ELSEVIER

Polymer 43 (2002) 5847–5854

polymer

www.elsevier.com/locate/polymer

Synthesis and physical properties of elastomeric polypropylene obtained in the presence of $TiCl_2(2\text{-}OC_6H_4OCH_3)_2$ and methylaluminoxane

Oriana Motta[a], Carmine Capacchione[b], Antonio Proto[b,*], Domenico Acierno[c]

[a]*Department of Physical and Chemical Methodology for Engineering, University of Catania, v.le A. Doria 6, 95125 Catania, Italy*
[b]*Department of Chemistry, University of Salerno, via S. Allende, 84081 Baronissi, SA, Italy*
[c]*Department of Materials and Production Engineering, University of Napoli "Federico II", Piazzale Tecchio 80, 80125 Napoli, Italy*

Received 23 January 2002; received in revised form 15 July 2002; accepted 16 July 2002

Abstract

In this work we present a new synthetic route to obtain elastomeric polypropylene with high molecular weight and narrow molecular weight distribution, in the presence of $TiCl_2(2\text{-}OC_6H_4OCH_3)_2$ and methylaluminoxane catalytic system. Moreover we focused on investigating the thermal, mechanical and rheological properties of the ELPP and its solvent fractions. The results demonstrate that the polymers exhibit high ultimate extension and excellent elastic recovery, due to the presence of microcrystalline domains dispersed in the amorphous phase. The elastic and viscous response has been found to depend upon the molecular weight, which changes with the polymerization temperature. © 2002 Published by Elsevier Science Ltd.

Keywords: Elastomeric polypropylene; Titanium guaiacolate; Rheology

---

1. Introduction

The microstructure of polypropylene obtained in the presence of homogeneous catalytic systems is related to the symmetry of organometallic precursor. In particular, for pseudo-tetrahedral compounds such as metallocenes, C_2, C_s and C_{2v} symmetry lead to isotactic, syndiotactic and atactic stereo-sequences of the monomer units, respectively. Recently Waymouth [1] has developed an oscillating catalyst which changes the symmetry between C_2 and C_{2v} during the growing of the chain, producing isotactic and atactic stereo-blocks. The polymer, which has M_w around 500,000 and $M_w/M_n < 3$, has an elastomeric behaviour similar to the stereo-irregular fraction obtained with heterogeneous Ziegler–Natta catalysts [2–4] and more recently by Collette [5]. Elastomeric polypropylenes (ELPPs) are also obtained in the presence of unsymmetrical ansa-metallocenes with convenient substituents to achieve the hemi-isotactic microstructure [6–9]. Recently interest has been moved on octahedral complexes with racemic C_2 symmetry. In particular Eisen and co-workers have produced ELPPs in the presence of acetylacetonate and phosphinoamide complexes of group 4 [10,11]. They have assumed that the stereo-chemical control on incoming monomer is given either by the symmetry properties of the organometallic precursor or by the intramolecular epimerization reaction of the last-inserted monomer. They have also showed, by ^{31}P NMR experiment on octahedral phosphinoamide compounds in the presence of methylaluminoxane (MAO), that the reaction product has a dynamic equilibrium between tetrahedral and octahedral configurations. The interconversion between these configurations should depend on the presence of a dynamic Lewis-base pendant group which can donate an electron ion pair to the electrophilic metal centre. Tetrahedral and octahedral configurations produce the atactic and isotactic stereo-sequences, respectively, in the elastomeric polymer chain.

In this work we present a new synthetic route to obtain PP with elastomeric behaviour by using a catalytic system based on $TiCl_2(2\text{-}OC_6H_4OCH_3)_2$ and MAO. Titanium compound which has octahedral structure and C_2 symmetry was first prepared by Gau and co-workers [12] and can be compared to the octahedral phosphinoamide compound above mentioned.

Moreover we found of interest to investigate the physical and mechanical behaviour of these ELPPs. In particular the dynamic rheological properties of two polypropylenes

---

* Corresponding author. Tel.: +39-89965234; fax: +39-89965296.
E-mail address: proto@chem.unisa.it (A. Proto).

0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00492-5

obtained at different polymerization temperatures have been analysed; the polymerization temperature has in fact a strong effect on the molecular weight of the polymer [13] and hence can also influence its rheological properties. Dynamic mechanical measurements and thermal characterization have been carried out in order to determine the transitions occurring upon heating and cooling and to provide information regarding the crystalline phase. Mechanical tests have been performed to monitor the elastomeric behaviour of these polypropylenes.

2. Experimental

2.1. Materials

Schlenk technique was used for all manipulations in nitrogen atmosphere.

