Dynamic-Mechanical Behavior of Highly Drawn Isotactic Polypropylene

F. DE CANDIA,[1,*] G. ROMANO,[2] A. O. BARANOV,[3] and E. V. PRUT[3]

[1]Dipartimento di Ingegneria Chimica ed Alimentare, Università di Salerno, 84081 Salerno, Italy,
[2]Istituto di Tecnologia dei Polimeri e Reologia CNR, Arco Felice, Napoli, Italy, and
[3]Institute of Chemical Physics, USSR Accademy of Sciences, Moscow, Russia

SYNOPSIS

Fibers of isotactic polypropylene were obtained by high-temperature drawing, adopting a two-stage process. Very high drawing degrees were achieved, more than 40. The physical behavior was analyzed by determining the dynamic-mechanical relaxation spectra in monoaxial stretching. The results obtained show that the elastic modulus reaches a saturation value at deformation degrees of about 20, well below the drawability upper limit, indicating that above 20 any further drawing does not affect the structure. Moreover the β transition appears weak or absent in the drawn samples, while the α transition is still readily detectable. Both effects agree with Peterlin's model of drawing and with the fiber structure. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

It is known that the cold drawing of crystalline polymers induces a deep morphological reorganization, and the initial spherulitic morphology is transformed into the final microfibrillar texture.[1] The morphological reorganization involves not only the crystalline phase but also the microstructure of the amorphous component, which is drastically changed by drawing. The first effect is the creation of tie molecules connecting different crystalline blocks along the drawing direction;[2] these molecules become more and more taut as the drawing degree is increased and are largely responsible for the achieved axial modulus. A second effect is a reduction of the molecular mobility, consequent to the compression that the drawing induces in the interfibrillar amorphous layers. The reduced molecular mobility affects the overall behavior but in particular some properties more directly related to the mobility phenomena, such as transport properties and glass transition temperature. In previous studies evidence of both effects was reported,[3-6] and the results obtained agree well with Peterlin's model of cold drawing. As reported by other authors,[7,8] in highly drawn samples obtained at high drawing temperature, besides the taut tie molecules (TTM), crystalline bridges connecting crystalline blocks along the fiber axis can also be observed. In the present study we report on the physical behavior of fibers of isotactic polypropylene (iPP) obtained with a two-stage drawing process carried out at different temperatures, some of them in the melting range. The two-stage process allows one to achieve very high drawing degrees.[9] The physical behavior was investigated analyzing the dynamic-mechanical relaxation spectra, with the aim of obtaining information on the effect that the two-stage drawing plays on the molecular mobility and on the sample morphology.

MATERIALS AND EXPERIMENTAL

The material used in this study was an isotactic polypropylene (iPP) indicated with the trademark "21020-16" (USSR), having the following characteristics: Molecular weight: $M_w = 2.29 \times 10^5$, $M_n = 7.76 \times 10^4$. Melting point: 163°C, obtained by differential scanning calorimetry (DSC). Melt flow index: 0.19 g min^{-1}. Degree of isotacticity: 93%.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 46, 1799–1806 (1992)
 CCC 0021-8995/92/101799-08

The undrawn sample (indicated as U) was obtained by melt extrusion at 190°C. The crystallinity of sample U, obtained by DSC, was 60.5%. The drawn samples were obtained from U sample by a two-stage isothermal drawing process. In the first stage the dumbell-shape sheets, with a gauge length of 35 mm, were drawn up to eight or nine times the initial length. In the second stage the sample (with a length of 50 mm) was drawn up to the final deformation degree, as determined by the displacement of ink marks placed 5 mm apart on the sample. The drawing was carried out at different temperatures, T_d: at 125°C (samples A), at 145°C (samples B), and at 165°C (samples C). In order to avoid melting of the undrawn sample in the clamps of the tensile testing instrument (Instron-1122), the first stage of samples C was carried out at 163°C. The elongation rate, measured on the clamp displacement, was 20 mm/min in each stage, and this gives an initial deformation rate of 0.57 min^{-1} in the first stage and of 0.40 min^{-1} in the second stage. The drawn samples are indicated by a code containing a letter and a number; as reported, the letter indicates the drawing temperature, while the number indicates the drawing degree. The analyzed samples are all reported in Table I, where the drawing temperature T_d and the drawing degree λ are reported; λ is the ratio between final and initial length.

