

Crystallization behaviour of syndiotactic poly-1,2(4-methyl-1,3-pentadiene)

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Different crystallization conditions were investigated for syndiotactic poly-1,2-(4-methyl-1,3-pentadiene) (P4MPD). The thermal crystallization is a slow process. At 60°C long times are needed to induce the structural rearrangements. Much shorter times are necessary for oriented samples, so that strain-induced crystallization occurs in a few hours. Solvent-induced crystallization produces a crystalline phase having small and poorly ordered crystallites. The crystallization process enhances the properties of the polymer, increasing both the modulus and the strength. © 1997 Elsevier Science Ltd.

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INTRODUCTION

In recent years it has been reported that the polymerization of a conjugated diolefin, as 4-methyl-1,3-pentadiene, obtained with heterogeneous catalysts from $\text{Al}(\text{C}_2\text{H}_5)_3$ and TiCl_4 , TiCl_3 or VCl_3 , gives polymers having almost exclusively 1,2 units and showing crystallinity attributable to 1,2 isotactic sequences¹. However, the same diolefin in the presence of typical catalysts producing syndiotactic polystyrene (e.g. CpTiCl_3 -MAO; Cp = cyclopentadienyl, MAO = methylaluminoxane) affords the 1,2 syndiotactic polymer^{2,3}.

The behaviour of 4-methyl-1,3-pentadiene is closer to that of polystyrene than to that of 1,3-butadiene or isoprene, which produce 1–4 *cis* polymers³.

The 1,2 structure of poly-1,2(4-methyl-1,3-pentadiene) (P4MPD) can be understood by considering that high substitution of one of the double bonds probably hinders 1,4 addition. The other unsaturation is conjugated and resembles, in reactivity, that of styrene. 2,1 insertion and syndiotactic arrangement would result from the non-bonded interactions between the incoming monomer and the active species, identical to those occurring in the polymerization of styrene⁴. As a matter of fact, styrene and 4-methyl-1,3-pentadiene resemble each other, having one conjugated unsaturation and being forced to undergo 2,1 insertion, thus giving polymers of similar stereochemical arrangement. It is therefore interesting to study the structural organization of this new polymer.

Very recently it has been reported that syndiotactic P4MPD, obtained as a highly oriented fibre, shows two crystalline modifications: a major one with a repeat of 1.173 nm, and minor amounts of a zig-zag planar polymorph⁵. Therefore, particular attention has to be paid to the crystallization of this polymer. Inducing crystallization is important both for theoretical and technological reasons. It is dependent on the physical treatments to which the polymer is subjected. In addition, the possibility of obtaining, through different treatments, either polymorph needs to be clarified.

In this paper the conditions under which thermal, strain-induced and solvent-induced crystallization occur will be presented and discussed in relation to the structure of the polymer.

EXPERIMENTAL

Polymerization of P4MPD was carried out in a 50 ml glass flask equipped with a magnetic stirrer, by introducing sequentially 2.5 ml of toluene, 6×10^{-3} mol of MAO (based on Al) dissolved in 3 ml of toluene, and 2 ml of 4-methyl-1,3-pentadiene. After thermostating at -20°C , the reaction was started by introducing 1.2×10^{-5} mol of CpTiCl_3 in 1 ml of toluene. The polymerization was stopped after 2 h by introducing a few millilitres of ethanol. The polymer was coagulated in acidified ethanol, washed several times, and dried *in vacuo* at room temperature. The yield was 0.450 g.

The structure of the polymer was assigned by its ^{13}C n.m.r. spectrum, comparing the chemical shifts of the resonances observed with data from the literature².

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The P4MPD powders were moulded into a film 0.10 mm thick, in a hot press at 160°C, and either quenched to 0°C, in an ice-water bath (Sample Q0) or slowly cooled to room temperature (sample SC). Sample Q0 was annealed for 2 days at 60°C (sample Q60), or immersed in dichloromethane for 2 h and dried (sample QS). Different strips of sample Q0 were drawn at room temperature and at 60°C, using an air-heated Instron stretching machine, at an initial drawing rate of 1 cm min⁻¹. The draw ratio was defined as $\lambda = l/l_0$ (l_0 is the initial length of the sample and l the length after drawing, measured by two ink marks printed on the sample). The sample was divided into four zones, and the draw ratio was recorded photographically, according to a previously reported procedure⁶.