Aromatic and aliphatic hydrocarbons (Carlo Erba) were refluxed 48 h under nitrogen atmosphere over sodium and benzophenone before using. Other reagents were purchased from Aldrich and used without purification. Toluene and $Al(CH_3)_3$ present in MAO 10% (Witco) solution were distilled under reduced pressure. The residual white powder was washed several times with *n*-hexane, dried in vacuum and stored in glove box. Deuterated solvents (Trimital) were stored in glove box and dried with molecular sieves 4 Å. Polymerization grade propylene was purchased from Società Ossigeno Napoli and used without purification. $TiCl_2(2\text{-}OC_6H_4OCH_3)_2$ was prepared according to the literature [12].

2.2. Polymerization procedure

The polymerizations of propylene were carried out in a 500 ml glass stirred autoclave at the temperatures of 25 and 50 °C. 2.9 g of MAO powder were dissolved in toluene (190 ml), 10 ml of a toluene solution 0.05 M of catalyst were added and the orange solution transferred in a thermostatic autoclave. The nitrogen was evacuated and the propylene was added at 5.0 bar. The flask was continuously fed with propylene. The polymerizations were stopped by removing the monomer and then injecting acidified methanol. The mixtures were poured into methanol and the polymers recovered by filtration, washed with fresh methanol and dried in vacuum oven at 70 °C. The polypropylene samples were fractionated by extraction with hexane under a nitrogen blanket at the boiling point of the solvent. The extracted polymer was recovered by evaporation of the solvent (60 °C in vacuo).

2.3. NMR analysis

^{13}C NMR spectra of the polymers were recorded on an AM 250 Bruker operating at 62.8 MHz in a Fourier transform mode at 378 K. The samples were prepared by dissolving about 30 mg of polymer in 0.5 ml of tetrachloro-1,2-dideuteroethane and 0.5 ml of 1,2,4-trichlorobenzene in the presence of hexamethyldisiloxane (HMDS) as internal chemical shift reference.

2.4. Molecular weight determination

Molecular weight and molecular distribution of the polymers were detected by Water 150 GPC instrument operating at 135 °C. Five milligrams of the samples were dissolved at 100 °C in 6.0 ml of 1,2,4-trichlorobenzene and automatically injected for the analysis.

2.5. Thermal analysis

The calorimetric measurements were carried out on a Mettler TC 11 differential scanning calorimeter operating under nitrogen flow and calibrated by the measurement of the melting point of indium. The samples were first heated at a rate of 10 °C min to 200 °C and held at this temperature for 10 min to allow the complete melting of the crystallites, then cooled to room temperature at 10 °C min. The values of crystallization temperature (T_c) and enthalpy of crystallization (ΔH_c) were collected during these cooling runs. The samples were then heated from -50 to 200 °C at 10 °C min and the results of the glass transition temperature (T_g), melting temperature (T_m) and enthalpy of melting (ΔH_m) referred to these traces are reported. Moreover in order to investigate the kinetic behaviour more accurately the samples were cooled at different cooling rates: 5, 10 and 20 °C min^{-1} and the data obtained were analysed adopting the Ozawa theory.

2.6. Dynamic mechanical characterization

Dynamic mechanical properties were determined on a dynamic mechanical analyser TA Instruments DMA 983 at the fixed frequency of 1 Hz and temperature ranging from -70 to 100 °C. The heating rate was 5 °C min^{-1} and samples of $10 \times 60 \times 1.2$ mm^3 were used.

2.7. Mechanical characterization

Mechanical tests were performed on an Instron Universal Testing Machine Mod. 4301 (Instron® Ltd, UK) equipped with a 1-KN tension load cell. Samples for mechanical tests were made by thermal compression moulding of the polymer at $T = 200$ °C. The sample was held for approximately 5 min to allow the powder to melt before applying pressure to the mould to force the polymer to flow into the shape of the frame. After 10 min the mould was cooled with circulating water and pressure was released. Tensile tests were performed according to ASTM D412 method with a crosshead speed of 500 mm min^{-1} on dumb-bell shaped specimens 4.4 mm wide and 1.4 mm thick. The specimen gauge length was 18 mm. For tensile set measurements the

Table 1
Polymerization results

Run	T (°C)	Yield (g)	Hexane insoluble (%)	M_w ($\times 10^3$)^a	M_w/M_n^{a}	M_w ($\times 10^3$)^b	M_w/M_n^{b}	mmmm^b (%)
1	25	3.8	>96	998	2.0	1198	2.0	25
2	50	1.9	70	573	3.3	647	3.1	18
3^c	25	3.6	48	860	2.0	n.d.	n.d.	19

All the runs were performed at 5.0 atm, in the presence of 5.0×10^{-5} mol of catalyst and Al(MAO)/Ti = 500 in 200 ml of toluene for 1 h.

[a] Whole polymer.

[b] Hexane insoluble fraction.

[c] Al(MAO)/Ti = 1000.

specimen (rectangular sample 30 mm long, 6 mm wide and 2 mm thick) was held at 200% elongation for 10 min and then allowed to rest for 10 min after the tension was released. The gauge length was 8 mm and the tensile set was defined as: $100 \times ((L_f - L_i)/L_i)$, where L_f and L_i are the final and initial distance between the bench marks on the specimen, respectively. At least five specimens were tested to obtain satisfactory statistics.