Samples A1, B1, and C1 were obtained by drawing in a single stage. The X-ray diffraction patterns indicated a value of 1 for the orientation factor of the crystalline phase in all the analyzed samples. The analysis was carried out using a flat camera assembled on a Seifert diffractometer. The distance of the sample to the recording film was 6 cm, and the radiation was the CuK_α. The patterns regarding samples A1 and C5 (the two extreme situations) are reported in Figures 1(a) and 1(b), respectively.

Table I Analyzed Samples

Sample	T_d (°C)	λ
U	—	1
A1	125	9.1
A2	125	15.0
A3	125	21.4
B1	145	8.2
B2	145	15.1
B3	145	20.3
B4	145	30.9
C1	165	7.8
C2	165	17.0
C3	165	23.3
C4	165	30.8
C5	165	43.7

The dynamic-mechanical behavior was analyzed in monoaxial stretching, with an excitation frequency of 110 Hz, in the temperature range −50 to 190°C. The analysis was carried out using the RheoVibron viscoelastometer of Toyo Instruments. The cross-sectional area of the different samples was in the range 1.4×10^{-3} to 7.0×10^{-4} cm^2, while the applied static stress was in the range 1.4 to 2.8 MPa.

RESULTS

The dynamic spectra were obtained by rapidly cooling the sample to the lower temperature of the analyzed range (−50°C) and then heating at a scanning rate of 3°/min, and detecting the complex modulus and the loss factor tan δ as a function of the temperature. In Figure 2, E', the elastic component of the modulus,[10] is reported as a function of temperature; Parts (a), (b), and (c) refer to different drawing temperatures. Two effects are visible in Figure 2: The first is a drastic increase of the modulus on increasing the drawing degree, as a consequence of the appearance of a fibrillar morphology. The second effect, observable at the higher drawing degrees, is a shift to higher temperatures of the modulus drop. This last effect is particularly evident for samples drawn at 165°C. From the data in Figure 2 the dependence of the elastic modulus on the drawing degree can be obtained. The isothermal data were obtained at three different temperatures: 50, 100, and 150°C, and are reported in Figures 3(a), 3(b), and 3(c), respectively. In each, three plots, referring to the three different drawing temperatures, are reported. The trend in the strain range below 9, which was not investigated, is represented by a dotted line. It is evident that the modulus is practically a single function of the drawing degree, the influence of the drawing temperature being weak. In Figure 4 the loss factor tan δ is reported as a function of the temperature; Figures 4(a) and 4(b) refer to T_d = 125 and 165°C, respectively. The undrawn sample U shows an intense loss band at 5°C, that can be identified with the glass transition, indicated in the literature as the β relaxation of iPP;[10] this transition is followed by a monotonic increase of tan δ, which can be associated to the α-relaxation process.[10] The β relaxation is lower in sample A1 and decreases below the limit of the instrument (tan $\delta < 0.01$) in all the other samples, where only the α relaxation is detectable.

The shrinking behavior of the fibers was also analyzed, detecting $\Delta L/L_0$ as a function of the temperature; L_0 is the initial length of the drawn sample,

