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Thermal and viscoelastic behaviour of copolymers of propene and 1-hexene

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Summary

The thermal and viscoelastic behaviour of several copolymers of propene and 1-hexene have been studied in a wide range of compositions. The samples were prepared with a Ziegler-Natta catalyst with both internal and external donors. A significant amount of crystallinity has been found for the sample with a comonomer content as high as 19 mol %. The dynamic mechanical results show a considerable decrease of the storage modulus in the copolymers in relation to that of iPP. A single relaxation, corresponding to the glass transition, has been found in all the samples. Only the copolymer with the highest hexene content seems to display the beginning of another relaxation at low temperature.

Introduction

Highly active and isospecific catalysts for olefin polymerization have attracted much attention from both industrial and academic laboratories. In the last two decades, many supported-type catalysts have been employed for the copolymerization of olefins.

The existence of centers with different activity in these catalysts is responsible for the usual heterogeneity in composition, with a higher concentration of comonomer units in the lower molecular weight chains (1,2). The activity of these centers can be changed by the nature and physical state of the support and by the addition of suitable electron-donor substances (3), which modify the structure of the copolymers.

The copolymerization of ethylene and propene as well as others alkenes, together with the thermal and mechanical properties of the copolymers, have been frequently reported (3,4). There are, however, only a few papers concerning the copolymerization of propene with high 1-alkenes (5), in spite of the fact that copolymers of propene with 1-alkenes are important commercial products. In particular, propene copolymers are suitable for films requiring good clarity, flexibility and mechanical strength (6). Therefore, efforts have been directed towards finding novel and more efficient catalysts for the synthesis of copolymers with the desired properties.

The aim of this work is to analyze the thermal and viscoelastic behaviour of

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several copolymers of propene and 1-hexene. They were synthesized by using $MgCl_2$/DIBP/$TiCl_4$-$AlEt_3$/PTES as catalyst, containing diisobutyl phthalate (DIBP) as internal Lewis base and phenyl triethoxysilane (PTES) as external base.

Experimental part

The details of the synthesis of the different polymers have been reported elsewhere (7). In summary, the copolymerizations were conducted in a 1 liter autoclave, with heptane as solvent, at 60°C. The $MgCl_2$-supported $TiCl_4$ catalyst contains DIBP as internal base. It was activated by $AlEt_3$, and PTES was used as external base.

The comonomer compositions and the isotactic triad fractions, [mm], were determined from the NMR spectra (7) in solutions of $C_2D_2Cl_4$. Table 1 shows the corresponding results.

Polymer films were prepared in a Collin press fitted with smooth-polished plates, by hot pressing at 5 MPa for 3 min, at a temperature 20°C above the melting temperature of the sample. The cooling process was carried out by quenching with water.

The thermal properties were measured by means of a Perkin Elmer DSC-7 calorimeter, interfaced to a data station and connected to a cooling system. The heating rate was 20°C/min. The weight of the samples ranged from 7 to 9 mg. Peak melting temperatures were considered. The value of the glass transition temperature, T_g, was considered as that temperature were the increment of the specific heat was half of the total at the transition.

X-ray diffraction patterns were obtained at room temperature with a Geiger counter X-ray diffractometer from Philips, employing nickel-filtered CuKα radiation.

Dynamic mechanical measurements were carried out with a Polymer Laboratories Mk II Dynamic Mechanical Thermal Analyzer working in the tensile mode. The complex modulus and the loss tangent of each sample were determined at 3, 10 and 30 Hz over a temperature range from -150 to 100°C. The experiments were carried out in a dry nitrogen atmosphere at a heating rate of 2°C/min. The specimens used were rectangular strips 2.2 mm wide with length and thickness around 14 mm and 0.3 mm, respectively. The relaxation intensities, based on loss tangent values, have been evaluated relative to the minimum value recorded for each experimental curve. The apparent activation energies were tentatively calculated according to an Arrhenius-type equation, from the maximum values of the loss tangent at the three mentioned frequencies.