2.8. Rheological measurements

The dynamic rheological measurements were carried out on a Rheometric ARES under a nitrogen atmosphere in order to avoid thermooxidative degradation. Strain sweep measurements were carried out in order to determine the region of linear viscoelasticity. Frequency sweeps were performed from 0.1 to 100 rad s^{-1} on 25 mm parallel plate at 5% strain and at different temperatures from 80 to 240 °C. The gap between plates was set to 1.2 mm and the polymer was equilibrated at the desired temperature before beginning the measurements.

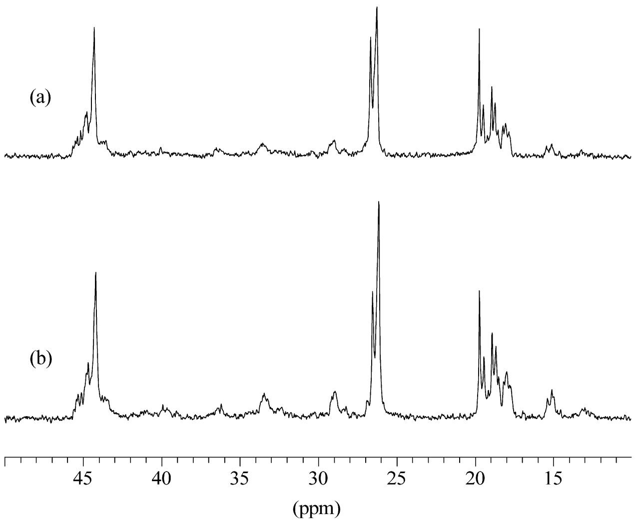

Fig. 1. NMR spectra of hexane insoluble fraction of (a) polymer **1** and (b) polymer **3**.

3. Results and discussion

3.1. Polymerization

In Table 1 the polymerization results of propylene in the presence of $TiCl_2(2\text{-}OC_6H_4OCH_3)_2$ and MAO catalytic system are reported. The polypropylene samples were fractionated by extraction with hexane under a nitrogen blanket at the boiling point of the solvent. From the table it is clear that the hexane soluble fraction of polypropylene increases either with reaction temperature or with Al(MAO)/Ti molar ratio. In Fig. 1 ^{13}C NMR spectra of the hexane insoluble fractions of polypropylene, prepared at the polymerization temperature of 25 °C and different Al(MAO)/Ti molar ratio, are reported (see run 1 and 3). The resonance with low intensities, about 10%, observed at $\delta = 15.1$, 15.5, 28,3, 29.4, 33.5, 33.7, 36.7, 40.1, are diagnostic of regio-irregularly arranged monomeric units, as reported in a previous paper [14]. In the spectrum of polymer **1**, the resonance of the *mmmm* (*meso*) stereochemical pentads at $\delta = 19.7$ is the most intensive one (about 25%), whereas that of polymer **3** is about 19%. These ELPPs are produced in mild pressure condition (5.0 atm) and have microstructures (same NMR signal pattern) similar to the elastomers prepared with acetylacetonate group 4 complexes [10].

GPC analysis shows high molecular weight polymers ($M_w > 10^5$) and narrow molecular weight distributions ($M_w/M_n = 2.0\text{–}3.3$), indicating that the polymers are produced by a single catalytic specie. The microstructure of the polymers could be derived either by considering the epimerization reaction of the last monomer unit into the polymer chain, or by an oscillating equilibrium between tetrahedral and octahedral configurations of the catalyst [10, 11]. In accord to the mechanism proposed by Eisen, a speculative consideration could be that the methoxy groups of guaiacolate complex, which are electron donors, in the reaction with MAO could afford to an equilibrium between tetrahedral configuration (atactic stereo-sequences), in which methoxy groups are far from the metal, or to C_2 octahedral configuration (isotactic stereo-sequences) with methoxy groups coordinated to the electrophilic metal centre. The lower amount of *meso* pentads in polymer **3**, prepared using higher Al/Ti molar ratio, could corroborate

Table 2
DSC data of elastomer PP and its solvent fractions obtained at: (**1**) $T = 25$ °C, (**2**) $T = 50$ °C

Sample	T_c (°C)	ΔH_c (J g^{-1})	T_m (°C)	ΔH_m (Jg^{-1})	T_g (°C)
Polymer **1**	84.5	3.4	129.7	2.3	−8.2
1 HS	–	–	–	–	−9.3
1 HI	87	2.1	136.7	2.0	−8.3
Polymer **2**	103.6	0.8	–	–	−11.3
2 HS	–	–	–	–	−8.3
2 HI	100.4	1.2	158	1.1	−9.6

the hypothesis of Eisen. In fact, in this case, the equilibrium between the two structures is moved toward tetrahedral arrangement which is responsible for atactic stereo-sequences. Of course this is matter of further investigation because it is not clearly known what really happens in the reaction between metal complex and MAO. In fact it is also plausible the hypothesis relative to the production in situ of multi-metallic specie. The presence of different amount of isotactic stereo-blocks (*mmmm* pentads) in these polymers, which are substantially regio- and stereo-irregular, accounts for the different physical properties which are discussed below.