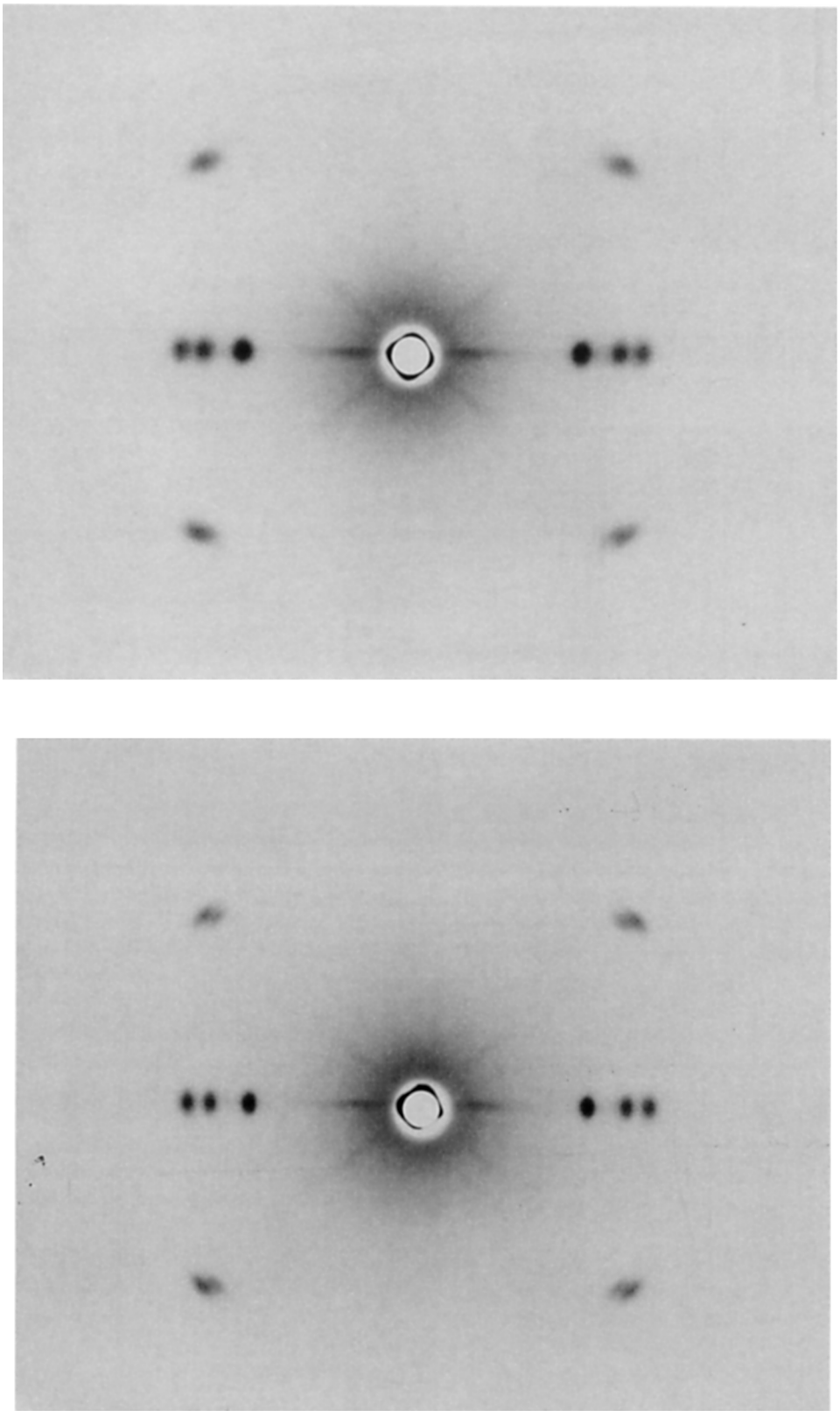

Figure 1 X-ray diffraction patterns of (a) sample A1 and (b) sample C5.