D.s.c. was carried out over the temperature range -100 to 300°C, using a Mettler differential scanning calorimeter, purged with nitrogen gas and chilled with liquid nitrogen. Runs were conducted on samples of about 10 mg at a heating rate of 20 K min⁻¹.

Wide-angle X-ray scattering spectra were carried out using a PW 1050/71 Philips powder diffractometer (Cu K α -Ni filtered radiation), in the reflection mode, at 2° of 2 θ min⁻¹.

Dynamic mechanical properties were measured using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer interfaced with a temperature controller. The measurements were performed in the tension mode, at a frequency of 1 Hz and a heating rate of 3 K min⁻¹, in the range -150 to 150°C.

RESULTS AND DISCUSSION

Thermal crystallization

The thermograms of samples Q0 and SC are shown in Figure 1. The two samples do not exhibit an endothermic peak, although sample SC was slowly cooled. The glass transition, centred between 25 and 30°C, is well evident, confirming that the samples are prevalently amorphous. The thermogram of sample Q60 is also shown in the figure, indicating that the long thermal treatment (2 days) led to the crystallization of the sample. A very sharp peak appears, at about 95°C, with an enthalpic content of 17.6 J g⁻¹. The glass transition is also evident, much reduced with respect to the amorphous sample.

In Figure 2 the wide-angle X-ray diffractograms (WAXD) of samples Q0 and Q60 are shown. The WAXD of sample SC is very similar to that of sample

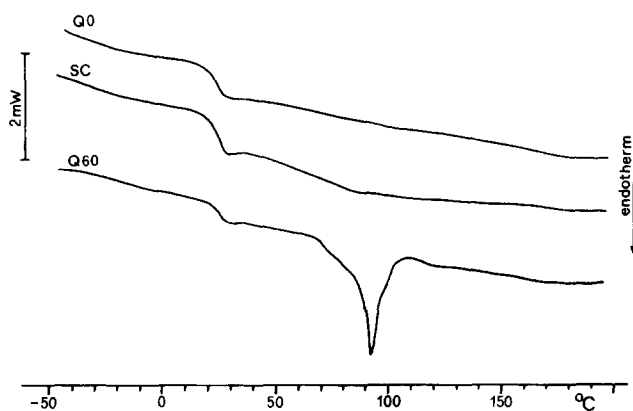


Figure 1 Thermograms of sample Q0, SC and Q60

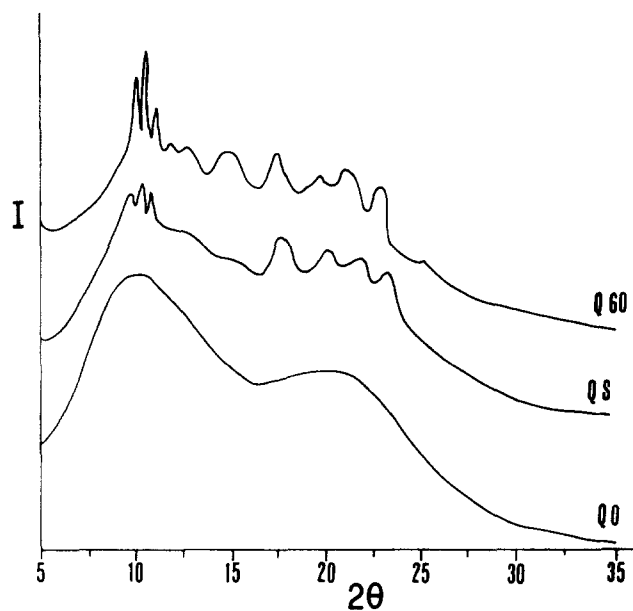


Figure 2 Wide angle X-ray diffractograms of sample Q0, QS and Q60

Q0, and is not reported on here. Sample Q0 shows only two broad peaks, centred at 10 and 20 of 2 θ . It is therefore an amorphous sample, as already revealed by the thermograms. At variance, sample Q60 shows a diffractogram in which many crystalline peaks are evident: some of them, at about 10, 10.5, and 11° of 2 θ are very sharp, whereas at higher angles they appear broad and not very well resolved. They correspond to the already reported form I of P4MPD, characterized by a repeat of 1.173 nm⁵. In fact, in the drawn samples we found the same identity period.

