JOURNAL OF MATERIALS SCIENCE **37** (2002) 1027–1032

The effect of concentration distribution of Gauche conformation on ultra-drawing of ultrahigh molecular weight polyethylene gel-films prepared from solution

WENMIN PANG, RONGRONG QI, QINGREN ZHU, CHENGGAO FAN
Structure Research Laboratory, University of Science and Technology of China,
Hefei, Anhui 230026, People's Republic of China
E-mail: zhuqr@ustc.edu.cn and pangwm@ustc.edu.cn

This paper reports the relationship between ultra-drawing and chain formation with gauche conformation in ultrahigh molecular weight polyethylene (UHMWPE) gel-films, which were prepared under several different concentrations, measured by infrared analysis. We demonstrated the effect of concentration distribution of gauche conformation on the ultra-drawing of UHMWPE gel-films. The relationship between the concentration distribution of gauche conformation and chain entanglement is also discussed here. It was found that the concentration of gauche conformation, defined by IR intensity ratio: $\sigma = I_{1303}/I_{1352}$, increased as the film-casting concentration increased. The UHMWPE gel-film prepared from the solution around the critical concentration (400–500 kg/m^3) showed the highest draw ratio ($\lambda > 300$). The changes of gauche conformation concentration correspond to that of chain entanglement number deduced by Matuso from specific viscosity. The σ value of UHMWPE gel-films decreased to a constant one after heat treatment. The heat treatment temperature affected the σ value more than the heat treatment time did. The σ value remained unchanged after heating the sample for 5 min at the drawing temperature. These results are consistent with the hypothesis that annealing at the drawing temperature is a prerequisite stage to reach ultrahigh draw ratio (Spells and Hill, *Polymer* **32** (1991) 2716). The UHMWPE gel-films could easily reach ultra-drawing ($\lambda > 300$) when they were drawn in the range of low σ values. These results were of great importance to detect and design the preparation conditions of UHMWPE gel-films deeply, the relationship between ultra-drawing and the structure texture and to ensure the ideal orientation of molecular chains.

---

1. Introduction

Flexible polymers will orient through uniaxial drawing, and the method of uniaxial drawing flexible polymers to increase the modulus and strength under appropriate conditions has been extensively applied, especially for UHMWPE quasi-dilute solution, which could form a gel through rapid cooling. From such gels have been obtained high modulus and high strength polyethylene material by spinning or ultra-drawing the UHMWPE gel-film. The modulus of the material could reach more than 200 GPa with its specific strength superior to that of high strength steel [1–5]. The significant mechanical property is due to approximately completely stretched molecular chains caused by ultra-drawing. The molecular chain is parallel to the direction of drawing and the repeat structure unit is trans-conformation. The ultimate mechanical property of drawn-orientated UHMWPE depends on the intrinsic property of its molecular chain. So, its theoretical strength should be equal to that of C—C single bond in diamond with 19 GPa in the *a*-direction and 340 GPa for the axial modulus. However, the strength and modulus of practically orientated UHMWPE samples are very inferior to the theoretical values mentioned above. To orient the molecular chain of UHMWPE as completely as possible is the key to our intention without considering the effect of chain-ends.

As shown in the previous research results, the preparation and structural morphology of the original film is of great importance for the ultra-drawing. It has been proved that the gel-film is of multi-layer-like crystalline structure and the film-casting concentration has a significant effect on obtaining the maximum drawing ratio [6, 7]. The ultra-drawing properties of UHMWPE gel-films depended on the different extents of chain entanglement between lamellar crystals caused by different solution concentrations when they were cooled to prepare gel-films. At the same time, the entanglement number was controlled to a small amount. Matsuo [4] measured the specific viscosity of UHMWPE solutions with some different molecular weights at several concentrations and found that each molecular weight UHMWPE corresponded to a specific critical concentration, at which the gel-film prepared could easily be drawn to the highest drawing ratio ($\lambda > 300$). Also he found that the value of the critical concentration (C_0) decreased as the molecular weight M_v increased. According to the above mentioned, Matsuo deduced that the chain entanglement number of each molecular chain decreased to a suitable value during the preparation of the most ideal UHMWPE gel-film which is suitable for ultrahigh drawing. However, he could not describe it quantitatively and no further experimental results has been reported thereafter. Moreover, the results of neutron scattering [8] showed that molten linear PE molecular chains entangled mutually and were in random coil confirmation; their radius of gyration did not change apparently after cooling to the solid state. It was regarded that the chain entanglement would be kept at the same position without any change. The maximum drawing ratio of PE samples crystallized from molten state was only 5–10. The assumption of chain entanglement mentioned above was often used to explain this fact [2]. Smith [2] gave the relationship between the maximum drawing ratio of gel-films prepared from solution ($\lambda_{\max}$) and the volume fraction of polymer φ in the following way:

$$\lambda_{\max} = \lambda'_{\max}\varphi^{-0.5} \qquad (1)$$

Here, $\lambda'_{\max}$ refers to the maximum draw ratio of melt-crystallized material. However, we found, from previous experimental data and the drawing results of UHMWPE gel-films, that the maximum drawing ratio of gel-film did not correspond to the extreme dilute solution from which the gel-film is prepared. To obtain ultra-drawing [6], the sample should be heated for some time at a specific temperature before it was drawn. We thought that the number of chain entanglements did not change during sample heating.

Kanamoto *et al.* [9] had obtained high draw ratios from the single-crystal-mats of UHMWPE. In the sample of single-crystal-mats, only loop chains on the surface of regular folded lamellae exists except trans-chain in the crystal lattice. No chain entanglement could be found in it. Kanamoto *et al.* explained its ultra-drawing as the inherent interaction between the chains. Recently, Matsuo *et al.* [10] tried to prove the assumption that chain entanglement affected draw ratio. They prepared single-crystal-mats with different numbers of chain entanglement by two means. They again proposed that a number of chain entanglements are necessary to obtain the ultra-drawing ratio during stretching because it could pass through the tensile stress evenly. But this was still an indirect deduction. Because of the above mentioned, we thought it possible to describe the mechanism of ultra-drawing of UHMWPE deeply and in detail if we consider the conformation of PE molecular chain in solid state.

In this article, UHMWPE gel-films with multi-layer-like lamellar structure were prepared from their quasi-dilute solutions by rapid cooling and crystallizing. These gel-films could obtain different highest drawing ratios respectively under appropriate conditions. The gauche (g) conformation between folded-chain lamellae varied with the solution concentrations because of the interaction between PE molecular chain and solvent. It is expected that this would affect the extent of chain entanglement and the ultradrawing of the gel-films. We here try to discuss it through IR results related to the "g" conformation combined with the experimental data of small-angle X-ray diffraction.

2. Experimental

2.1. The preparation of UHMWPE gel-film

UHMWPE powder with M_w of 5.2×10^6, was abstracted for 24 hours in CH_3OH then dried for 48 hours at 50°C. It was dissolved in decalin with concentration varying from 100 to 800 kg/m^3, stirred at 140°C and dissolved completely at 160°C. The solution was cast into an Aluminum bowl (120×120 mm^2) cooled by ice-water rapidly after being kept for 10 min at 150°C. The crystallizing film began to appear after 2 hours. The film was dried for 15 days at room temperature and soured in CH_3OH for 24 hours, then it was dried for 40 hours at 50°C in a vacuum oven. Then we got a dried gel-film with thickness of about 110 μm. The drawing and orientation of the gel-film were performed in a silicone-oil bath at the chosen temperature using a self-made hand-operating drawing device [6].

IR analysis was performed on a Nicolet 170SX FT-IR with resolution of 1 cm^{-1}. Many crystalline samples showed that the absorption bands between 1250–1400 cm^{-1} were that of CH_2 wagging region absorption in the amorphous region related to different "g" conformation sequences in crystalline PE. At least 4 kinds of different vibration mode absorption have been found in the region up until now [6]; they all relate to the folded-chain conformation on the surface of PE crystals and chains in the amorphous region. Further study is needed to identify the "g" conformation sequence in the area [11]. It is possible to study the change of "g" conformation by the ratio $\sigma = I_{1303}/I_{1352}$ (I_{1303}, I_{1352} represents the peak intensity at 1303 cm^{-1}, 1352 cm^{-1} in IR spectra respectively). Because the σ value is related to the selection of the base line [12], we measured the peak intensity according to the method shown in Fig. 1 in order to compare it with that in reference [12].