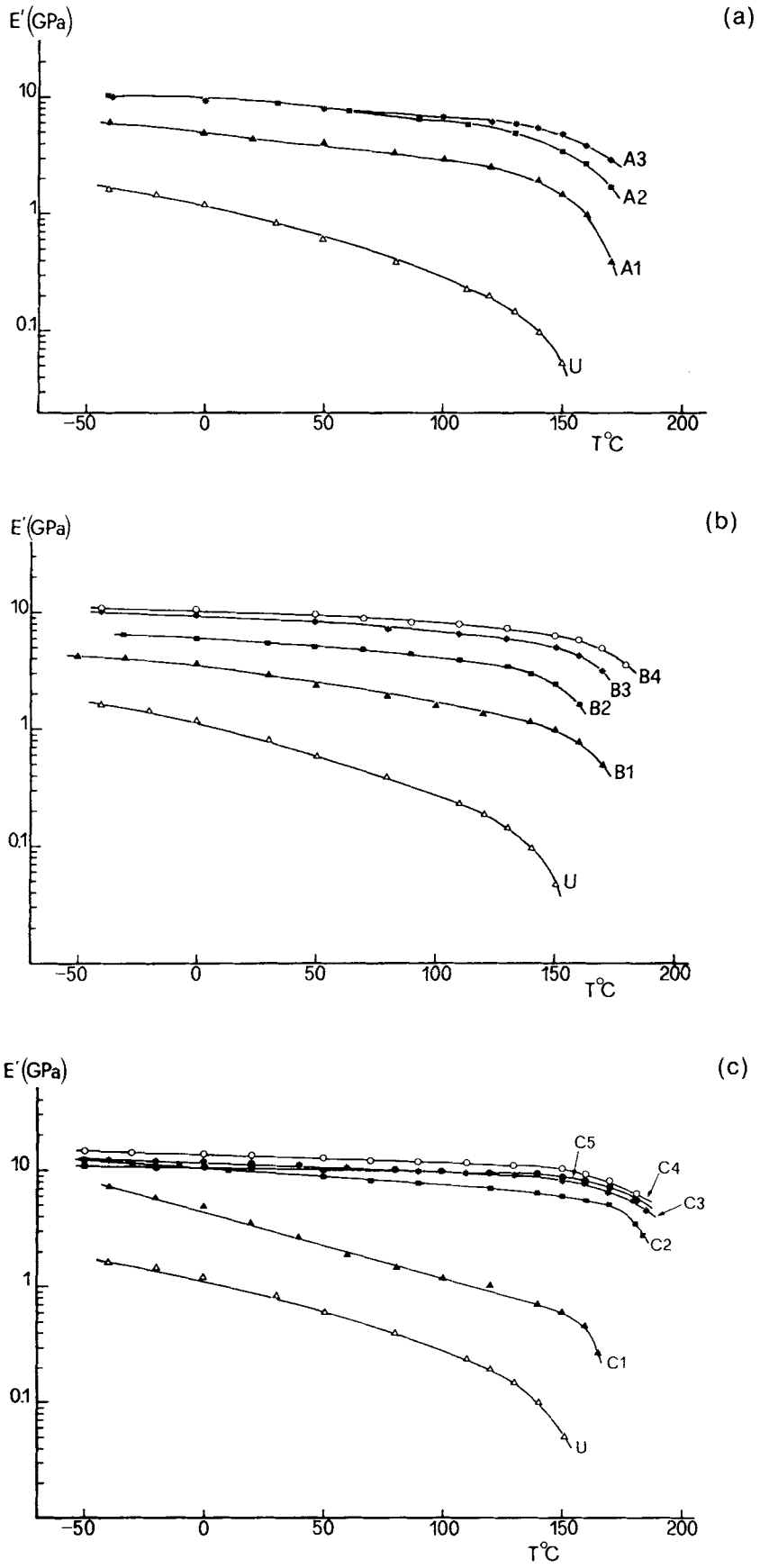

Figure 2 The elastic component E' of the dynamic modulus is reported as a function of the temperature. Parts (a), (b), and (c) refer to different drawing temperatures: 125, 145, and 165°C, respectively. The samples code is explained in Table I.

and ΔL is the length reduction at any given temperature, after thermosetting for 10 min. The temperature range analyzed was 25–160°C. The results obtained can be summarized as follows: The shrinkage behavior agrees well with the trend observed for the elastic modulus, in the sense that where the modulus drop is more intense, a stronger effect on the sample shrinkage is observed. In particular at higher drawing degrees the shrinking effect is weaker and, analogous with the modulus, appears to be shifted to a higher temperature.

DISCUSSION

According to Peterlin's model of cold drawing and fiber morphology,[1,2] the drawing process, carried out on semicrystalline polymeric systems, induces a deep structural rearrangement, which leads to microfibrils as new morphological units. The new morphology is characterized by high orientation of the crystals along the drawing axis, as shown by the X-ray diffraction patterns. However, the structural rearrangement plays a relevant role on the amorphous component too, which is also oriented by the drawing process, and whose molecular mobility is drastically reduced. In previous studies evidence of this phenomenon was shown on the basis of transport parameters, such as diffusion and sorption coefficients, detected using methylene chloride as permeant.[3-5] A relevant effect was also observed analyzing the EPR spectra of drawn samples;[11,12] the effect was explained on the basis of the relationships between correlation times and molecular mobility in the medium where the paramagnetic probe is dissolved. According to this picture, the dynamic-mechanical analysis showed a relevant effect on the intensity of the β band, which appeared drastically reduced in the drawn samples,[6] as observed also by other authors.[13,14]

The dynamic-mechanical behavior of ultradrawn samples here described confirms, with some further evidence, previously obtained results and general knowledge of the structural organization of highly oriented samples.