3.2. Thermal behaviour

In Table 2 the numerical data of the crystallization and melting parameters, obtained by means of DSC, relative to the polypropylenes prepared at different polymerization temperatures are reported. In order to erase all previous thermal history the samples were heated up to 200 °C and held at this temperature for 10 min to allow complete destruction of the crystals. After this treatment cooling and heating traces were recorded at a scanning rate of 10 °C min^{-1}. As can be seen polymer **1** exhibits a single crystallization temperature at $T_c = 84.5$ °C with an enthalpy of crystallization $\Delta H_c = 3.4$ J g^{-1}. Upon heating a glass transition temperature at $T = -8.2$ °C and a melting peak corresponding at $T = 129.7$ °C with a $\Delta H_m = 2.3$ J g^{-1} can be observed. The area under the melting endotherm (enthalpy of fusion) is a measure of the amount of the polymer crystallinity. The degree of crystallinity can be calculated from the following relation

$$\phi_c = \frac{\Delta H_m}{\Delta H_m^0(\mathrm{iPP})} \times 100$$

where ΔH_m^0(iPP) is the equilibrium heat of fusion for isotactic polypropylene which is 209 J g^{-1}, as reported in Ref. [15]. The degree of crystallinity for polymer **1** is 1.1%. This low value of crystallinity, coupled with the observation of low isotactic content (< 25% by NMR) suggests that the polymer has a stereo-block structure of crystallizable isotactic blocks and non-crystallizable atactic blocks [16]. The thermoplastic elastomer behaviour has been proposed to arise from the presence of microcrystalline domains (isotactic stereo-sequences) acting as physical crosslinks in prevailingly amorphous samples (atactic stereo-sequences) [2–4]. Giving a closer look to the behaviour of the hexane fractions one can see that the soluble fraction of polymer **1** (**1** HS), which is less than 4%, does not show thermal transitions upon heating and cooling with the exception of the glass transition at $T = -9.3$ °C, so this fraction can be considered as fully amorphous, in accord with NMR experiment. On the other hand the hexane insoluble fraction (**1** HI), which is more than 96%, behaves like the elastomer polypropylene, in fact it has a $T_c = 87$ °C with the enthalpy of crystallization $\Delta H_c = 2.1$ J g^{-1}, a $T_g = -8.3$ °C and a $T_m = 136.7$ °C with an enthalpy of fusion $\Delta H_m = 2.0$ J g^{-1}. In Table 2 the DSC data of polypropylene obtained in the same polymerization condition but at higher temperature (polymer **2**) are reported. This sample shows a small enthalpy of crystallization ($\Delta H_c = 0.8$ J g^{-1}) during the cooling run whereas no melting transition is detected upon the subsequent heating. The hexane fractions of polymer **2** have also been analysed and reveal that the hexane insoluble fraction (**2** HI) has a higher degree of crystallinity with respect to the unfractionated polymer, in fact it has an enthalpy of crystallization $\Delta H_c = 1.2$ J g^{-1} and an easily recognizable melting peak with an enthalpy of fusion $\Delta H_m = 1.1$ J g^{-1}. On the other hand the soluble fraction (**2** HS) shows only the glass transitions at $T = -8.3$ °C; this fraction, which is around 30%, has been found from NMR analysis to have few stereo-regular blocks (< 10%). A possible explanation for the observed lack of crystallinity of the soluble fraction, still containing stereo-regular blocks, is that the isotactic sequences could be significantly shorter than in the insoluble fraction.

To better understand the kinetic behaviour of these polymers the non-isothermal crystallization route were analysed more accurately and data obtained by DSC at different cooling rates were analysed adopting Ozawa equation [18]. From a technological point of view the non-isothermal crystallization behaviour of polymers is of great importance since most of the processing techniques occur under non-isothermal conditions. Ozawa theory is based on the acceptance that crystallization occurs under constant cooling rate and proceeds by nuclei being formed randomly and growing in three dimensions. The parameters determining the crystallization kinetics are the Avrami exponent n, which can be related to the type of nucleation and to the geometry of crystal growth, and the cooling crystallization function χ. These parameters can be determined from the slope and the intercept of the straight line obtained by plotting the double logarithm of the amorphous fraction $\ln[-\ln(1 - X_c)]$ against the logarithm of the cooling rate $\ln a$. The Ozawa theory can be expressed by the following equation

$$\ln[-\ln(1 - X_c)] = \chi - n \ln a$$

where X_c is the volume fraction of the material crystallized at a given temperature T and a is the cooling rate. The DSC