SAXD testing was performed on a WAXD spectrometer by self-made sample frame with slit system of (1/6)°, (1/6)°, 0.15 mm. The diffraction plane is parallel to the sample surface by symmetric reflection, while it is perpendicular to the sample surface when operating in transmission. Continuous scanning step by step with starting angle of (0.6)°(2θ) was used here.

3. Results and discussion

The IR absorption band between 1300–1400 cm^{-1} is very sensitive to the all different trans-conformation in crystalline PE. Among them are bands at 1352 cm^{-1}, 1303 cm^{-1} representing Infrared 'defect modes' of "g" conformation in PE single crystals which were

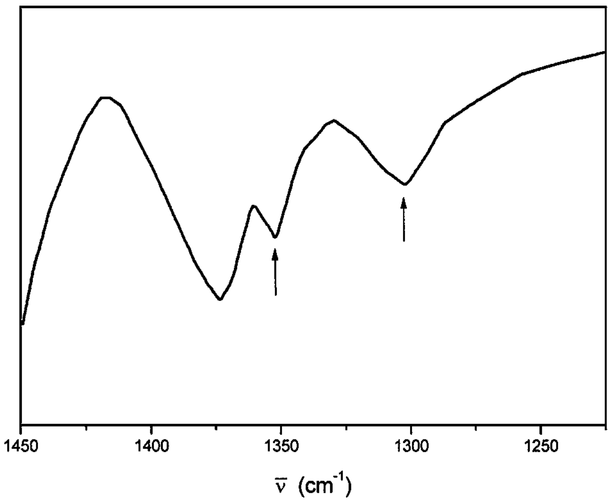

Figure 1 Determination of the base line for W_{CH2} in UHMWPE gel-film IR absorption spectrum.

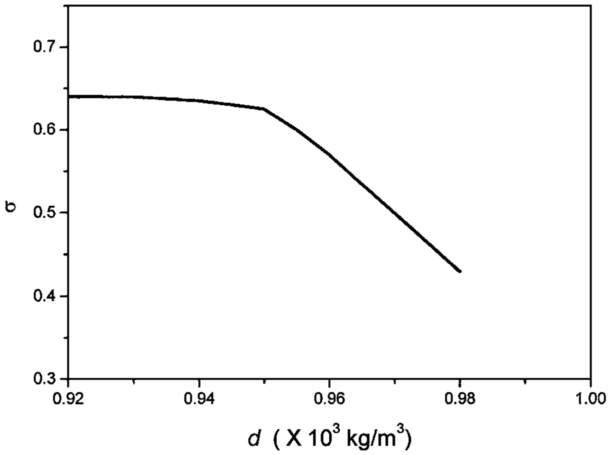

Figure 2 The curve of σ vs. d (density of PE).

regarded as GG (1352), GTG/GTG′ (1303) [10]. Hagele *et al.* [11–14] tested the IR spectrum of PE single crystals from PE dilute solution and n-alkane model compounds, and separated a band at 1346 cm^{-1} from the 1352 cm^{-1} band and attributed it as corresponding to regular neighbor folding. They regarded the conformation of folded chains on the surface of the lamellae as GGTGG. It was calculated by Krimm [16] that the CH_2 wagging mode frequency-shift of GG conformation of folded-chain plane, including chain-end GG conformation and unsaturated end GG conformation which cannot be ignored for general PE samples, varied from 1342 to 1352 cm^{-1} because of deformation. We use UHMWPE as the sample, so chain end effects could be ignored. And the absorption band 1352 cm^{-1} in Fig. 1 was mainly related to the "g" conformation of the surface of the folded chain.

