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Mechanical properties of thermotropic polybibenzoates

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The mechanical properties of different samples of two thermotropic polybibenzoates (poly(heptamethylene) *p,p*'-bibenzoate) (P7MB) and poly[oxybis(trimethylene) *p,p*'-bibenzoate] (PDTMB) were analysed at several temperatures and deformation rates. One of the polymers presents a very slow transformation of the mesophase into three-dimensional crystal, so that it can be analysed either in the pure mesophase state or in semicrystalline samples. The stress–strain behaviour of a PDTMB sample where only a mesophase is present is intermediate between that of amorphous and semicrystalline polymers, since low values of the Young modulus and high deformation at break are obtained but the deformation takes places through necking even at temperatures above T_g. Moreover, when these thermotropic polymers are allowed to crystallize, their behaviour is typical of semicrystalline polymers. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The interest in liquid crystal polymers (LCPs) is in connection with the properties of the mesophase, together with the specific behaviour of the polymer. The anisotropy of the LC phase opens the possibility of manufacturing new high-performance materials, exhibiting excellent properties related to an appropriate disposition of macromolecules in the mesophase during the processing. Owing to this fact, the LCPs show a low viscosity, long relaxation times and a high molecular alignment, which enhance their processability by conventional techniques (extrusion, injection and spinning).

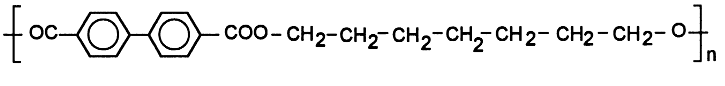
LCPs containing the biphenyl group as a rigid mesogen in the main chain and alkylene or oxyalkylene chains as spacers are convenient models for the study of phase transitions of LCPs with semiflexible chains. The biphenyl group in these polymers is able to generate smectic mesophases with isotropization temperatures which generally decrease as the length of the alkylene spacer increases[1–6], although the typical even–odd effect is also observed[3,7,8]. The influence on the phase behaviour of the replacement of the central methylene in the spacer of poly(heptamethylene *p,p*'-bibenzoate) (P7MB) by an oxygen atom, to give poly[oxybis(trimethylene) *p,p*'-bibenzoate] (PDTMB), was reported previously[9–12], as well as the difference in stability between the various phases of P7MB and PDTMB. It was found that the flexibility introduced by the ether group has a marked effect on the temperature range of stability of the mesophase, since the presence of the ether group in the spacer of PDTMB results in the suppression of the three-dimensional crystalline state. A similar effect has also been reported for polybibenzoates with flexible spacers having a different number of oxyethylene groups[4,5]. It should be considered that the knowledge of the phase behaviour is important because it is reflected in the mechanical properties. For instance, the presence of ordered crystalline regions results in a mechanical behaviour very different from that of amorphous polymers[13].

The aim of this paper is to study the effect of structural modifications (e.g. different spacers) on the phase behaviour and, consequently, on the mechanical properties of polybibenzoates. Taking into account that, in addition to the structural factors, there is a strong dependence of some of the mechanical properties with thermal history and temperature, we present in this work the results of tensile properties obtained in two polybibenzoates with different thermal histories and stretched at different crosshead speeds and drawing temperatures.

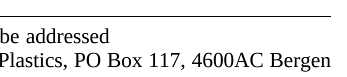
EXPERIMENTAL

The two polybibenzoates, P7MB and PDTMB, were obtained by melt transesterification as reported previously[9,10]. The viscosities, measured in chloroform at 25°C, were found to be 1.03 and 1.05 dL g^{-1} for P7MB and PDTMB, respectively. Their structural formulae are:

P7MB



PDTMB



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The polymer samples were placed in a Collin press fitted with smooth-polished plates and hot-pressed at 20–30 MPa and 200°C for 5 min. Cooling was carried out by quenching the molten polymer between water cooled plates (samples P7MB-Q and PDTMB-Q). In the case of P7MB the quenching was also achieved in liquid nitrogen (sample P7MB-QN). A second sample of PDTMB was analysed after storing it for 2 yr at room temperature (sample PDTMB-RT).