Figure 2 shows that the modulus is drastically increased by the drawing process, as expected for the appearance of fiber texture. Moreover, an effect on the relationship between modulus and temperature is also observable; in the undeformed sample the modulus monotonically decreases with temperature in all the analyzed range, and an increase of its derivative is observable at about 120–130°C. In the drawn samples, and in particular at high drawing, the modulus is substantially constant over a wide temperature range, where only a weak decrease is observable, while significant reduction appears shifted to the melting range. Similarly, the shrinkage is shifted into the melting range. This result clearly suggests the presence of crystalline bridges connecting different crystalline blocks along the fiber axis. The presence of such morphological units previously suggested[7] has been recently confirmed on the basis of the thermal behavior.[8] The activation of the sample shrinkage, based on the conformational relaxation of the TTM[15] is hindered by the crystalline bridges, whose melting is required to allow shrinkage. This effect can be explained on the basis of the Takayanagi model.[16] In fact, according to Takayanagi, a fiber can be represented with an ideal model, where a hard element is coupled in parallel with a bicomponent hard–soft element, characterized by serial coupling. The hard element can be identified with crystalline bridges and TTM, while the bicomponent element can be identified with the crystalline blocks, alternating with the amorphous layers. This model is generally adopted in describing the modulus of a highly oriented fibrous system. The axial modulus of such a system is largely affected by the modulus of the hard elements assembled in parallel; therefore melting of the crystalline bridges, and the following relaxation of TTM, is required to observe a well-detected effect both on modulus and shrinking, as actually found.

According to other authors,[13] Figure 3 shows that the modulus is substantially a single function of the drawing degree. Particularly interesting is the saturation effect observable in Figure 3; in fact, after an initial sharp increase, the modulus tends to assume a saturation value at about $\lambda = 20$. This is evident at 50°C [Fig. 3(a)], where the modulus is about 10 GPa for $\lambda = 20$, and is only 12 GPa for $\lambda = 43.7$. At 100°C [Fig. 3(b)] the modulus reaches 10 GPa for $\lambda = 24$ and remains constant for any further drawing. The tendency to assume a saturation value is still present at 150°C [Fig. 2(c)], even if less evident. At least on the basis of the dynamic analysis, the existence of a saturation effect suggests that the structure is not further modified by drawing higher than some limit value, in the present case about 20. Any further drawing induces a shear of the formed fibrils, without any further increase of tie molecules and crystalline bridges. The shear of the fibrils generally increases the tension acting on the interfibrillar TTM,[17] inducing the sample fracture. However, in the present case the drawing is performed at temperatures where the α