Besides, Fig. 2 from reference 13 showed the curve of $\sigma = I_{1303}/I_{1352}$ versus density (d) of PE. It could be seen from Fig. 2 that the σ value is about 0.65 and keeps constant when $d < 960$ kg/m^3; σ decreases as d increases when $d > 960$ kg/m^3. The σ value for PE single crystal is 0.46. So, d is closely related to the crystallinity of PE, which practically demonstrates the change and distribution of "g" conformation on the surface of folded lamellae and the amorphous region. The gel-film prepared here is consisted of lamellae with thickness of about 11 nm and molecular chains perpendicular to the film plane. The lamellae were stacked in multi-layers and linked by random molecular chains in the amorphous region [5, 7]. This kind sample has high crystalline degree (87–90%), high density ($d > 960$ kg/m^3). The interaction between "g" conformation, in the amorphous region among the surface of multi-layer lamellae and interface, and the environment around the molecular chain is different, i.e. the change of σ would reflect directly the different conformations on the surfaces of lamellae and the randomly arranged chains in the amorphous region.

Fig. 3b shows the relationship between σ measured by IR and the solution concentration, C, when preparing the gel-film. The σ value varies from 0.46 to 0.52 within the concentration range from 100 to 400 kg/m^3 and it increases as C increases. This shows that the crystalline morphology of the gel-film prepared from this range of concentration is similar to that of a single crystal. At the same time, it is consistent with the results from X-ray diffraction and solid state high resolution NMR, i.e. the lower the film-casting concentration, the more the neighbor regular fold percentage. When C is above 400 kg/m^3, σ value increases rapidly and it seems that a critical concentration (C_0) also exists. Matsuo [4] and we all have observed the relationship between the maximum drawing ratio ($\lambda_{\max}$) and the film-casting concentration. To UHMWPE with M_{w} of 5.2×10^6 used here in our experiment, $\lambda_{\max}$ appears when C is in the range 400–500 kg/m^3 ($\lambda_{\max} > 300$) while it could hardly reach this value at other concentrations. Matsuo *et al.* [4] proposed that ultra-drawing of gel-films relied on a most suitable entanglement number which is correlated with the film-casting concentration, based on the relationship between specific viscosity (η_{sp}/C) of the film-casting solution and the film-casting concentration [See Fig. 3a]. The critical concentration point

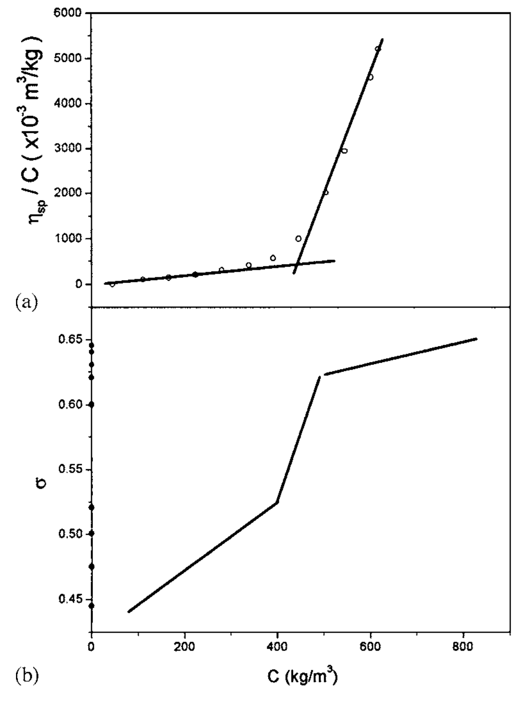

Figure 3 The curves of η_{sp}/C–C (a) and σ–C (b).

in Fig. 3 corresponds to the most suitable chain entanglement number. Chain entanglement concentration would be more or less than the most suitable one when the film-casting concentration is higher or lower than the critical concentration. This model can explain the ultra-drawing of UHMWPE gel-films well, but it could not give a satisfactory explanation for the ultra-drawing of polymer materials prepared at other conditions.

From Fig. 3a and b, it could be found that σ values characterizing the change of "g" conformations and the chain entanglement concentrations were linked in nature. It could be practically thought that the chain entanglement concentration would certainly increase as the "g" conformation in the amorphous region increases. At the same time it should be considered that the σ value also demonstrates a change in distribution of "g" conformation on the lamellae surface and in the amorphous region, regularity of folded chain surface and deformation. In Fig. 3b, films prepared from solutions with concentrations higher than C_0 are of incomplete multi-layer lamellar structures and their σ values are close to that of PE samples prepared by quenching the melt. Under such circumstances, the decreased microcrystal dimension of the sample may be attributed to loose-loops with different conformation for its surface folded chain [7].