The moulded polymers were characterized by DSC and X-ray diffraction. The thermal properties of the samples were measured by means of a Perkin Elmer DSC-7 calorimeter connected to a cooling system. The heating rate was 20°C min^{-1} and the temperatures ranged between − 40°C and 200°C. X-ray diffractograms at wide angles were recorded at room temperature with an X-ray diffractometer from Philips Co. equipped with a Geiger counter detector, using nickel-filtered CuKα radiation.

Dumb-bell specimens, cut from sheets around 0.5 mm thick by using a standardized die (15 mm long and 1.9 mm wide in the narrow section), were uniaxially drawn in an Instron dynamometer at deformation rates, v_d, of 0.1, 1 and 10 cm min^{-1}. No slippage in the clamps was detected. The samples were stretched at different temperatures, T_d, after previous conditioning in a thermostatic chamber. These temperatures are: 23°C (lower than T_g for P7MB and in the critical region for PDTMB), 40°C (above T_g for PDTMB and in the critical region for P7MB) and 65 and 80°C (above T_g for the two polymers).

A high chart speed was used at the beginning of the stretching process in order to obtain a reliable Young modulus (the slope of the stress–strain curve) from the initial portion of the recorded traces. Yield is measured as the point where the force–elongation curve shows a maximum. All the stresses are nominal values, calculated from the initial cross-section of the sample, and the results were determined by averaging three experiments. The elongation of the samples will be given either by per cent of drawing (ϵ) or by draw ratio (λ). The relation between these parameters is:

$$\epsilon(\%) = 100(\lambda - 1)$$

where $\lambda = l_f/l_o$, where l_f = final length and l_o = initial length. The actual draw ratio, λ, was determined from the displacement of parallel ink marks.

The following mechanical parameters were obtained from the stress–strain curves: Young modulus (E), stress and deformation at the yield point (σ_Y and λ_Y, respectively), break stress (σ_B) and strain at breaking (λ_B).

RESULTS

The mechanical properties of the two polybibenzoates were studied at different temperatures and deformation rates. The drawing temperatures were chosen below and above the T_g of the polybibenzoates. When the drawing temperature is below T_g the polymer is in the glassy state and the deformation will lead to rupture or require excessively high stresses, owing to the fact that the material is too rigid. With an increase in the temperature the pass from the brittle to ductile states will occur but the neck does not stabilize and the specimen also breaks. Above a certain temperature, slippage of the material occurs and the drawing process takes place.

Mechanical properties of P7MB

The X-ray diffractogram (upper curve in *Figure 1*) of a P7MB sample quenched in water (P7MB-Q) shows the existence of a small crystal fraction ($\alpha \approx 17\%$) together with the liquid crystalline phase. In an attempt to obtain only the mesophase, the polymer was quenched from the melt in liquid nitrogen (P7MB-QN). However, the X-ray diffractogram of this sample (lower curve in *Figure 1*) also shows 15% of crystallinity and reveals the difficulty of obtaining P7MB without a small content of three dimensional crystallinity. Therefore, the P7MB samples under study present a liquid crystal (LC) phase in addition to a three-dimensional crystal (3D) phase. In principle, the difficulty in quenching out crystallinity in P7MB might be related to the existence of some preordering in the melt. However, conformational factors seem to play a more important role, since similar preordering is envisaged in PDTMB and this polymer can be easily quenched without any three-dimensional order. The flexibility of the central ether group in the spacer of PDTMB is responsible for this behaviour.

The DSC melting curves of the two P7MB samples are similar and *Figure 2* shows the curve corresponding to the sample P7MB-Q. The glass transition is observed at about 46°C, followed by an endotherm at 168°C. We have shown