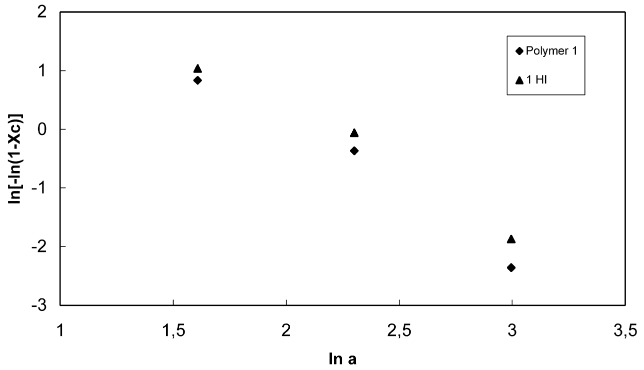

Fig. 2. Ozawa plot of polymer **1** and its hexane insoluble fraction (**1** HI), at the temperature of 84 °C.

data obtained in the dynamic cooling crystallization at 5, 10 and 20 °C min^{-1} were analysed according to this equation. The value of the Avrami exponent n is 2.5 for polymer **1**, and the cooling crystallization function χ decreases with increasing the temperature of analysis. In Fig. 2 the Ozawa plot for polymer **1** and its hexane insoluble fraction (**1** HI) is reported at the temperature of 84 °C. The lines are similar and the value of the Avrami exponent n for the insoluble fraction is 2.1. This indicates that the nucleation mechanism does not change appreciably. Ozawa plot of the ELPP obtained at the polymerization temperature of 50 °C (polymer **2**) was not feasible due to the very low level of crystallization enthalpy.

3.3. Dynamic mechanical measurements

The dynamic mechanical properties of polymer **1** were determined as a function of temperature and at the frequency of 1 Hz. As expected, inspection of the loss modulus E'' trace reveals the occurrence of only one mechanically active transition, characterized by its maximum, which corresponds to a value of $T = -5$ °C. This value is associated with the glass transition of the polymer, in good accord with the value found by DSC analysis. Moreover the spectrum does not reveal other transitions confirming that a single phase is present. These findings are in accord with the results of GPC analysis which reveals a narrow distribution and hence evidences that the polymer is constituted by macromolecules of the same microstructure.

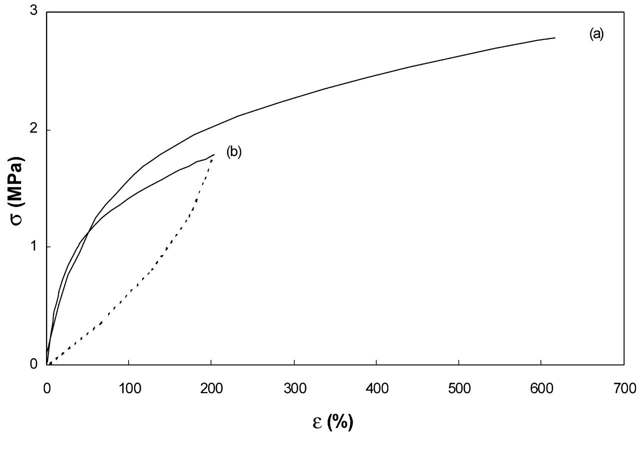

Fig. 3. Stress–strain curve of polymer **1**: (a) the curve has been obtained at a rate of 500 mm min^{-1}; (b) the curve has been obtained at a rate of 50 mm min^{-1} and stopped at 200% elongation to measure the elastic recovery (the dotted line is not obtained experimentally).

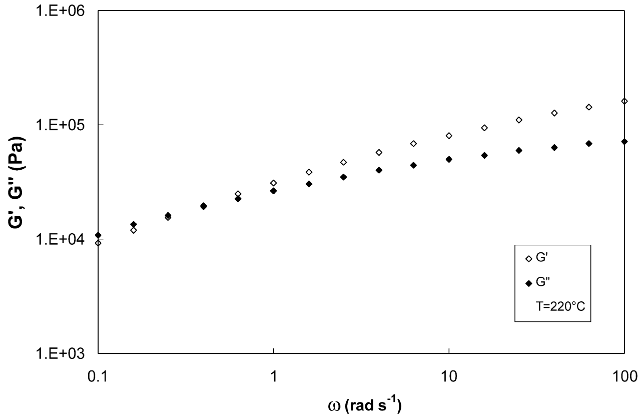

Fig. 4. Storage and loss modulus for polymer **1** obtained at $T = 220$ °C.