Fig. 4 showed the SAXD results of UHMWPE gel-films with different film-casting concentration by symmetrical diffractometer reflection. The curve gives diffraction intensity distribution of planes parallel to the film plane. The first, the second and the third diffraction peak in curve c, whose film-casting concentration is C_0, are apparently visible. While for other curves for samples whose film-casting concentrations are higher than C_0, especially for those from higher concentrations, other diffraction peaks disappear except that the first diffraction peak with low diffraction angle still keeps certain intensity. The experimental results demonstrated that films prepared from around the critical concentration possessed the most regular multi-layer lamellar structure parallel to the plane. Though the multi-layer lamellar structure is also observed in the films prepared from the solution concentrations lower than C_0, it still has many defects compared with that of film prepared at C_0. We also found during drawing tests that $\lambda_{\max}$ more than 300 could easily be achieved for films prepared from around the film-casting concentration, meanwhile $\lambda_{\max}$ could hardly reach 150 at $C = 100$ kg/m^3 and $C = 700$ kg/m^3.

The relationship between "g" conformation and concentration mentioned above makes it possible to understand the stacking process of molecular chains during the forming process of multi-layer lamellae. In relatively dilute solution of practical UHMWPE molecular chains, the gelation/crystalization process mainly depends on the cohesive forces between molecular chains. In this work the thickness of inter-phase which is between lamellae of samples prepared from film-casting concentration lower than C_0 is around 2 nm, which is consistent with the theoretical value calculated from the lattice model proposed by Flory [15], illustrating that the motives to form multi-layer lamellae are mainly intra-molecular cohesive forces when UHMWPE gel crystallizes at film-casting concentrations lower than C_0. However, the inter-phase thickness is higher than the theoretical value by Flory when C is more than C_0. Besides intermolecular cohesive forces, the effects of increase in rotation energy and motion restraint and intra-chain interaction should also be considered and the plane structure of films and changes of conformation are results of comprehensive interactions of every element.

Moreover, even for films prepared from solution of film-casting concentration, the highest drawing ratio could be obtained only by treating the sample at an appropriate temperature (120–135°C) for some time. Fig. 5 shows the curve of σ value of the film (whose film-casting concentration is 400 kg/m^3) heated for 4 min at different temperatures. The σ value decreases before 110°C and reaches its lowest point at 137°C

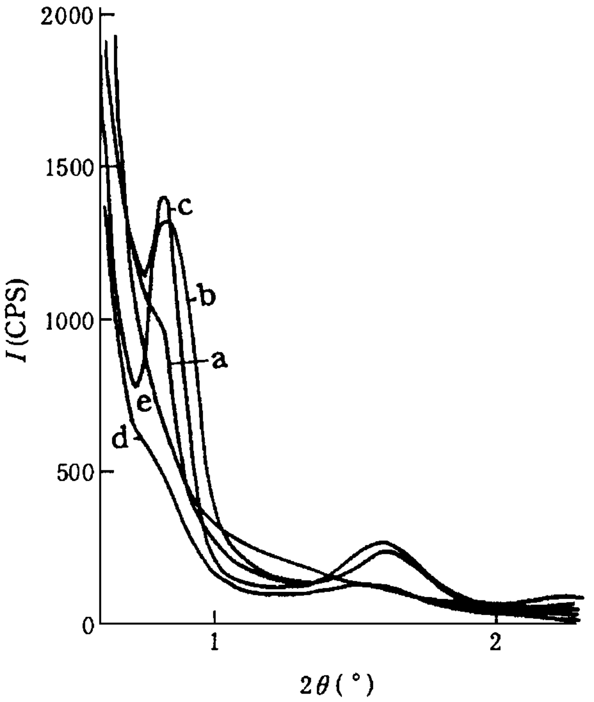

Figure 4 SAXD curves of UHMWPE gel-films prepared from different concentrations: (a) 100; (b) 300; (c) 400; (d) 500; (e) 700 kg/m^3.