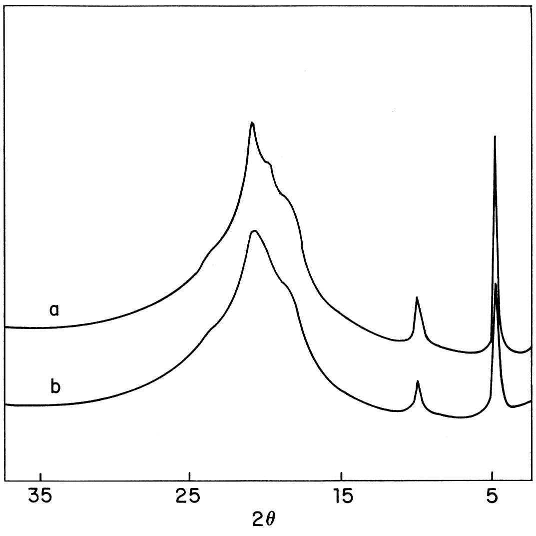

Figure 1 X-ray diffractograms corresponding to: (a) sample P7MB-Q and (b) P7MB-QN

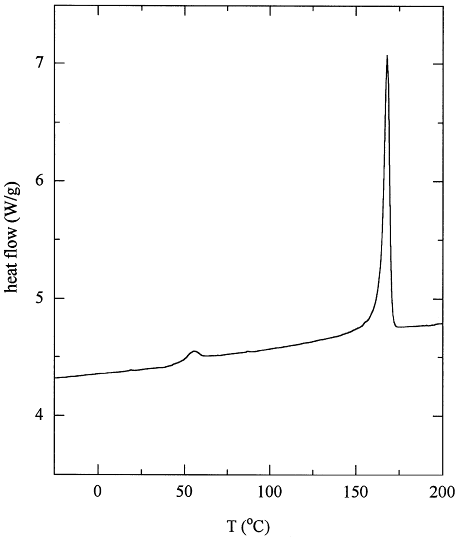

Figure 2 DSC melting curve of sample P7MB-Q

previously[9,11] that P7MB presents a monotropic behaviour and that the crystal melts directly into the isotropic phase, so that the mesophase is only observed on cooling. Therefore, the endotherm at 168°C represents the melting of the crystals directly into the isotropic melt.

The stress–strain plots corresponding to sample P7MB-Q are shown in *Figure 3*. The plot at $T_d = 23°C$ was omitted because the deformation at break is very small ($\lambda_B \approx 1.02$). This behaviour is attributed to the fact that the drawing temperature is much lower than T_g . The mechanical parameters obtained from these plots are listed in *Table 1* and represent the average of three experiments, as it was mentioned in the experimental part, while the curves in *Figure 3* correspond to a specified experiment.

At 40°C the stretching process takes place through necking (probably more than one neck) and is clearly dependent on strain rate[14]. It can be seen in the upper part of *Figure 3*, that the intensity of the main neck increases with the rise of the strain rate. Further extension occurs by the displacement of the neck through the sample, when the plastic deformation is concentrated in a small region of the sample[15]. The Young moduli at this temperature (*Table 1* and *Table 2*) are lower than those at 23°C and increase with the strain rate when passing from 0.1 to 1 cm min^{-1}. However, the low value of the Young modulus at 10 cm min^{-1} is probably a result of adiabatic heating[16,17].

At 65°C and 80°C the stretching process also takes place through necking, although T_d is higher than T_g, because of the presence of crystallinity in the polymer, but the necking process is less pronounced at those temperatures in comparison with the drawing at 40°C. It is known that very drastic reorganization may occur at the morphological level and structure may change from a spherulitic to a fibrillar type as the degree of plastic deformation increases. At those temperatures a process of annealing in P7MB and the subsequent increase of crystallinity cannot be disregarded and will be reflected in some properties.

The yield peak in the stress–strain curve, the point at which plastic flow becomes dominant, depends on the temperature and on the strain rate (*Table 1*). This dependence follows the usual trend: the yield stress increases when the drawing temperature decreases or when the strain rate increases. The deformation at yield, λ_Y, generally decreases when increasing the temperature for amorphous polymers, but the opposite effect can be found with some crystalline polymers[13]. No clear trend can be deduced for P7MB from the data in *Table 1*. Moreover, the breaking of the specimens takes place before the yield point when they are stretched at 23°C, i.e., at a temperature below T_g.