3.4. Mechanical behaviour

Mechanical tests were performed on the polymer obtained at $T = 25$ °C in order to investigate on the elastomeric behaviour. The stress–strain curve of polymer **1** is reported in Fig. 3. The curve does not show a yield point and, as expected, the specimen exhibits high ultimate extension and excellent elastic recovery. The elastic recovery is 98% after elongation to 200% for 10 min (curve b) whereas following break the tension set value obtained is 3.3%. Low tension set value (and hence good elastic behaviour) is generally related for uncrosslinked samples to the presence of physical crosslinks, which in this case are the microcrystalline domains in the amorphous phase. It has been demonstrated that the drawability becomes very small when the samples are fully amorphous at room temperature and unable to crystallize under stretching [19] and only low crystallinity and isotacticity polymers exhibit elastomeric properties [17]. The tensile modulus obtained for this polymer was 4.2 MPa and the ultimate strength 2.7 MPa while the elongation at break measured at a crosshead speed of 500 mm min^{-1} was 622%, as can be observed from the figure (curve a). The tensile properties of the hexane insoluble fraction of polymer **1** were also investigated. The results show that mechanically the HI fraction resembles ELPP, in fact also in this case the sample exhibited high ultimate extension and excellent elastic recovery (tension set = 3, ultimate extension 800%).

3.5. Rheological properties

Usually the viscoelastic behaviour can be determined by

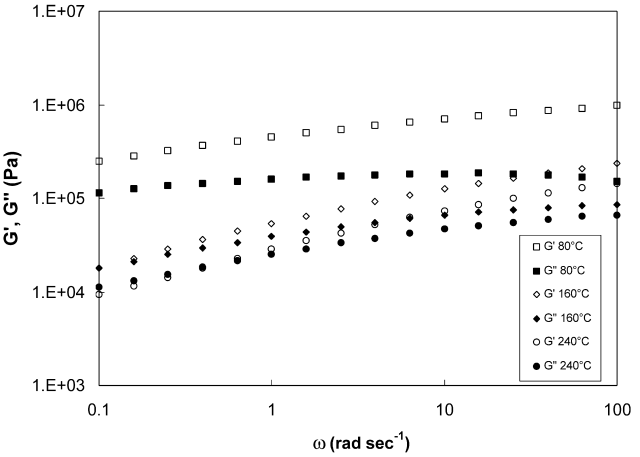

Fig. 5. Storage and loss modulus for polymer **1** obtained at different temperatures.

measuring the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ over a wide range of frequencies ω and temperatures T. The storage modulus is proportional to the energy stored in a cycle deformation reflecting a certain degree of elasticity of the system, the loss modulus is proportional to the dissipation of energy as heat in a cycle deformation reflecting a certain degree of viscosity of the system. Cross point value $[G'(\omega) = G''(\omega)]$ separates viscous-like and elastic-like behaviour [20]. In Fig. 4 the storage and loss modulus for polymer **1** obtained at $T = 220$ °C are reported versus the angular frequency ω. It can be clearly seen that at frequency below $\omega_{\text{cross}} = 0.31\ \text{rad s}^{-1}$, G'' dominates and the polymer is able to relax, while at frequencies higher than ω_{cross} relaxation is inhibited ($\tan\delta < 1$).

In general, the rheology of polymer melts depends strongly on temperature. Dynamic rheological measurements were performed on the same samples at different temperatures ranging from 80 to 240 °C. Data of storage and loss moduli for polymer **1** collected at the temperature of 80, 160 and 240 °C (the rest have been omitted to avoid crowding) are shown in Fig. 5. It can be observed that for tests measurements performed at temperature higher than 160 °C a cross point value $[G'(\omega) = G''(\omega)]$ can be detected and the curves are very similar, whereas at temperatures below 160 °C they differ substantially. Considerably higher values of both G' and G'' are obtained at temperatures lower than 160 °C and the curves do not contain a crossover frequency (the storage modulus overcomes the loss modulus in the whole frequency range and continues to increase in relative importance as the temperature is decreased). At low temperatures polymer **1** behaves as an elastomer that does not flow or relax even at low frequencies. Indeed relaxation may take place on longer time scales than those employed in these oscillatory experiments. In the range of temperatures above 160 °C ω_{cross} increases with the increasing of temperature, as can be observed in Fig. 6. Dynamic rheological measurements were also performed on polymer **2** with the attempt to investigate on the effect of polymerization temperature on the viscous and elastic response of the polymer. The obtained data show that the rheological behaviour of polymer **2** is similar to that of polymer **1** but all the curves relative to the rheological parameters (η^*, G', G'') are shifted towards lower values. These lower values can be accounted for the lower molecular weight of the polymer obtained at the higher polymerization temperature, following the inverse relationship between molecular weight and reaction temperature. Also in this case ω_{cross} strongly depends upon temperature and the diagram is reported in Fig. 6. It shows that at the same test temperature the values of ω_{cross} for polymer **2** are higher than that of polymer **1**. This interesting finding can be explained by considering that lower molecular weight implies lower network constraints and point restrictions. Moreover DSC analysis has shown that the degree of crystallinity of polymer **2** is very low compared to that of polymer **1**; thus the lower amount of crystallite fillers should enable the polymer to flow and relax in a higher frequency range at the same temperature. Moreover for polymer **2** the temperature at which the moduli do not contain a crossover frequency