Table 1. Comonomer composition, isotactic triad fractions, maximum of tan δ for the α relaxation (at 3 Hz) and apparent activation energy of this relaxation for the different samples

sample	mol % hexene	[mm]	tan δ_α	ΔH_α (kJ/mol)
iPP	0	0.88	0.07	310
C05	4.7	0.88	0.27	250
C12	12.0	0.88	0.30	200
C19	19.4	0.83	0.39	210

Results and discussion

The DSC melting curves, normalized with respect to the mass of the samples, of the four quenched samples are presented in figure 1. It is observed that the relative proportion of the low temperature tail in the copolymers is higher than that in the homopolymer. This behaviour is characteristic of heterogeneous olefin copolymers. As expected, a considerable decrease of both the melting temperature, T_m, and the enthalpy of melting, ΔH_m, is obtained with increasing hexene content (see figure 2). Due to the heterogeneity of the copolymers, the variation of the melting temperature with the composition is not smooth, and the most significant decrease is obtained on passing from iPP to C05, while the values for the three copolymers are very close. This reflects the increasing importance of the low-temperature tail in the endotherms as the hexene content is increasing. The crystallinity, f_c, of the samples has been estimated from the values of the enthalpy of melting together with that reported for a perfect crystal of iPP (8). The corresponding values of f_c are plotted in figure 2.

The amplified inset in figure 1 shows the glass transition of the samples. The specific heat increment at the transition increases with the hexene content, since this transition is produced in the amorphous phase. The values for that increment are 0.08, 0.21, 0.24 and 0.26 J/g°C for samples iPP, C05, C12 and C19, respectively (with an error of the order of ±0.05 J/g°C). The variation of the glass transition temperature with the composition is shown in the lower part of figure 2, showing that T_g decreases when the hexene content increases (we found a value of -43°C for the T_g of a poly(1-hexene) sample synthesized with a similar, but not the same, Ziegler-Natta catalyst).

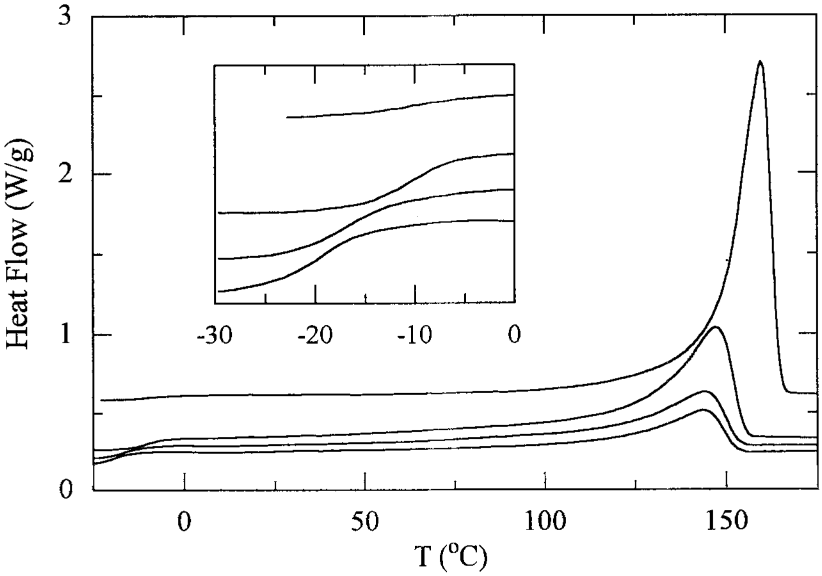

Fig. 1. Normalized DSC melting curves of the samples quenched from the melt. From top to bottom: iPP, C05, C12 and C19.