The conformations of syndiotactic vinyl polymers have been recently summarized⁷. Syndiotactic polystyrene (sPS) and polypropylene (sPP) show two low-energy conformations: the all-*trans* T4 sequence, with a repeat of 0.505 nm^{8,9} and the two-fold helical conformation (s(2/1)2), with a repeat of 0.71 and 0.74 nm, respectively^{10,11}. These conformations were the most stable by energy calculations, too^{12,13}. Recently a new crystalline form was identified in sPP exposed to solvent vapour, characterized by a repeat of 1.16 nm, and a (T6G2T2G2) conformation¹⁴. In analogy to this form of syndiotactic polypropylene, Meille *et al.*⁵ suggested for oriented P4MPD, showing a repeat of 1.173 nm, a similar conformation, which can be described as a combination of the T4 and (T2G2)₂ conformations.

We can conclude that the thermal crystallization of non-oriented P4MPD produces the same crystalline form. It is a slow process, not occurring during the film preparation, and a long time at the crystallization temperature is needed for the polymer to crystallize.

It is worth remembering that our polymer was synthesized at a temperature (-20°C) for which Meille *et al.* found a less crystallizable sample⁵.

Strain-induced crystallization

To investigate the strain-induced crystallization, sample Q0 was drawn at room temperature and at 60°C, and the drawing behaviour analysed in terms of the stress-strain curves. The drawing occurs homogeneously: as matter of fact, the strain inhomogeneity is not concentrated in any particular zone, and macroscopically

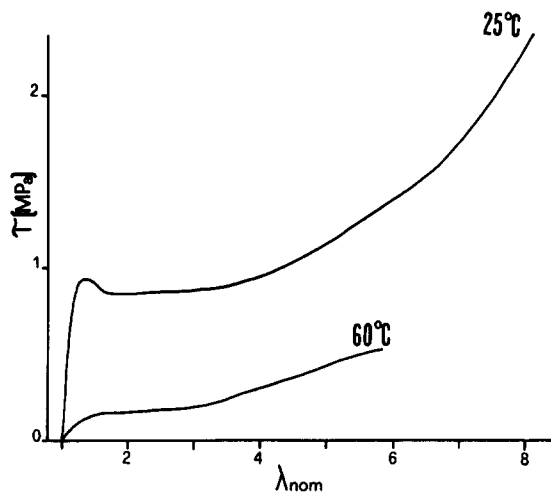


Figure 3 Stress-strain curves for P4MPD, drawn at room temperature (25°C), and at 60°C

the deformation is characterized by the absence of a localized visible neck.

In Figure 3 we report the tensional stress τ (force on the initial undeformed cross-sectional area) (in megapascals) as a function of the nominal strain λ_N , for the drawing either at room temperature (25°C) or at 60°C. The drawing occurs by yielding, well evident in the drawing at room temperature. The yield tension decreases markedly on increasing the temperature. After the yielding, the drawing occurs at constant τ in a strain range depending on the temperature. At higher strains, τ steeply increases on increasing the strain up to the fracture. Strain hardening occurs after $\lambda = 3$ and 4 for the drawing at 60°C and at room temperature, respectively. This phenomenon can be associated with the orientation and, possibly, the crystallization of the originally amorphous sample, and therefore could be indicative of strain-induced crystallization. It is evident that the strain hardening occurs earlier at 60°C with respect to that at room temperature, indicating that the crystallization is, in any case, favoured at higher temperatures. In order to investigate the strain-induced crystallization the drawn samples were analysed by d.s.c.

In Figure 4 the thermograms of the samples drawn up to different draw ratios, at room temperature and at 60°C, are reported.

