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Study of Nucleation Induced Structure Modification in Isotactic Polypropylene by DMTA and Solid State NMR

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Summary: Isotactic polypropylene (iPP) modified by heterogeneous nucleation and molten state drawing was investigated using the DMTA and NMR methods. The nucleation was realized by specific α and β nucleating agents, 1,3,2,4-bis(3,4-dimetylobenzylideno) sorbitol (Millad 3988, Miliken) leading to the creation of the α phase, and N,N'-dicyklohexylo-2,6-naftaleno dikarboxy amid (NJ100) as the β phase promoter. The processing induced modification was performed by molten state drawing during an extrusion in the range between the die exit and the calibration unit. An increase of the glass transition temperature of iPP was found to be drawing independent for the β-nucleated samples, and dependent in the case of the α-iPP. Changes in the macromolecular mobility, depending on the α/β iPP structure and molten state drawing, was found by NMR lineshape and second moment measurements.

Keywords: chain mobility; DMTA; glass transition; NMR; poly(propylene) (PP); specific α and β nucleation

Introduction

The heterogeneous nucleation presents a very efficient approach to structure modification for polymers, characterised by a relative low crystallisation rate, and by significant supercooling. This is the case of an isotactic polypropylene.[1-7]

The addition of even of very low amount, like 15 to $30x10^{-4}$ parts, of low molecular substances (*called nucleating agents(NA)*) results in an increase of the nucleation density, and therefore leads to effects like a rise of the crystallisation temperature (*an important processing parameter*), production of fine spherulitic morphology (*an optical effect, but also modification of the properties*), and in specific condition to the modification of the crystal structure, e.g. creation of various crystallographic forms, like α, β or γ crystal phase in polypropylene. For isotactic polypropylene (iPP) and for related copolymers a huge family of nucleating agents was developed and examined.[8-13]

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Both crystal phases in iPP (α and β phase) differ by macromolecular chain conformation, crystallographic form, elementary unit density and therefore by molecular mobility, thus consequently by the physical properties. Huge research was published concerning possible applications of iPP crystallised in both crystal forms.[1,2,14-19]

The crystal structure modification, related to the changes of the chain conformation and of the geometry of elementary units, e.g. consequently changes of the interchain distances, may be determined by the measurements of the chain mobility.[20-23]

Significant differences in chain mobility may be awaited if structure of an isotactic polypropylene is modified by both specific nucleating agents and by molten state processing. Especially the different chain arrangement of iPP macromolecules which are in general heterogeneous may be studied by means of broad line NMR spectra giving rise to the multiple transitions occurring in the temperature range around and above glass transition of PP. Three components of the rotating frame spin-lattice relaxation times $T_{1\rho}$ with several relaxation minima in their temperature dependences also confirmed such relaxation behaviour.[24,25] The minimum of T_1 spin-relaxation in laboratory frame being appeared in the temperature range above the glass transition of PP corresponds to the β relaxation which was assigned to the glass transition phenomena.[26,27] The influence of NA on relaxation processes in PP was found out by rotating frame spin-lattice relaxation times $T_{1\rho}$.[25] In this case only the small shifts between β relaxation corresponding to the segmental motion and α relaxation which was ascribed to the motion of the whole amorphous chains were observed. On the other hand broad line NMR spectra provide data which are helpful to interpret also the temperature dependences of the relaxation times. Therefore we used the broad line NMR techniques to estimate the changes due to NA addition to iPP and to processing.

To study the role of both modifying parameters, e.g. of the heterogeneous nucleation and processing the dynamic mechanical thermal analysis (DMTA) and nuclear magnetic resonance (NMR) measurements were realized. Especially the DMTA is commonly applied when the information about the glass transition temperatures (T_g)[28-31] for investigated samples should be delivered, and the NMR for the manifestation of chain mobility in the investigated temperature range.

The aim of our studies was to describe the mechanism of structure modification on the molecular level by the iPP samples, and especially the influence of the nucleating agent on the macromolecular transition.

Materials

An isotactic polypropylene (NOVOLEN 1100H, BASF Germany) with a MFI = 2.4 cm^3/10 min (230°C, 2.16.kg, and density ρ = 910 kg/m^3) was used in our experiments. This polymer was modified by the heterogeneous nucleation using two additives: 1,3,2,4-bis(3,4-dimetylobenzylideno) sorbitol (DMDBS) leading to the creation of the α phase in iPP, and N,N'-dicyklohexylo-2,6-naftaleno dikarboxy amid as a β phase promoter. The DMDBS was Millad 3988 (Miliken), a white powder with a melting temperature T_m = 277°C and crystallization temperature T_{cr} = 214°C. The β-phase nucleate with a commercial name NJ 100 was also a white powder with a T_m = 387°C and T_{cr} = 137°C.

The inclusion of the NJ 100 into the isotactic polypropylene leads to the creation of a high content of the hexagonal β-phase. According to our previous investigations,[14,15,16,31] depending on the concentration of particular nucleating agent and of the processing condition, the β-phase content may reach values over 90%.

