase of anneal time, the reflection (100) of the δ-form split into two reflections when the anneal time was long enough such as 12 h (sample e) and these two reflections split more obviously with the increase of annealing time (sample f). Annealing of the sample increased the reflection intensity and the two reflections separated more obviously, which indicated that the sample crystallized in the triclinic α-form structure. Structural investigation showed that the crystal transition occurred during the annealing process from the pseudo-hexagonal δ′-form structure to the triclinic α-form structure. These results also indicated that the prolonged annealing of Nylon 11 improved the order of the hydrogen bonds within the sheets and increased the crystal perfection of the polymer [17].

The pseudo-hexagonal δ′-form, produced by quenching the melt into an ice bath [3], was referred to be a “smectic phase”. Fig. 2 showed the WAXD patterns of the δ′-form Nylon 11 annealed at 165°C for different times. It can be seen that the original δ′-form sample (sample a) showed one strong and broad reflection (100) with the $d$ spacing of 0.42 nm. The hexagonal δ-form, produced from the δ′-form at 165°C, was observed with a stronger and sharper reflection at 0.43 nm (sample b). The (100) reflection split into two reflections within a short time when the δ′-form films were annealed at 165°C. The two-peak nature of the WAXD pattern indicated that the sample had crystallized in the triclinic α-form.

### 3.2. Crystal transitions at the same temperature with different drawing ratios

The α-form Nylon 11 films were drawn with $n = 2, 3, 5$ at the same drawing temperature ($T_d = 80°C$) and their WAXD patterns were shown in Fig. 3. Sample a was the original one (α-form) and the drawing ratios $n$ were 2, 3, and 5 for samples b–d, respectively. The (001) reflection of the α-form ($d_{001} = 1.18$ nm) disappeared and the other two reflections (100) and (010,110) broadened and approached each other with the increase of drawing ratio. The plot of the $d$ spacings of (100) and (010,110) reflections of the α-form vs. drawing ratios were shown in Fig. 4. It revealed the approach trend of the (100) and (010,110) reflections, which also showed the triclinic α-form to the pseudo-hexagonal δ′-form transition trend during the drawing process.

The WAXD patterns of the δ′-form Nylon 11 with various drawing ratios at the same drawing temperature

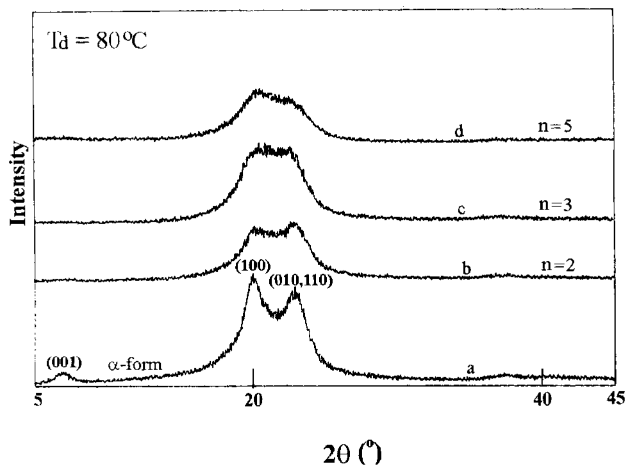


Fig. 3. WAXD patterns of α-form Nylon 11 drawn at 80°C with different drawing ratios: (a) original sample, (b) $n = 2$, (c) $n = 3$, (d) $n = 5$.

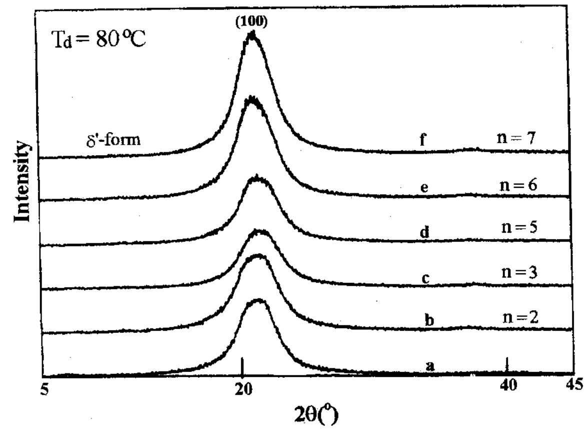


Fig. 5. WAXD patterns of δ′-form Nylon 11 drawn at 80°C with different drawing ratios: (a) original sample, (b) $n = 2$, (c) $n = 3$, (d) $n = 5$, (e) $n = 6$, (f) $n = 7$.