In the drawing at room temperature (Figure 4a), we observe that, up to $\lambda = 4$, no clear evidence of crystallization is present in the thermograms. For the samples with $\lambda = 2$ and 4, only the glass transition, extending between 20 and 30°C, is well evident, demonstrating that the samples are prevalently amorphous. A very broad and small endothermic signal indicates that some structural organization is present in these drawn samples. The sample drawn at $\lambda = 6$ shows the endotherm of the crystalline phase, centred at about 100°C. The enthalpic content of this endotherm, integrated between 70 and 120°C is 12.0 J g⁻¹. The enthalpic content and the form of the endotherm indicate that the strain-induced crystallization at room temperature produced smaller and more defective crystals with respect to the thermal crystallization.

The drawing at 60°C does not induce crystallinity in the samples drawn up to $\lambda = 2$ and 4 (Figure 4b) whereas a broad endothermic peak appears at $\lambda = 5$. In the

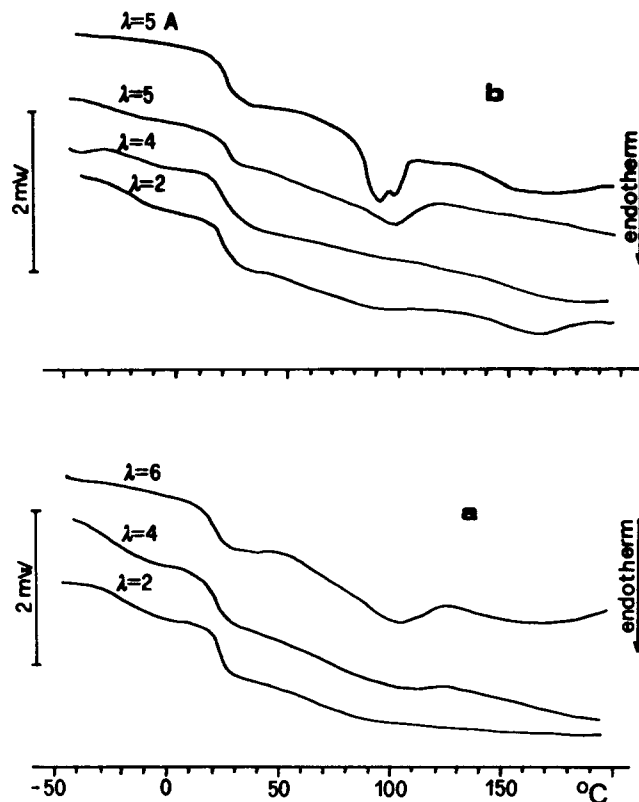


Figure 4 Thermograms of the samples drawn (a) at room temperature up to $\lambda = 2, 4$ and 6 and (b) drawn at 60°C up to $\lambda = 2, 4$ and 5, and $\lambda = 5$ kept with fixed ends for 2 h at 60°C (5A)

figure, the thermogram of the sample with $\lambda = 5$ was carried out after keeping the sample for 2 h with fixed ends in the drawing camera, to improve the crystallinity ($\lambda = 5A$). In fact, a sharp endotherm with two peaks appears after the short thermal treatment. These results also show that the strain-induced crystallization is a quite difficult process, although crystallization occurs more easily than that observed without orientation. It occurs after $\lambda = 4$, and the obtained crystallinity is improved by a following thermal treatment, keeping the sample with fixed ends. Returning to the stress-strain curve (Figure 3), we can conclude that the strain hardening is principally due to the orientation process, and less to the development of crystallinity. In agreement with the results of Meille *et al.*⁵, the X-ray fibre diffraction pattern, not reported here, shows in the drawn samples the prevalent presence of crystallinity of form I, with a small amount of form II.

Solvent-induced crystallization

As shown by d.s.c., at room temperature the P4MPD is slightly below its glass transition temperature. It is, therefore, necessary to increase the temperature to allow segmental mobility, which is needed for the crystallization process, to occur. Interaction between polymer chains and solvents may disrupt the intermolecular cohesive forces, increasing the chain mobility and allowing crystallization at a temperature much lower than that needed for thermal crystallization. This process, called solvent-induced crystallization (SINC), is very interesting, not least because it can lead to different morphologies of the crystalline samples.