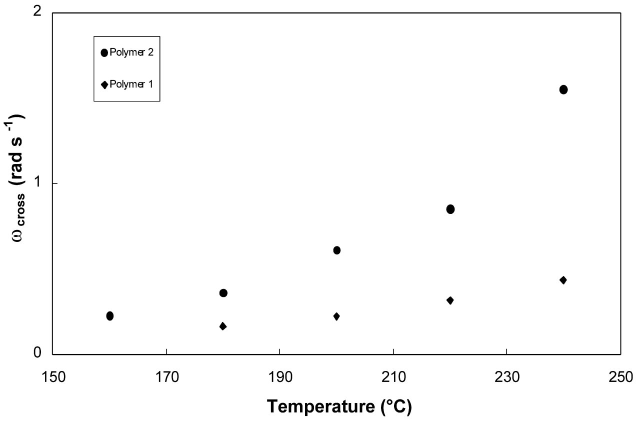

Fig. 6. Crossover values $[G'(\omega) = G''(\omega)]$ of polymers **1** and **2** versus temperature.

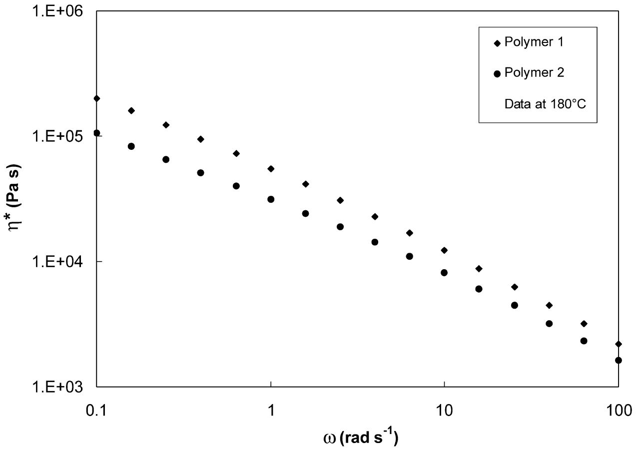

Fig. 7. Complex viscosity η^* versus the angular frequency ω for polymers **1** and **2** obtained at $T = 180$ °C.

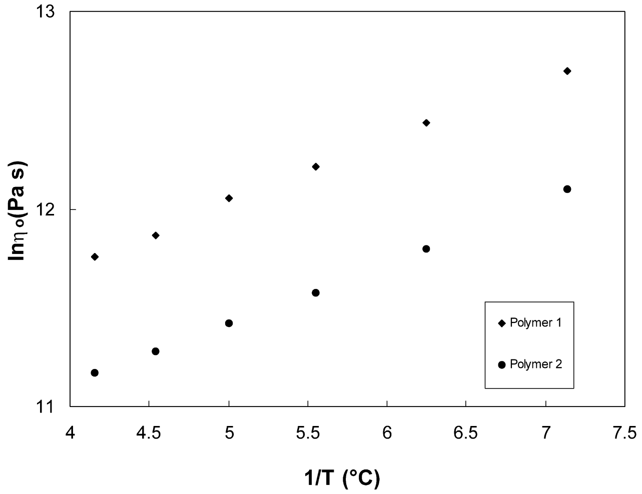

Fig. 8. Logarithm of viscosity (calculated at $\tau = 5 \times 10^3$) versus reciprocal temperature for polymers **1** and **2**.

has been found to be 140 °C (20 °C lower than that of polymer **1**).

Fig. 7 shows the complex viscosity, η^*, collected at $T = 180$ °C, for both polymers **1** and **2**. In the frequency range explored the polymers show typical pronounced non-Newtonian (shear thinning) behaviour thus it is not possible to obtain frequency independent viscosity. The temperature dependence of the zero shear viscosity above melting can be expressed by the Arrhenius equation, that is $\eta_0 \propto \exp(E_a/RT)$. Hence a semilog plot of η_0 versus $1/T$ yields a line which slope permits to calculate the flow activation energy E_a. E_a is a measure of the temperature sensitivity of viscosity; small values imply little effect of temperature on the viscosity while large values imply strong dependence. Due to the impossibility of dealing with Newtonian viscosities we have plotted the complex viscosity against the shear stress (τ) and calculated the value of the viscosity at different values of τ. A representative plot of ln η versus $1/T$ for both polymers **1** and **2** at a fixed value of τ is reported in Fig. 8. From it a value of $E_a = 39 \pm 2$ kJ mol^{-1} is obtained. The plot clearly shows that the temperature sensitivity of viscosity is quite similar for both the two polymers and independent of the molecular weight. This value is in good agreement with values of E_a typical of isotactic polypropylenes which have been reported to be in the range 39–43 kJ mol^{-1} [21,22]. Moreover in the work of Eckstein [21] a value of 39 kJ mol^{-1} has been reported also for the atactic polypropylene, calculated by the WLF equation.