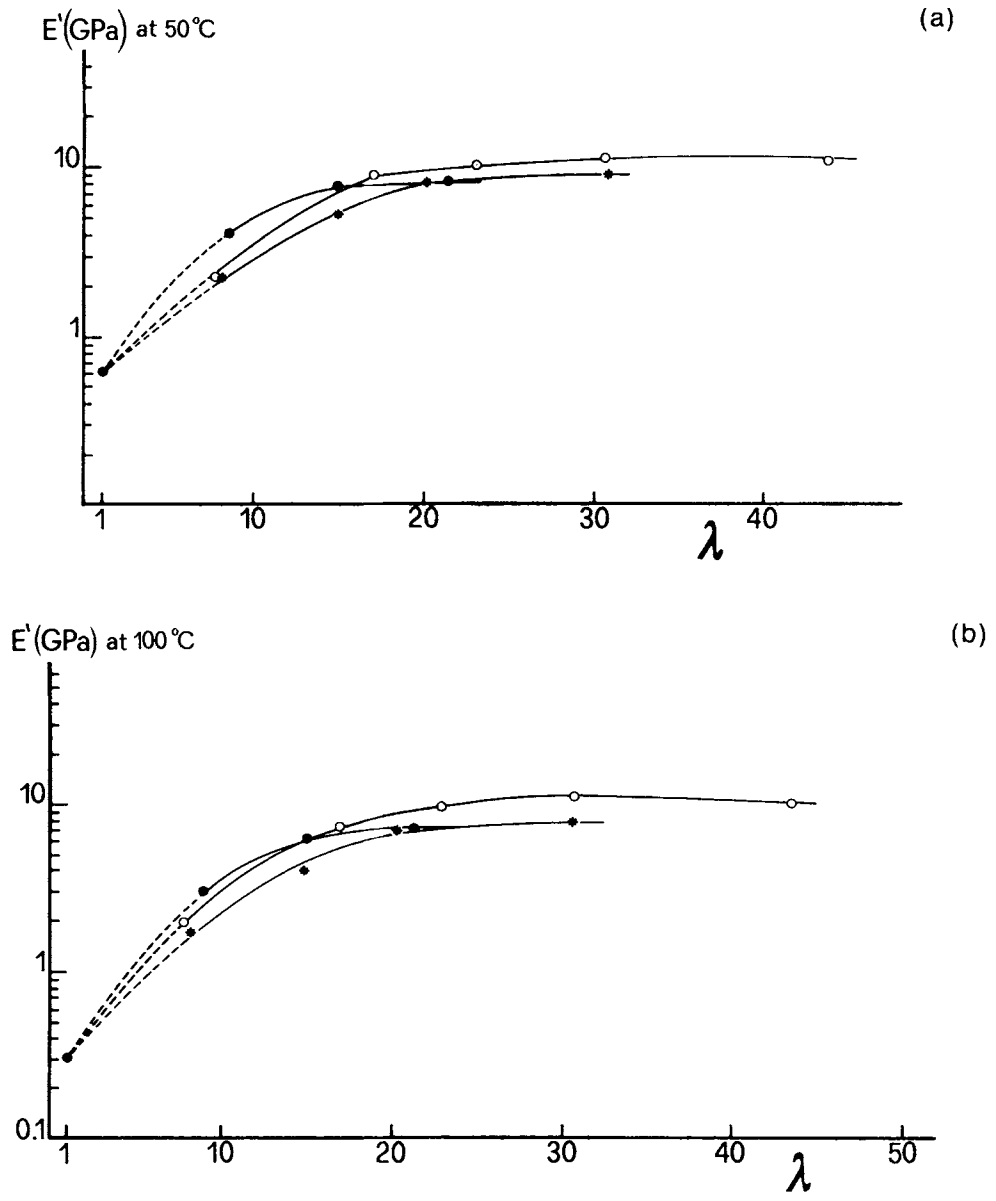

Figure 3 The modulus E' is reported as a function of the drawing degree. Parts (a), (b), and (c) refer to different temperatures; 50, 100, and 150°C, respectively. In each three plots are reported referring to different drawing temperatures: (●) 125°C, (*) 145°C, (○) 165°C.

mechanism is active; this mechanism, as known,[10] is based on the pulling of chain sequences out of the crystalline blocks. Therefore the tension can be relaxed delaying the sample fracture. Moreover phenomena of melting and recrystallization can be active during the drawing process, reducing the axial tension, and therefore cooperating in delaying the sample fracture. This means that very high deformations, more than 40, that can be achieved by the two-stage process, do not reflect to a similar extent on the achievable modulus values. In this sense the drawing procedure adopted seems not to be particularly efficient; in fact a single-stage die drawing, for drawing degree of about 20, allows modulus values of about 18 GPa,[14] that is higher than the limit of 12 GPa observed for sample C5 drawn up to $\lambda = 43.7$.