To verify if P4MPD undergoes this process, the amorphous sample Q0 was exposed to dichloromethane

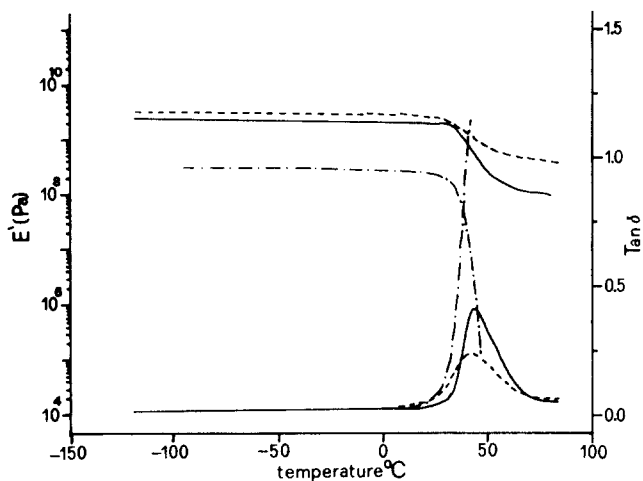


Figure 5 Dynamic mechanical spectra of sample Q0 (· · · · ·), Q60 (—), and Q0 drawn at room temperature up to $\lambda = 7$ (— · — · —)

vapour for 2 h, and dried under vacuum for many hours. Dichloromethane was used because it is a small molecule that interacts highly with the polymer.

In Figure 2 the WAXD of sample QS is reported, showing that the amorphous sample crystallized in the solvent into a crystalline form more disordered than that obtained by thermal crystallization. In fact the crystalline peaks, appearing on the amorphous halo, are very broad and not well resolved as the others. The d.s.c. thermogram, not reported here, indicates a poor crystalline sample, too. However, this result is very important, because it shows that the SINC process is a possible route to the crystallization of P4MPD. Although dichloromethane induces a very disordered crystalline form, it is worth remembering that this process occurs at room temperature, without the use of thermal energy. Furthermore, the solvent-polymer interaction, allowing the crystallization process, depends on many factors: among them a very important role is played by the solubility parameter of the solvent. Generally, the closer the solubility parameters of the solvent and the polymer, the higher the concentration of solvent in the polymer, and therefore the higher the chain mobility. Other solvents have to be analysed in order to find the best conditions.

Dynamic mechanical analysis

In Figure 5 the dynamic mechanical spectra of samples Q0, Q60 and Q0 drawn at room temperature up to $\lambda = 7$ are shown. The elastic moduli of samples Q60 and $\lambda = 7$ are much higher, throughout the analysed temperature range, than the amorphous sample Q0. The decrease in modulus, due to the glass transition, is dramatic for sample Q0, and determines the loss of the mechanical resistance. The sample flows, and we observe a break in the curve. This is another indication that the sample does not crystallize during the heating run. Instead, the

crystalline sample Q60 after T_g shows a constant modulus up to the melting point. The modulus after T_g of the drawn sample is still higher; the drop at T_g is very much reduced, due to the oriented crystals in the sample. The behaviour of the loss factor, $\tan \delta$, follows that of the elastic modulus. A very intense peak is observed for the amorphous sample, which is interrupted just after T_g , due to the flowing of the sample. The intensity of the peak is very much reduced in sample Q60 and in the drawn sample. The intensity of the loss band is indicative of two structural features: the amount of amorphous component, and the molecular mobility within it. According to the other results, the drawn sample shows the lowest intensity of the peak.

CONCLUSIONS

The crystallization of syndiotactic P4MPD can be obtained either thermally or by strain-induced and solvent-induced processes. In the first case, long times are needed to induce the structural rearrangements, leading to the crystallization. As expected, much shorter times are necessary for oriented samples; therefore, the drawing greatly accelerates the crystallization process, giving much better crystalline forms, too.

The solvent-induced crystallization is a possible route for obtaining crystallization of P4MPD, although this process produces a less crystalline form.

Work is in progress to investigate other crystallization conditions, and to clarify the structural organization of the crystalline samples.

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