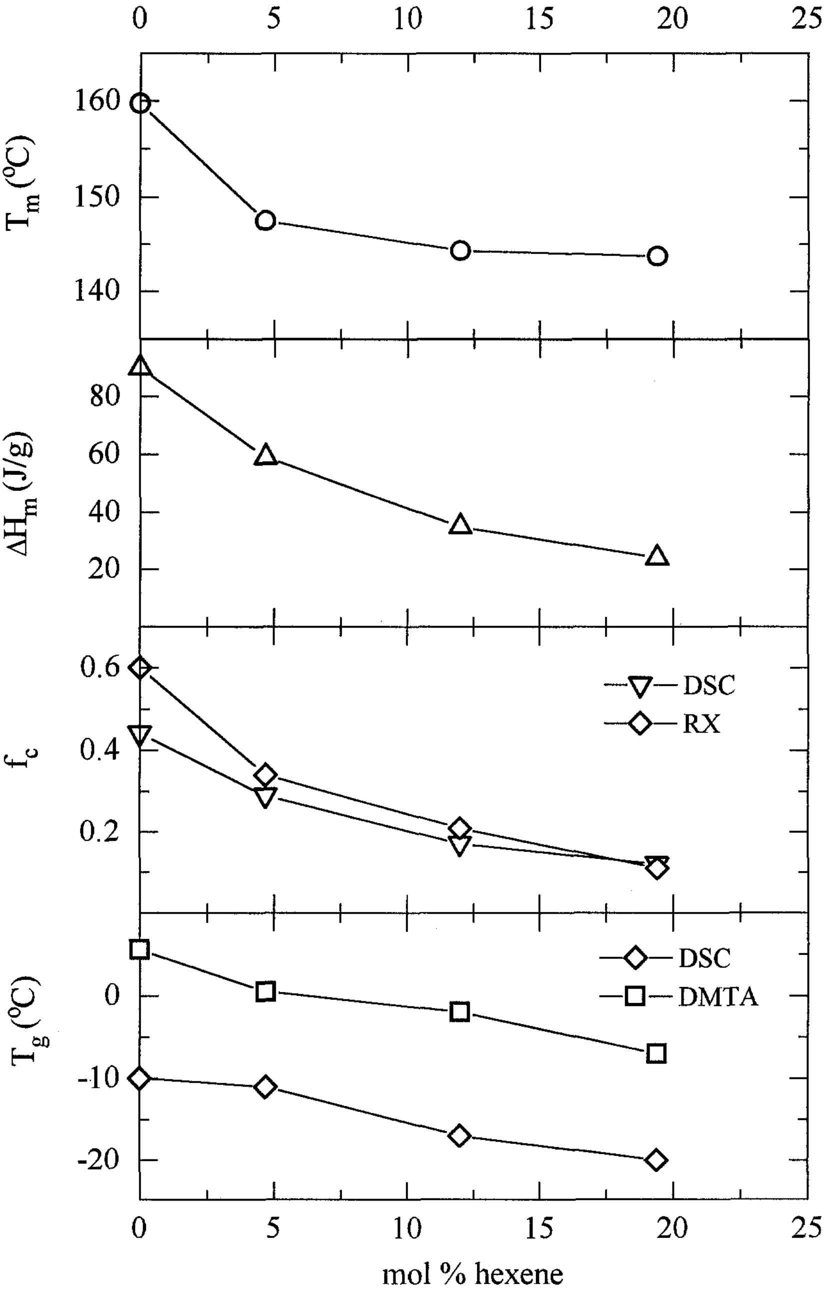

Fig. 2. Variation of the melting temperature, enthalpy of melting, degree of crystallinity and glass transition temperature with the composition.