($T_d = 80°C$) were shown in Fig. 5. All the WAXD patterns showed a similar strong reflection at about $2\theta = 21°$ which corresponded to the $d$ spacing of about 0.42 nm. The reflection became sharper and stronger with the increase of drawing ratios, which indicated that the degree of crystallinity of the pseudo-hexagonal δ′-form increased.

In order to test the stability of the drawn δ′-form Nylon 11 films, we placed them at room temperature for more than 2 months without any drawing stress. The WAXD patterns of these samples changed little, which indicated that the δ′-form produced by drawing at low temperature ($<T_g$) was stable. It was a useful method to produce the piezoelectric films because only the δ′-form Nylon 11 films were found to exhibit obvious piezoelectric property [15].

### 3.3. Crystal transition of Nylon 11 at different temperatures with the same drawing ratio

Fig. 6 showed the WAXD patterns of α-form Nylon 11 films drawn at different temperatures with the same drawing ratio ($n = 5$). It could be seen the original sample (sample a) exhibited two strong reflections (100), (010,110) at the $d$ spacings of 0.42 and 0.38 nm. Samples b–f were drawn at 40, 80, 100, 120, and 160°C, respectively. Sample b only showed one strong reflection (100) which was very similar to the pseudo-hexagonal δ′-form structure. With the increase of $T_d$, the reflection (100) began to separate and two reflections appeared as shown in Fig. 6. Moreover, the (100) reflection of sample f drawn at 160°C showed more obviously and the (010,110) reflection became very sharp and strong. These results indicated that the α-form transformed into the δ′-form when they were drawn at low temperature, but the content of the α-form increased with the increase of $T_d$.

The quenched films of Nylon 11 (δ′-form) were drawn at different $T_d$ with the same drawing ratio ($n = 5$), and the results were presented in Fig. 7. Sample a was the original one and samples b–g were drawn at 40, 80, 95, 100, 120,

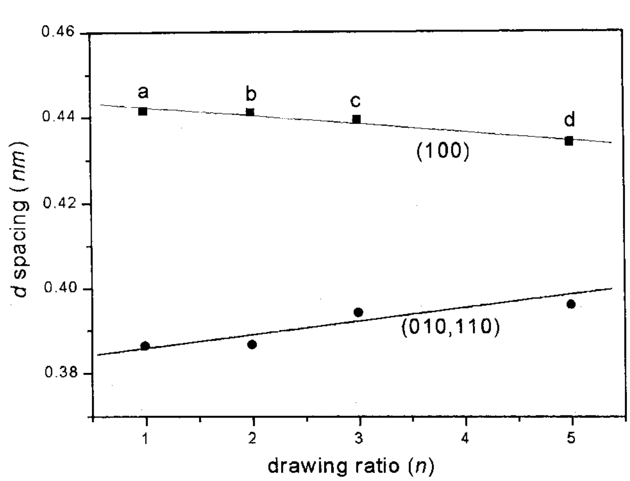


Fig. 4. $d$ Spacings of (100) and (010,110) reflections of Nylon 11 with various drawing ratios.

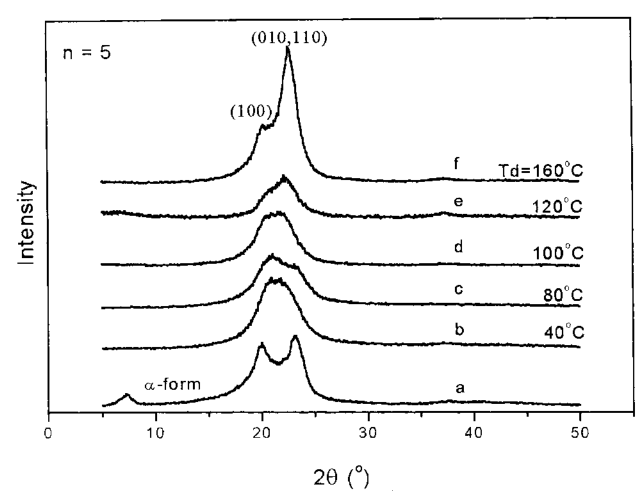


Fig. 6. WAXD patterns of α-form Nylon 11 drawn at different temperatures with the same drawing ratio ($n = 5$) : (a) original sample, (b) $T_d = 40°C$, (c) $T_d = 80°C$, (d) $T_d = 100°C$, (e) $T_d = 120°C$, and (f) $T_d = 160°C$.