An interesting feature in the drawing behaviour of P7MB is the presence of double yield points. This phenomenon was also found in polyethylene[18,19], considering the first yield point as a result of a strain-softening process and the second one, appreciable by a geometric change of the specimen shape, a result of the necking process[19]. *Figure 3* shows that the stress–strain plots of P7MB samples drawn at low temperatures display a smooth maximum just after the main yield point and before the strain hardening process. This second maximum is less pronounced when increasing the drawing temperature and decreasing the strain rate.

The mechanical parameters for sample P7MB-QN are shown in *Table 2*. It can be observed that these values are of the same order as those for P7MB-Q in all the cases, except for the deformation at break. These values of λ_B are very small for sample P7MB-QN at all temperatures, while those for P7MB-Q are considerably higher at temperatures above 23°C. This difference is a result of the appreciably high number of voids (inhomogeneous texture) appearing in sample P7MB-QN. The very low deformation at break exhibited by this sample prevents the determination of σ_Y and λ_Y at the two lower temperatures.

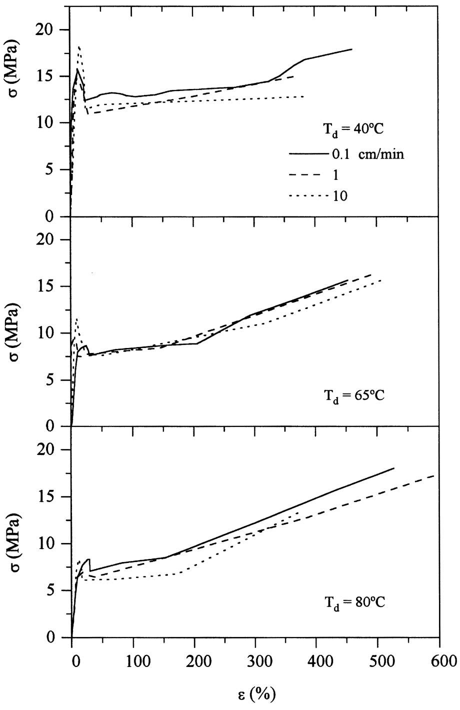

Figure 3 Stress–strain curves of sample P7MB-Q at the indicated temperatures and deformation rates

Table 1 Mechanical parameters of sample P7MB-Q

T_d(°C)	v_d (cm min^{-1})	E (MPa)	σ_Y (MPa)	λ_Y	σ_B (MPa)	λ_B
23	0.1	930[a]	—	—	16.4	1.02
	1	810[a]	—	—	15.0	1.02
40	0.1	195	15.4	1.16	17.9	5.61
	1	245	14.8	1.10	14.3	4.34
	10	140[b]	18.4	1.15	—	4.83
65	0.1	125	8.5	1.23	15.0	5.43
	1	140	9.4	1.05	16.2	5.92
	10	155	11.2	1.11	16.3	6.58
80	0.1	90	8.0	1.28	18.0	6.27
	1	115	7.5	1.10	17.3	6.93
	10	125	8.6	1.12	13.3	4.73

[a] Broad dispersion of the values

[b] Adiabatic heating

Table 2 Mechanical parameters of sample P7MB-QN

T_d(°C)	v_d (cm min^{-1})	E (MPa)	σ_Y (MPa)	λ_Y	σ_B (MPa)	λ_B
23	0.1	800	—	—	16.9	1.03
	1	840	—	—	18.0	1.03
40	10	245	—	—	12.2	1.06
65	10	155	11.4	1.16	8.3	1.97
80	10	130	11.6	1.08	8.1	1.40

Mechanical properties of PDTMB

This polybibenzoate displays a mesophase at room temperature which is fairly stable during several days (while P7MB always presents some crystalline content owing to its high crystallization ability). When PDTMB is stored at room temperature for a long time the crystallization takes place, as a result of the fact that the glass transition of this polyester is lower than room temperature[11]. This behaviour is very interesting because it is possible to study the mechanical properties both in the pure LC phase (sample PDTMB-Q) and in a semicrystalline sample (sample PDTMB-RT).