4. Conclusions

The catalytic system based on $TiCl_2(2\text{-}OC_6H_4OCH_3)_2$ and MAO produces polypropylene with high molecular weight and narrow molecular weight distribution. The *mmmm* (*meso*) stereo-chemical pentads observed for the polymers produced in different condition of temperature and Al(MAO)/Ti molar ratio are in the range 18–25%. Further experiments are in progress in order to deeply investigate on the reaction mechanism using these octahedral catalytic systems.

From GPC analysis it has been found that increasing the polymerization temperature leads to a decrease in the molecular weight of the polymer and to a broadening of the molecular weight distribution. The thermal analysis has shown that the polymers exhibit a very low level of crystallinity, which coupled with low isotactic content (<25% by NMR) produces a polymer with thermoplastic elastomeric characteristics. Dynamic mechanical analysis has confirmed the value of the glass transition temperature obtained by DSC and revealed that a single phase is present. Mechanical tests have shown that the polymer exhibits high ultimate extension and excellent elastic recovery and no yield is evidenced.

Dynamic rheological measurements have revealed that the polypropylenes have temperature dependent properties. At low temperatures ELPP behaves like an elastomer that does not flow or relax on the time scale of the experiment, even at low frequencies, whereas at high temperatures a cross point value can be detected and the loss modulus overcomes the storage modulus at frequencies lower than ω_{cross} (the polymer is able to relax). Comparison with the polymer obtained at higher polymerization temperature (50 °C) shows that lower values of all the rheological parameters are obtained as a consequence of the lower molecular weight. The melt flow activation energy was found to be independent of the molecular weight and in good accord with values typical for isotactic and atactic polypropylenes.

Acknowledgements

This work was supported by National Research Council (CNR). The authors are grateful to Mr Ennio Comunale for GPC analyses and Dr Patrizia Oliva for NMR analyses.

References

[1] Coates GW, Waymouth RM. Science 1995;267:217.
[2] Natta G. J Polym Sci 1959;34:231.
[3] Natta G, Crespi G. US Patent 3:175; 1965.
[4] Natta G, Mazzanti G, Crespi G, Moraglio G. Chim Ind (Milan) 1957;39:275.
[5] Collette JW, Tullock CW, MacDonald RN, Buck WH, Su ACL, Harrel JR, Mulhaupt R, Anderson BC. Macromolecules 1989;22:3851.
[6] Lin GY, Dong S, Chien JCW. J Am Chem Soc 1990;112:2030.
[7] Gauthier WJ, Collins S. Macromolecules 1995;28:3779.
[8] Bravakis AQM, Bailey LE, Pigeon M, Collins S. Macromolecules 1998;31:1000.

[9] Dietrch U, Hackmann M, Rieger B, Klinga M, Leeskela M. J Am Chem Soc 1999;121:4348.

[10] Shmulinson M, Fereres MG, Lisovskii A, Nelkenbaum E, Semiat R, Eisen MS. Organometallics 2000;19:1208.

[11] Kühl O, Koch T, Somoza Jr. FB, Junk PC, Hey-Hawkins E, Plat D, Eisen MS. J Organomet Chem 2000;604:116.

[12] Kuo CH, Huang TY, Shao MY, Gau HM. Inorg Chim Acta 1999;293:12.

[13] Jordens K, Wilkes GL, Janzen J, Rohlfing DC, Welch MB. Polymer 2000;41:7175.

[14] Grassi A, Zambelli A, Resconi L, Albizzati E, Mazzocchi R. Macromolecules 1988;21:617.

[15] Carlson ED, Krejchi MT, Shah CD, Terakawa T, Waymouth RM, Fuller GG. Macromolecules 1998;31:5343.

[16] Legge NR, Holden G, Schroeder HE, editors. Thermoplastic elastomers: a comprehensive review. New York: Hanser; 1988.

[17] Wunderlick B, Macromolecular physics, vol. 3. New York: Academic Press; 1980.

[18] Ozawa T. Polymer 1971;12:150.

[19] Guerra G, Ruiz De Ballesteros O, Venditto V, Galimberti M, Sartori F, Pucciariello R. J Polym Sci, Part B 1999;37:1095.

[20] Vega JF, Munoz-Escalona A, Santanaria A, Munoz ME, Lafuente P. Macromolecules 1996;29:960.

[21] Eckstein A, Suhm J, Friedrich C, Maier RD, Sassmanshausen J, Bochmann M, Mulhaupt R. Macromolecules 1998;31:1335.

[22] Wasserman SH, Graessley WW. Polym Engng Sci 1996;36:852.