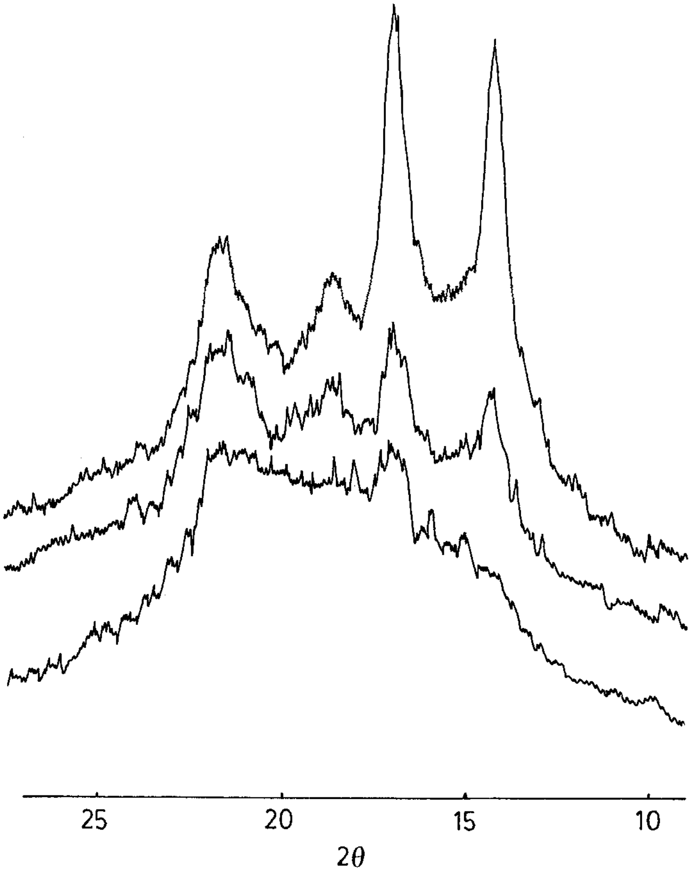

Fig. 3. X-ray diffractograms of the three copolymer samples quenched form the melt. From top to bottom: C05, C12 and C19.

The X-ray diffractograms corresponding to the three copolymer samples are shown in figure 3. It is evident that the crystallinity decreases when the hexene content increases. Thus, the diffraction pattern for C19 shows a broad amorphous peak with barely defined crystalline peaks. These crystal diffractions are rather wide, as expected for small crystals. A rough deconvolution of the amorphous and crystal components allows estimation of the crystallinity of the samples. The corresponding values have been plotted in figure 2, compared with those obtained from the enthalpy. For the iPP sample, it is observed that the crystallinity obtained from X-rays is considerably higher than that obtained from the enthalpy measurement, since the former value presumably includes the interfacial content, which is not considered in the enthalpy measurements (9,10). However, the difference between the two estimations becomes smaller with increasing hexene content, and similar values have been obtained for copolymer C19. This is contrary to expectations, because higher interfacial contents have been reported for copolymers (10). We think that the reason for this unexpected result lies in the difficulty of the deconvolution in the X-ray diffractogram. The fact that the crystal diffractions become broader with increasing comonomer content may lead to underestimations of the X-ray crystallinity. Alternatively, one can think that for these broad crystal diffractions, the interfacial content is now included in the amorphous peak and therefore the two determinations tend to coincide. We are planning to analyze other propene copolymers, synthesized with different catalyst systems, in order to clarify this point.

It has been reported that iPP exhibits polymorphic behaviour (11-15) and the so called γ modification can be obtained under certain conditions, in addition to the more common α form. For instance, we have found significant amounts of the γ modification in iPP homopolymers with very low isotactic contents or in those obtained with metallocene catalysts. The most important factor for the obtention of the γ modification seems to be the occurrence of disruptions in the iPP chain. The presence of a randomly distributed comonomer leads, evidently, to such disruptions, and the γ form is expected to be favoured in iPP copolymers. It has been shown (12,14) that it is difficult to distinguish between the α and γ modifications by DSC, since their melting temperatures are very close. However, the X-ray diffractogram of the γ form presents a characteristic peak at $2\theta \approx 20$ degrees, and the γ content can be calculated from this peak (13,16). The diffractograms of the copolymers presented in figure 3 show the diffraction peaks corresponding to the α modification (11), although they are rather broad. However, considering the noise level in the diffractograms, the presence of a signal from the γ modification cannot be excluded.