However, as observed,[18] the dynamic analysis in forced vibration can underestimate the modulus values, particularly when one operates, as in the present case, with very thin sections. This technical limitation can be the effect of many different problems, such as sample clamping and uniformity of applied stress as observed.[19,20] This is noted just to

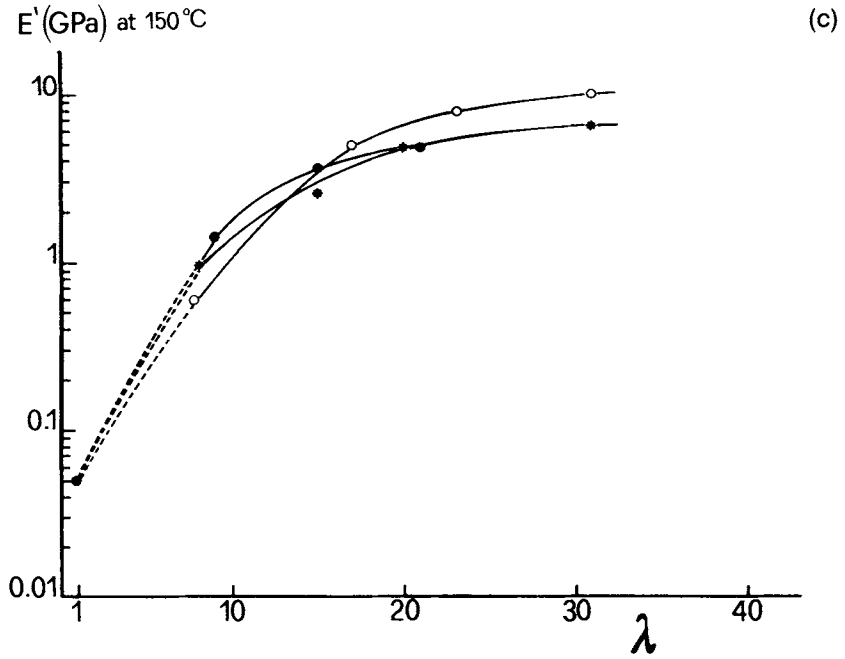

Figure 3 *(Continued from the previous page)*

point out that the actual modulus reached could be higher than the 12 GPa that we found.

Another effect shown by the results obtained concerns the drastic reduction of β transition. As previously observed,[6] this phenomenon is the consequence of two factors. The first is the reduced molecular mobility consequent to the presence of TTM, and to the compression induced by drawing on the interfibrillar amorphous layers. This microstructural condition affects the conformational mobility, and therefore the intensity of the β band. The second factor is related to the analytical technique adopted. In fact we analyze the dynamic-mechanical behavior in monoaxial vibrational stretching imposed along the fiber axis. Therefore the technique mainly "sees" the relaxation phenomena along the axis. In this direction the stress is mainly concentrated on crystalline bridges and TTM, and therefore the possi-

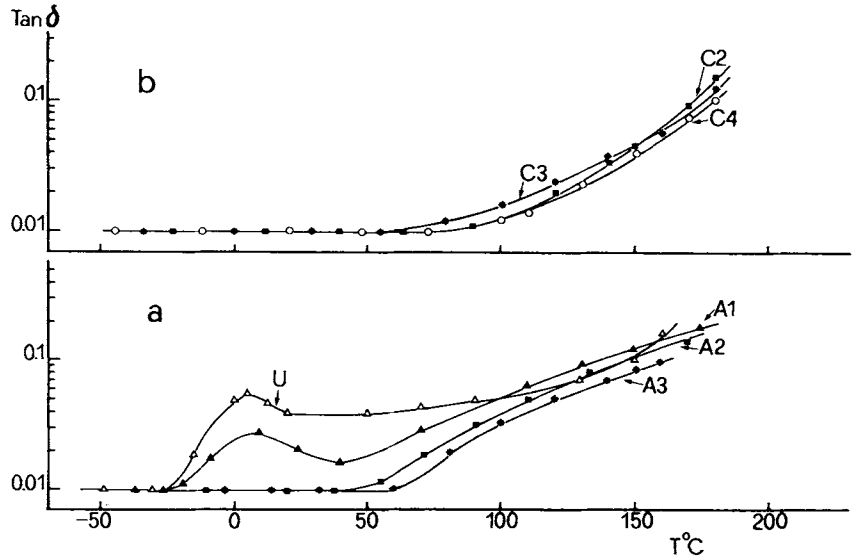

Figure 4 The loss factor tan δ is reported as a function of the temperature. Parts (a) and (b) refer to samples of A and C series, respectively.

bility to detect a dissipation band, is mainly related to relaxation phenomena occurring in these structural elements. In these elements the relaxation mechanisms are activated in the temperature range of α transition, largely above the glass transition. In agreement with this picture, the α transition is readily detectable also in the highly drawn samples. In fact, according to the mechanism, this transition, observable also in isotropic films, is favored in the oriented systems by the tension acting on the crystalline blocks, particularly where the tie molecules are clamped; the effect on the dynamic behavior is expected to be readily detectable, particularly observing the relaxation phenomena along the fiber axis, as we do. Therefore the disappearance of the β transition, and the readily detectable α band, both agree with the structural model.