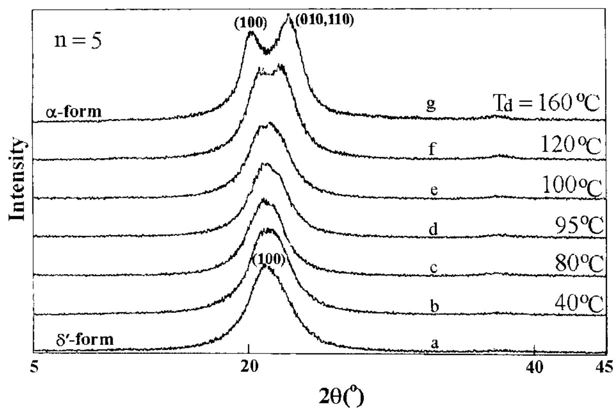


Fig. 7. WAXD patterns of α-form Nylon 11 drawn at different temperatures with the same drawing ratio: (a) original sample, (b) $T_d = 40$°C, (c) $T_d = 80$°C, (d) $T_d = 95$°C, (e) $T_d = 100$°C, (f) $T_d = 120$°C, and (g) $T_d = 160$°C.

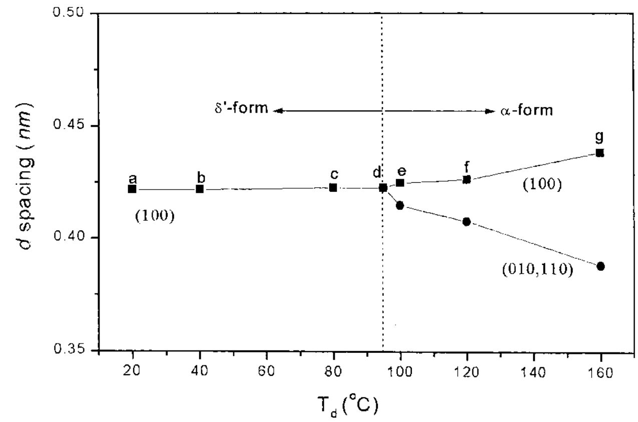


Fig. 8. $d$ spacings of (100) and (010,110) reflections of Nylon 11 drawn at different drawing temperatures.

and 160°C, respectively. The δ′-form films were stable after being drawn at low temperatures (samples b and c), but its reflection (100) began to split at $T_d = 95°C$ (sample d) and the splitting trend was more obvious with the increase of $T_d$ (sample f). The WAXD pattern of sample g drawn at 160°C was the same as that of the α-form. It could be seen that the δ′-form Nylon 11 drawn with a certain drawing ratio transformed into the α-form when it was drawn at high temperature. The δ′–α transition took place when $T_d$ was above 95°C and this transition became more obvious at high $T_d$. The $d$ spacings of (100) and (010,110) reflections at various $T_d$ were shown in Fig. 8, which also obviously indicated the δ′–α form transition at $T_d > 95$°C.

## 4. Discussion

In general, Nylon 11 crystallizes into a structure consisting of a three-dimensional order of the hydrogen-bonded sheets with maximum coupling between adjacent amide groups within a hydrogen-bonded sheet [7]. The methylene segments and amide groups would get more kinetic energy at high temperature. The α-form and δ′-form exhibited the similar transition behavior of transforming into δ-form if they were heated to high temperature. But with the increase of anneal time, the metastable δ-form transformed into the α-form. Balizer et al. [14] reported the triclinic α-form of Nylon 11 was stable below 95°C and the hexagonal δ-form was stable from 95°C to the melting temperature. However, on the basis of our experimental results, the hexagonal δ-form was metastable at high temperature and it was only a production on terms of dynamics, and the triclinic α-form was the stable structure for Nylon 11 from room temperature to its $T_m$ in terms of thermodynamics.

The above results also indicated that there was a competition between the thermal inducement and drawing inducement. On the basis of these WAXD results, a conclusion could be drawn that the thermal inducement was favorable to forming the α-form within a certain drawing ratio. The stable δ′-form Nylon 11 could be produced by being stretched at low temperature (see Fig. 5) which indicated the drawing inducement was favorable to forming the δ′-form. However, when the thermal inducement and the drawing inducement coexisted during the crystallization process, the competition of both effects would coexist together. When $T_d$ was below 95°C, the drawing inducement was dominant during the transition process, and the characteristic reflection of the δ′-form appeared in WAXD patterns, there was only a single reflection at $2\theta = 21°$ approximately. With the increase of $T_d$ ($T_d > 95°C$), the single reflection was gradually divided into two reflections and the distance of these two reflections increased too. At high drawing temperature, for example $T_d = 160°C$, only the α-form was produced, but because the (010) plane was a hydrogen-bond plane, the priority growth direction was changed by stretching and the reflection of the (010,110) plane became more intense.