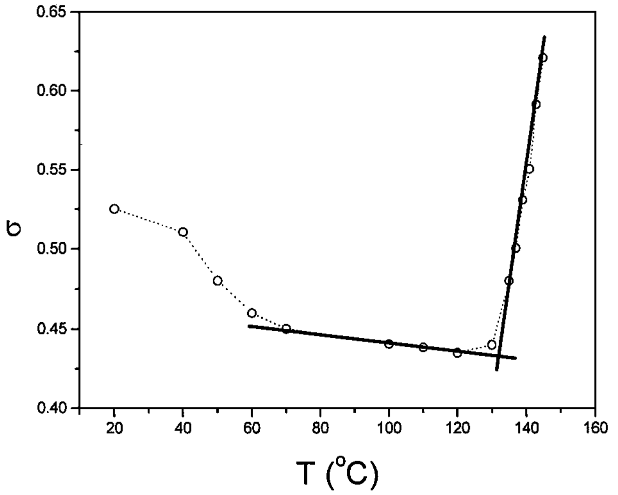

Figure 5 The curve between σ value of UHMWPE and heat treatment temperature.

TABLE I Maximum drawing ratio obtained when samples were drawn at different temperatures after heat treatment (129°C/5min)

T(°C)	25	60	90	129	140
$\lambda_{\max}$	12	30	90	300	150

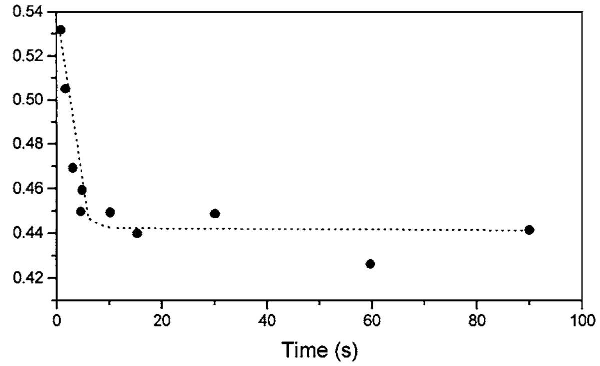

Figure 6 Time dependence of σ value for samples heated at 129°C.

($\sigma = 0.43$), which is near to the results for PE single crystal. The heat treatment temperature range corresponds to the range within which the highest drawing ratio could be obtained (see Table I), it is also consistent with the range within which the folded chains thicken and lamellae become more perfect, as detected by X-ray diffraction. The changes of σ values reflect the changes of surface folded chain conformation between multi-layer lamellae and in amorphous regions. When samples were heated at above 138°C, the σ value increased rapidly and approached gradually that of PE samples crystallized by quenching. The increase of σ value is due to the destruction of the multi-layer structure of the films when the heat treatment temperature approaches or is higher than the melting point of PE.

The σ value decreases rapidly first when the sample is heated, and reaches its lowest value after 4–5 min as shown in Fig. 6. Fig. 6 shows the relationship between σ values and the heat treatment time at 129°C. The results demonstrated that the single-crystal-like multi-layer structure of UHMWPE gel-film became perfect quickly when the sample was heated under the drawing temperature, and the consequent heat treatment temperature affects the changes and distribution of "g" conformation in the sample more than the heat treatment time does. In fact, when we determined the optimal drawing orientating conditions, we have found that heat treatment temperature affects the ultra-drawing and condensed structure of UHMWPE gel-films more than heat treatment time does [6].

To determine the effect of the changes of "g" conformation concentration on the crystalline region, the change curve of crystallite sizes in three axial dimensions measured by WAXD with heat treatment temperature was shown in Fig. 7.

In Fig. 7, the lattice constant of the (001) plane changes little, but, for the (100) and (010) planes, appear observable changes in lattice parameter at temperature ranges corresponding to that in Fig. 5. The results show the changes of "g" conformation does not affect the dimension in the chain-axis direction (c-axis), rather it shows effects in the a-axis and b-axis directions. The (010) lattice parameter decreases with decreasing "g" conformation concentration, while that in the [100] direction increases first and then decreases. Whether or not the changes of lattice parameters assist chain unfolding during the process of ultrahigh drawing is still a problem that still needs further investigation.