Both nucleating agents were incorporated into the iPP matrix in the molten state by extrusion. The high melting temperature of both nucleating agents signifies that during melt mixing both NA where in a solid state, *e.g.* a distribution of the solid nucleating additives, in a form of powder, in the molten iPP matrix has taken place. The studies were carried out for two concentrations of the NA: 0.1 wt. % and 0.5 wt. %, respectively. Pure iPP samples were investigated as well.

Processing

To determine the influence of the molten state processing on the glass transition by iPP some of the samples were extruded and drawn in molten state, in the region between the die exit and the beginning of the cooling bath. The elongation, estimated as the ratio between the average pulling velocity and the average die output velocity, was in the range from λ=1 (reference samples produced by compression moulding without elongation) to λ = 7.11.

Methods

The dynamic mechanical thermal analysis (DMTA) test was performed by torsion with a frequency of 1 Hz, in the temperature region between 240 K and 423 K. The aim of these measurements was to detect the influence of processing and nucleation induced structure modification on the glass transition temperature of iPP, as well on the position of the characteristic relaxation maximum.

The solid-state nuclear magnetic resonance (NMR) broad line investigations were performed with a continuous wave spectrometer[32] operating by frequency of 30 MHz, with frequency sweep and data acquisition performed with PC. The measurement of NMR lineshape was made in the temperature range between 227 K and 403 K, with the task to detect the influence of NA's on the possible changes of temperature dependent NMR second moment.

The Glass Transition Temperature and Relaxation Temperature for Nucleated and Drawn iPP Samples

On Figure 1 the run of the loss factor tan δ, as a function of temperature for both, non-nucleated and nucleated iPP is presented. The NA content (NJ and DMDBS) was 0.1 wt % and 0.5 wt %, respectively. It may be noted that the addition of the NJ (as β phase nucleate in iPP) leads to a shift of the glass transition temperature T_g towards higher values. Depending on the NA content the maximum on the curve tan δ was observed in the range between 275 K and 280 K for the β-nucleated iPP and between 270 K and 275 K for the α-phase iPP.

The crystal phase depending changes of the T_g, may be attributed to the interaction created between the amorphous and crystalline domains in the specific β-nucleated iPP. As it was proposed by Labour et al.[33] and discussed previously[34] the great number of tough tie molecules in the β-structure iPP may be the origin of the chain mobility modification. The macromolecular chains passing partly by the amorphous domains may give a rise of the structure rigidity and therefore of the changes of the T_g observed in this case. Such an assumption may be comprehended as contradictory to the effect of an increased impact resistance of the β-form of iPP.[1,6,7,14,18,19] Although, as it was shown by Aboulfaraj et al,[18] and confirmed,[14,19] the dependability of the impact resistance should be predominantly recognized to the spherulitic morphology, e.g. to the existence of radial and/or tangential lamellae, and to a lower extent to the chain conformation.

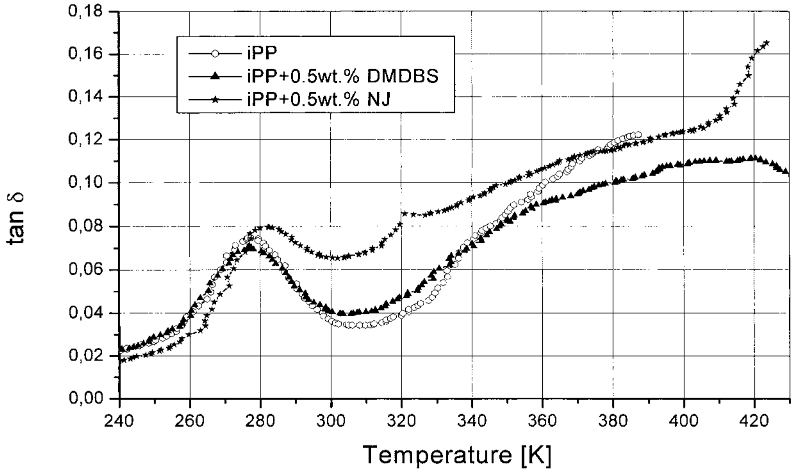

Fig. 1. The loss factor tan δ as a function of temperature for pure iPP, iPP nucleated with DMDBS and NJ.

Similar effects, e.g. an increase of the T_g were observed if in the α-iPP the molten state elongation was applied to modify the crystal order (Figure 2) in both, non-nucleated and α-phase nucleated iPP. As a consequence of drawing a shift of the T_g towards higher temperature of about 283 K, in comparison with the temperature of about 278 K observed for non-stretched samples was noted. In this case a similar explanation may be proposed as before, e.g. the creation of a certain number of tough tie macromolecules in the crystalline domains which provoke the decrease of the mobility in the amorphous phase, e.g. the rise of the T_g.