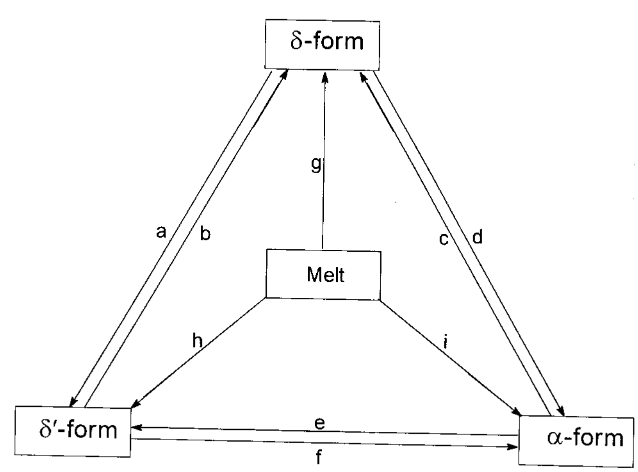


Fig. 9. Crystal transitions of Nylon 11: (a) quenching into ice bath, (b) heating to high temperature (>95°C), (c) heating to high temperature (>95°C), (d) isothermal crystallization at high temperature (>95°C), (e) drawing at low temperature (<95°C), (f) annealing at high temperature (>95°C), (g) cooling to high temperature (>95°C), (h) quenching into ice bath, and (i) isothermal crystallization at high temperature (>95°C).

## 5. Conclusions

The crystal transitions of Nylon 11 at high temperature were studied by wide-angle X-ray diffraction (WAXD). The pseudo-hexagonal $\delta'$-form transformed into the $\alpha$-form when it was annealed at high temperature. The crystal transitions of Nylon 11 drawn at various temperatures with different drawing ratios were investigated. The results showed that the crystal transitions of Nylon 11 strongly depended on the thermal history and the conditions of hot drawing. The $\delta'$-form Nylon 11 could be gradually transformed into the $\alpha$-form when it was drawn at high temperature. This could be due to the effect of the competition between thermal inducement and drawing inducement. The thermal inducement was favorable to producing the $\alpha$-form, while the drawing inducement was favorable to producing the $\delta'$-form and the results of crystal transitions of Nylon 11 were summarized in Fig. 9.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 59873023) and subsidized by Special Funds for Major State Basic Research Projects.

## References

[1] Newman BA, Chen PK, Pae KD, Scheinbeim JI. J Appl Phys 1980;51(10):5161.
[2] Mathur SC, Scheinbeim JI, Newman BA. J Appl Phys 1984;56(9):2419.
[3] Lee JW, Takase Y, Newman BA, Scheinbeim JI. J Polym Sci Polym Phys 1991;29:273.
[4] Takase Y, Lee JW, Scheinbeim JI, Newman BA. Macromolecules 1991;24:6644.
[5] Scheinbeim JI, Lee JW, Newman BA. Macromolecules 1992;25:3729.
[6] Schmidt GF, Stuart HZ. Z Naturforsch (A) 1958;13:222.
[7] Slichter WP. J Polym Sci 1959;36:259.
[8] Sasaki T. J Polym Sci B 1965;3:557.
[9] Chen PK, Newman BA, Scheinbeim JI, Pae KD. J Mater Sci 1985;20:1753.
[10] Kawaguchi A, Ikawa T, Fujiwara Y, Tabuchi M, Monobe K. J Macromol Sci Phys B 1980;20(1):1.
[11] Newman BA, Sham TP, Pae KD. J Appl Phys 1977;48(10):4092.
[12] Kim KG, Newman BA, Scheinbeim JI. J Polym Sci Polym Phys 1985;23:963.
[13] Mathias LJ, Powell DG. Macromolecules 1990;23:963.
[14] Balizer E, Fedderly J, Haught D, Dickens B, Dereggi AS. J Polym Sci Polym Phys 1994;32:365.
[15] Wu SL, Scheinbeim JI, Newman BA. J Polym Sci Polym Phys 1999;37:19.
[16] Mathur SC, Newman BA, Scheinbeim JI. J Polym Sci Polym Phys 1988;26:447.
[17] Statton WO. J Polym Sci C 1967;18:33.