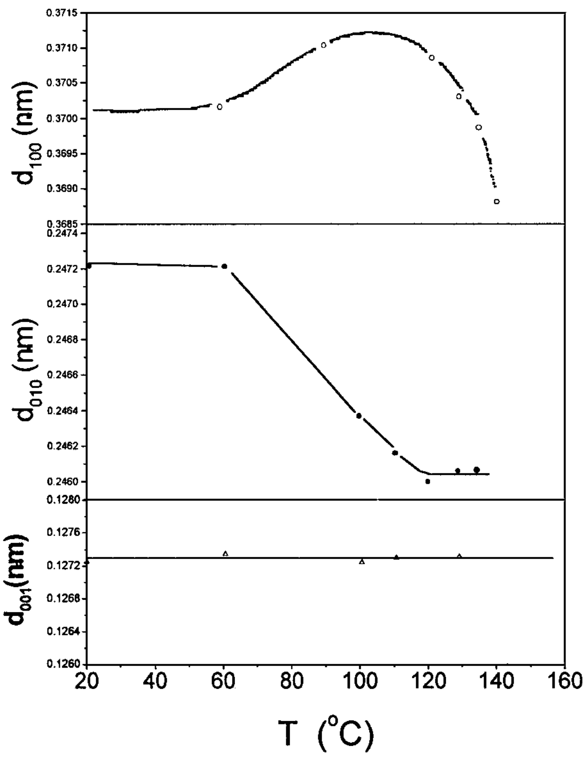

Figure 7 Lattice parameters for UHMWPE gel-film vs. heat treatment temperature.

4. Conclusions

Here we proposed a σ value measured by IR to characterize the "g" conformation changes and its distribution in UHMWPE gel-films. It can explain the relationship between the ultra-drawing of UHMWPE gel-film and its condensed structure more completely and more naturally than the viscosity method does. However, further study combined with other methods should be done because it is difficult to give the absolute distribution of "g" conformation quantitatively in UHMWPE gel-films by IR method only.

Acknowledgement

We are grateful to the National Natural Science Foundation of China for the financial support.

References

1. A. J. PENNING and A. ZWIJNNENBURG, *J. Polym. Sci., Phys. Ed.* **17** (1979) 1011.
2. P. SMITH and P. LEMSTRA, *J. Mater. Sci.* **15** (1980) 505.
3. M. MATSUO, K. INONE and N. ABUMIYA, *Sen-i Gakkaaishi* **40** (1984) 275.
4. T. OGITA, R. YAMAMOTO, F. SUZUKI and M. MATSUO, *Polymer* **32** (1991) 822.
5. Q. R. ZHU, F. HORII, M. TSUJI and R. KITAMARU, *J. Rheol. Soc., Japan* **17** (1989) 35.

6. G. E. ZHOU, Q. R. ZHU, J. F. GAO, R. R. QI, K. L. HONG and Z. F. YE, *Journal of China University of Science and Technology* **22** (1992) 425.
7. Q. R. ZHU, R. R. QI, K. L. HONG, J. F. GAO, G. E. ZHOU and M. S. SONG, *ACTA: Polymerica Sinica* **5** (1994) 552.
8. L. FISCHER, R. HASCHBAGER, A. ZIEGERLDOR and W. RULAWD, *Colloid Polym. Sci.* **260** (1982) 174.
9. T. KANAMOTO, A. TSURUTA, K. TANAKA and R. S. PORTER, *Polym. J.* **15** (1983) 327.
10. T. OGITA, Y. KAWAHARA, R. NAKAMURA, T. OCHI, M. MINAGAWA and M. MATSUO, *Macromolecules* **26** (1993) 4626.
11. Q. R. ZHU, K. L. HONG, L. Q. JI, R. R. QI, G. E. ZHOU, M. S. SONG and Y. W. WONG, *J. Polym. Sci.* B **33** (1995) 739.
12. S. SPELLS, C. SCHMID and P. C. HAGELE, *Polymer* **28** (1987) 697.
13. S. WOLF, C. SCHMID and P. C. HAGELE, *ibid.* **31** (1990) 1222.
14. A. R. WEDGEWORD and J. C. SEFERIS, *Pure and Appl. Chem.* **55** (1983) 873.
15. P. J. FLORY, D. Y. YOON and K. A. DILL, *Macromolecules* **17** (1986) 862.
16. S. KRIMM and J. JAKES, *ibid.* **4** (1971) 605.

Received 12 August 2000
and accepted 23 October 2001