The dynamic mechanical behaviour of the samples is shown in figure 4. The tan δ plots show only one clear maximum for each sample, which is close to the temperature of the DSC glass transition, and is accompanied by a sharp decrease of the storage modulus, E'. Moreover, high values of the apparent activation energy, ΔH_α, have been found for this relaxation (see Table 1). Consequently, we have assigned this relaxation to the glass transition, and named it α (it has been reported (17) that some iPP samples display a relaxation at higher temperatures, which was called α and the glass transition was then named β).

The α relaxation (glass transition) temperature, T_α, decreases as the comonomer content increases (lower part of figure 2) in a similar trend exhibited by the DSC glass transition, although the DMTA values (tan δ basis) are about 15°C higher than those from DSC. The intensity of the α relaxation (see Table 1) increases significantly with the hexene content, owing to the increase in the amorphous content.

Close inspection of figure 4 (see tan δ inset) shows that the C19 copolymer displays an increase of tan δ with decreasing temperature from about -100°C. This increase seems to be outside the experimental error and points to the existence of a mechanical relaxation. We assign this relaxation to crankshaft motions of methylenic

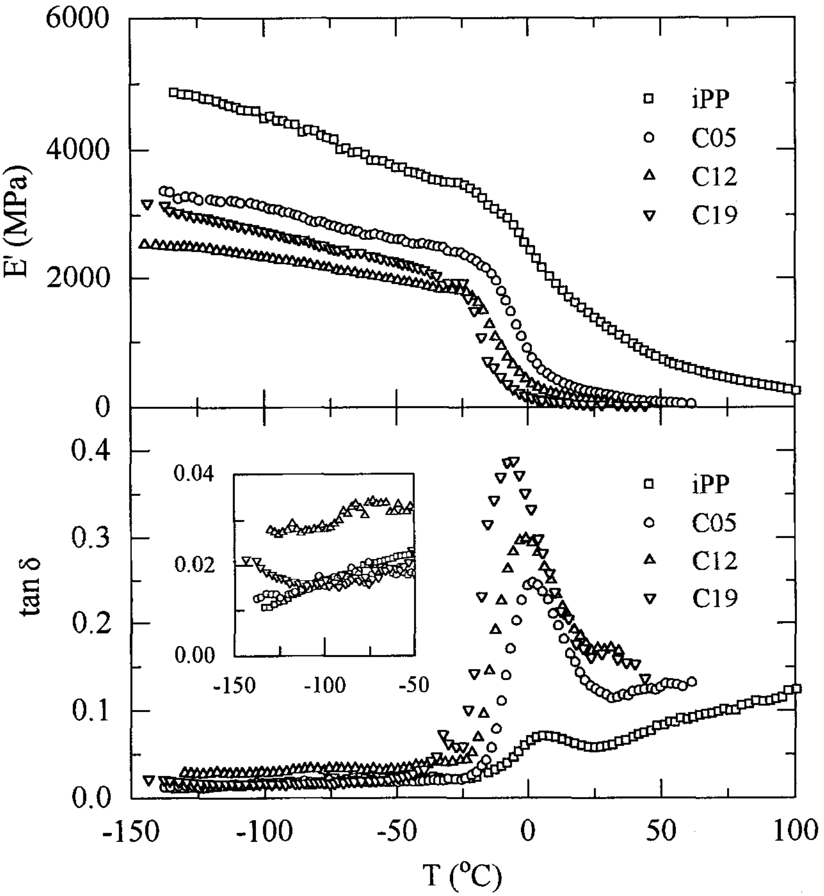

Fig. 4. Temperature dependence (at 3 Hz) of the storage modulus (upper) and loss tangent (lower) for the different samples quenched from the melt.

segments in the amorphous phase, which are characteristic of the γ relaxation reported in both polymethylenic (4,18) or polyoxyethylenic (19) sequences at temperatures around -120°C. This relaxation has been also reported for poly(1-olefin)s with the exception of polypropene (20).

Regarding the storage modulus, it can be observed in the upper part of figure 4 that a considerable decrease of this parameter, in relation to that for the homopolymer, is found for the copolymers, even for the one with the lowest hexene content.

Acknowledgment

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