The X-ray diffractogram of the sample PDTMB-Q shows only the LC phase, with two sharp diffractions assigned to the characteristic length of the smectic phase and its second order[11] (only the second order is displayed in *Figure 4*) and a broad peak arising from the disordered lateral arrangement of the chains in the smectic mesophase. The corresponding DSC trace (lower curve in *Figure 5*) shows a glass transition at 17°C, in addition to the isotropization endotherm at 172°C. Therefore, the only structure obtained for PDTMB is a smectic liquid crystalline phase, stable at room temperature during the measurement time.

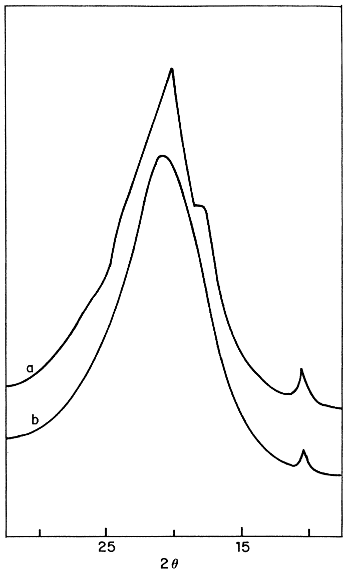

Figure 4 X-ray diffractograms corresponding to: (a) sample PDTMB-Q and (b) sample PDTMB-RT

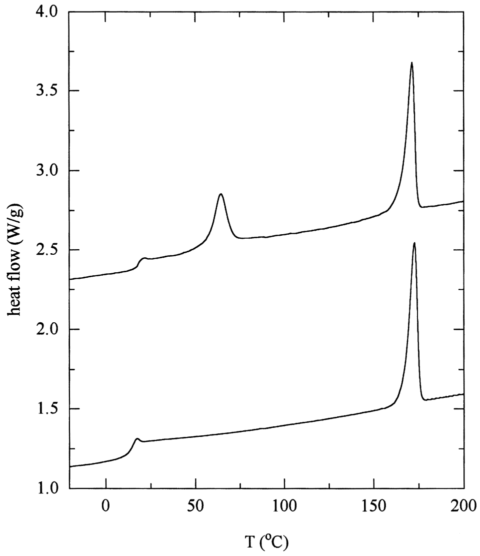

Figure 5 DSC melting curves of samples PDTMB-Q (lower) and PDTMB-RT (upper)

The stress–strain plots for the sample PDTMB-Q are displayed in *Figure 6*. The upper part of this figure shows the influence of the deformation temperature on the stretching process at the highest cross-head speed. It can be observed that the deformation occurs through necking in all cases, even though T_d is higher than T_g. The influence of the drawing rate is depicted in the lower part of *Figure 6*. These results show that the ductile behaviour (through necking) at 10 and 1 cm min^{-1} is transformed in an elastomeric behaviour (homogeneous drawing able to sustain large deformations without necking) at 0.1 cm min^{-1}. This feature is reflected in the lowest values of E and σ_y and the highest ones for λ_B at this speed.

The mechanical parameters corresponding to sample PDTMB-Q are shown in *Table 3*. It has to be considered in this case that all the drawing temperatures are above the T_g of the sample, in contrast to the case of P7MB. The Young moduli for sample PDTMB-Q are low, corresponding to a non-crystalline sample, and the deformation at break values

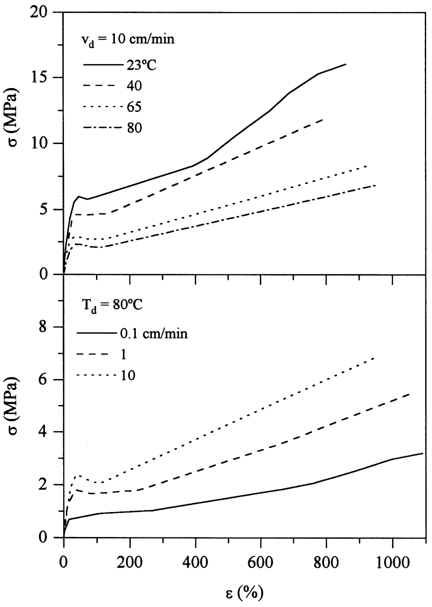

Figure 6 Stress–strain curves for samples PDTMB-Q at the indicated temperatures and deformation rates