CONCLUSIONS

The ultradrawing of isotactic polypropylene, carried out adopting a two-stage process, allows one to achieve very high drawing degrees, more than 40. This possibility does not reflect in the modulus, which reaches a saturation value at about $\lambda = 20$, indicating that any further drawing does not affect the structure.

Moreover, according to Peterlin's model of cold drawing, the molecular mobility in the amorphous component is drastically reduced by drawing. This phenomenon, and the adopted analytical technique, both affect the β transition, which is very weak or absent in the drawn samples. On the other hand the α transition appears to be readily detectable also in the drawn samples, as expected on the basis of the transition mechanism and according to the model of the fiber structure.

The authors wish to thank Dr. L. Guadagno for the X-ray analysis. This work was supported by Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate" of CNR, Italy.

REFERENCES

1. A. Peterlin, *Colloid Polym. Sci.*, **253,** 809 (1975).
2. A. Peterlin, *J. Appl. Phys.*, **48,** 4099 (1977).
3. L. Araimo, F. de Candia, V. Vittoria, and A. Peterlin, *J. Polym. Sci. Phys. Ed.*, **16,** 2087 (1978).
4. F. de Candia, R. Russo, V. Vittoria, and A. Peterlin, *J. Polym. Sci. Phys. Ed.*, **20,** 269 (1982).
5. F. de Candia, V. Vittoria, and A. Peterlin, *J. Polym. Sci. Phys. Ed.*, **23,** 1217 (1985).
6. F. de Candia, A. Botta, and V. Vittoria, *J. Polym. Sci. Phys. Ed.*, **24,** 2145 (1986).
7. A. G. Gibson, G. R. Davies, and I. M. Ward, *Polymer,* **19,** 683 (1978).
8. A. K. Taraiya, A. P. Unwin, and I. M. Ward, *J. Polym. Sci. Phys. Ed.*, **26,** 817 (1988).
9. A. A. Turetskii, S. N. Chvalun, A. O. Baranov, Yu. Zubov, and E. V. Prut, *Polym. Sci. USSR,* **30,** 1993 (1988).
10. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids,* Wiley, New York, 1967.
11. F. de Candia, R. Russo, V. Vittoria, B. E. Krysiuc, A. A. Popov, and G. E. Zaikov, *Polymer,* **27,** 1743 (1986).
12. B. E. Krisyuc, A. A. Popov, G. E. Zaikov, F. de Candia, R. Russo, and V. Vittoria, *Colloid Polym. Sci.*, **265,** 220 (1987).
13. A. J. Wills, G. Capaccio, and I. M. Ward, *J. Polym. Sci. Phys. Ed.*, **18,** 493 (1980).
14. A. K. Taraiya, A. Richardson, and I. M. Ward, *J. Appl. Polym. Sci.*, **33,** 2559 (1987).
15. F. de Candia, G. Romano, V. Vittoria, and A. Peterlin, *J. Appl. Polym. Sci.*, **30,** 4159 (1985).
16. M. Takayanagi, K. Imada, and T. Kajiama, *J. Polym. Sci.*, **C15,** 263 (1966).
17. F. de Candia, R. Russo, V. Vittoria, and A. Peterlin, *J. Polym. Sci. Phys. Ed.*, **20,** 269 (1982).
18. D. J. Massa, *J. Appl. Phys.*, **44,** 2595 (1973).
19. A. R. Wedgewood and J. C. Seferis, *Polymer,* **22,** 966 (1981).
20. K. Pournoor and J. C. Seferis, *Polymer,* **32,** 445 (1991).

Received September 23, 1991
Accepted February 18, 1992