Table 3 Mechanical parameters of sample PDTMB-Q

T_d (°C)	v_d (cm min^{-1})	E (MPa)	σ_Y (MPa)	λ_Y	σ_B (MPa)	λ_B
23	1	20	4.3	1.50	12.5	10.57
	10	25	5.3	1.40	14.2	8.93
40	0.1	20	2.5	1.41	—	9.02*
	1	20	3.2	1.36	7.6	9.56*
	10	25	4.1	1.38	9.3	7.84*
65	1	12	2.5	1.45	6.9	10.35
	10	25	2.7	1.38	6.9	8.90
80	0.1	8	0.9	1.23	—	11.90*
	1	13	1.8	1.36	5.6	11.75
	10	19	2.5	1.32	6.4	9.43

*No break

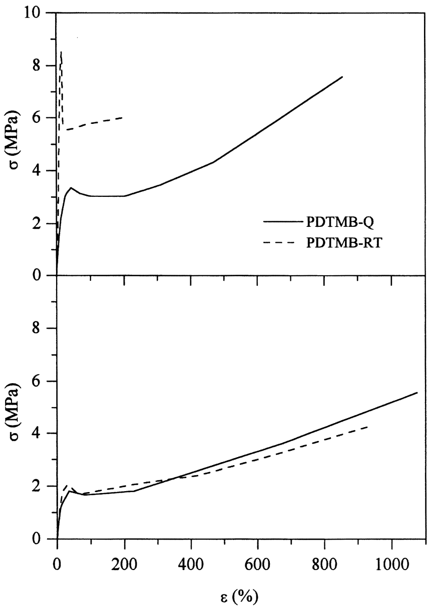

Figure 7 Stress–strain curves for sample PDTMB-RT compared with those of PDTMB-Q, deformed at 1 cm min^{-1}. Upper part: $T_d = 40$°C; lower part: $T_d = 80$°C

Table 4 Mechanical parameters of sample PDTMB-RT

T_e (°C)	V_d (cm min^{-1})	E (MPa)	σ_Y (MPa)	λ_Y	σ_B (MPa)	λ_B
40	1	130	8.5	1.15	5.9	2.94
	10	120[a]	9.4	1.14	9.1	6.25
80	1	18	2.0	1.32	4.3	10.46

[a] Adiabatic heating

are considerably high. Moreover, for drawing temperatures above T_g, these values are higher than those of other LC polybibenzoates with oxyalkylene spacers[20].

These results and the fact that PDTMB-Q, with only the pure LC phase, deforms through necking, reflect an intermediate behaviour between amorphous and semicrystalline polymers: in amorphous polymers homogeneous deformation takes place at $T_d > T_g$ while semicrystalline polymers keep the deformation through necking.

When PDTMB is left at room temperature a slow transformation into a three-dimensional crystal takes place. *Figure 4* shows the diffractogram of sample PDTMB-RT together with the one for PDTMB-Q. A degree of crystallinity comparable to that for the quenched samples of P7MB can be deduced from the upper diffractogram of *Figure 4*. The corresponding DSC melting curve (upper curve in *Figure 5*) shows the glass transition of PDTMB-RT at 18°C, followed by the crystal–mesophase transition at 63°C and the final isotropization of the sample, which is similar to that one for sample PDTMB-Q. Therefore, PDTMB presents a regular enantiotropic behaviour, in contrast to the case of P7MB, where the crystal experiences a monotropic transformation directly into the isotropic melt. The presence of crystallinity is clearly reflected in the mechanical properties. *Figure 7* shows the comparison of the stress–strain plots of samples PDTMB-Q and PDTMB-RT at two deformation temperatures. Moreover, the mechanical parameters for sample PDTMB-RT are presented in *Table 4*. The results show that, at $T_d = 40$°C, there is a considerable increase in E and σ_Y as a result of the presence of crystallinity. This is also responsible for the decrease of the deformation at break. The mechanical parameters for sample PDTMB-RT at $T_d = 40$°C are, however, not very different from those of sample P7MB-Q (compare *Tables 1, and 4*), especially if the comparison is made with $T_d = 65$°C for P7MB-Q, because this latter deformation temperature (65°C) for P7MB-Q is about 20 degrees above its T_g. This is similar to the case of $T_d = 40$°C for PDTMB-RT that is also about 20 degrees above the T_g of this polymer. This result is not surprising if we consider that those two samples, PDTMB-RT and P7MB-Q, exhibit similar degrees of crystallinity.

If we now focus the attention on the lower part of *Figure 7*, we can see that at $T_d = 80$°C the two curves for samples PDTMB-Q and PDTMB-RT are practically identical, and similar values of the mechanical parameters are obtained at this temperature for both samples (see *Tables 3 and 4*). The reason for this is that at 80°C the crystal–mesophase transition has occurred, as observed in the upper curve of *Figure 5*. Therefore, at this temperature the crystallites of samples PDTMB-RT were destroyed and only the mesophase is present, and the structures of the two PDTMB samples are identical at that temperature (80°C).

In conclusion, the stress–strain behaviour of a PDTMB sample where only a mesophase is present is intermediate between that of amorphous and semicrystalline polymers, since low values of the Young modulus and high deformation at break are obtained but the deformation takes places through necking even at temperatures above T_g. Moreover, when these thermotropic polymers are allowed to crystallize, their behaviour is typical of semicrystalline polymers.

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REFERENCES

1. Meurisse, P., Noel, C., Monnerie, L. and Fayolle, B., *Br. Polymer J.*, 1981, **13**, 55.
2. Krigbaum, W. R. and Watanabe, J., *Polymer*, 1983, **24**, 1299.
3. Watanabe, J. and Hayashi, M., *Macromolecules*, 1988, **21**, 278.
4. Pérez, E., Benavente, R., Marugán, M. M., Bello, A. and Pereña, J. M., *Polymer Bull.*, 1991, **25**, 413.
5. Pérez, E., Riande, E., Bello, A., Benavente, R. and Pereña, J. M., *Macromolecules*, 1992, **25**, 605.
6. Bello, A., Pereña, J. M., Pérez, E. and Benavente, R., *Macromol. Symp.*, 1994, **84**, 297.
7. Ober, C. K., Jin, J., Fhou, Q. and Lenz, R. W., *Adv. Polymer Sci.*, 1984, **59**, 103.
8. Nöel, C., *Makromol. Chem., Macromol. Symp.*, 1988, **22**, 95.
9. Peréz, E., Bello, A., Marugán, M. M. and Pereña, J. M., *Polym. Comm.*, 1990, **31**, 386.
10. Bello, A., Pérez, E., Marugán, M. M. and Pereña, J. M., *Macromolecules*, 1990, **23**, 905.
11. Bello, A., Riande, E., Pérez, E., Marugán, M. M. and Pereña, J. M., *Macromolecules*, 1993, **26**, 1072.
12. Pérez, E., Marugán, M. M., Bello, A. and Pereña, J. M., *Polymer Bull.*, 1994, **32**, 319.
13. Nielsen, L. E., *Mechanical Properties of Polymers and Composites*, 2nd Edition. Marcel Dekker Inc., New York, 1994.
14. Marugán, M. M., Pereña, J. M., Benavente, R., Pérez, E. and Bello, A., *Progress and Trend in Rheology IV*, ed. C. Gallegos. Steinkopff, Darmstadt 1994, p. 332.

15. Ward, I. M. *Mechanical Properties of Solid Polymer*, 2nd Edition. J. Wiley & Sons, Chischester, 1985.
16. Marshall, I. and Thompson, A. B., *Proc. Royal Soc.*, 1954, **A221**, 541.
17. Vincent, P. I., *Polymer*, 1960, **1**, 7.
18. Seguela, R. and Rietsch, F., *J. Mater. Sci. Lett.*, 1990, **4**, 46.
19. Brooks, N. W., Duckett, R. A. and Ward, I. M., *Polymer*, 1992, **33**, 1872.
20. Benavente, R., Pereña, J. M., Bello, A. and Pérez, E., *Polymer Bull.*, 1995, **34**, 635.