The increase of the glass transition temperature as well for the β-nucleated iPP samples as for the α-drawn iPP, signify that higher temperature (e.g. higher thermal energy) has to be provided in order to prevail over this mobility transition barrier. On the contrary no changes of the T_g was noted for β-nucleated and subsequently drawn iPP samples (Figure 3). In this case once the higher value of T_g was obtain, due to the β-nucleation, no changes may be observed after drawing. This observation may indicate also that no significant changes of the β-phase content, for the uniaxial molten state drawn iPP, should be awaited.[31,35] Other way, the specific α and/or β nucleation, and the subsequent molten state drawing may be an origin of several changes of the lamellar distribution in the iPP.[36]

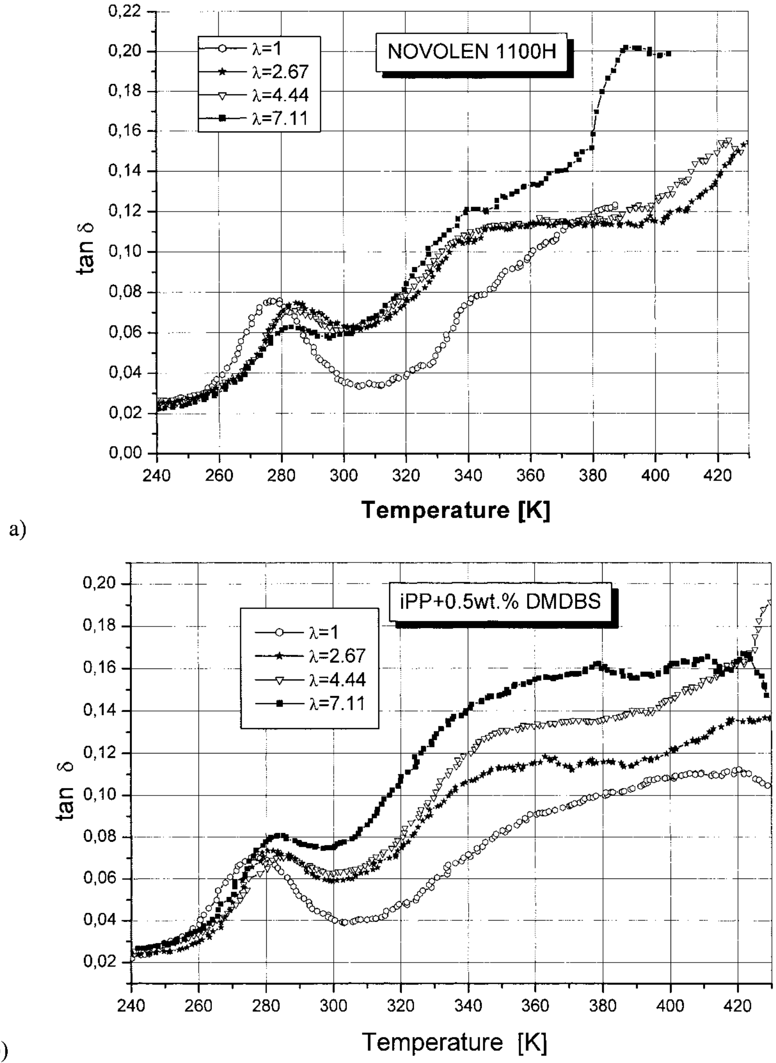

Fig. 2. The loss factor tan δ as a function temperature for molten state elongated samples: a) pure iPP, b) iPP nucleated with 0.5 wt. % of DMDBS.

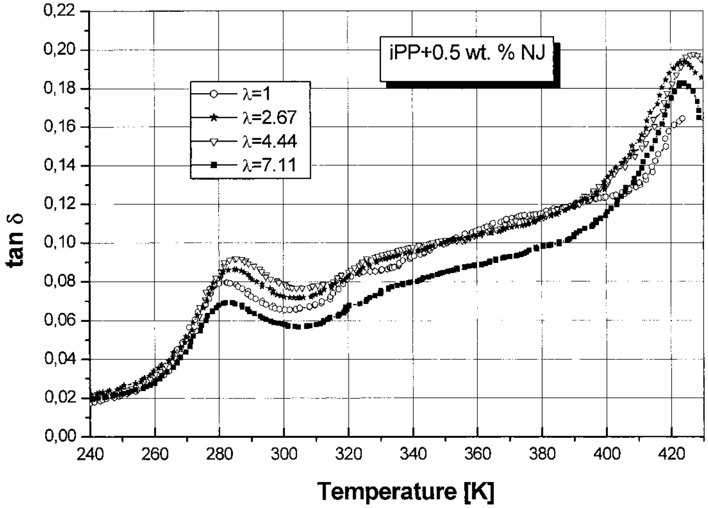

Fig. 3. The loss factor tan δ as a function of temperature for molten state drawn samples of iPP nucleated with 0.5 wt. % of NJ (β-phase iPP).

Another, less expressed maximum on the tan δ-curves may be seen for the temperature range between 320 K and 360 K. This maximum is much wider than those significant for the glass transition, and corresponds probably to the relaxation effect in the iPP. As well the position, as the intensity of the maximum is also nucleation and processing dependent.

NMR Broad Line Investigation

To explain the nature and the character of the appearance of the maximum by 320 K to 360 K, the NMR measurements in the solid state, as a function of temperature were realised.

A significant change of the NMR lineshape (Figure 4), observed for the same temperature range as the maximum on the DMTA curves, allows to relate this structural effect to the changes in the macromolecular mobility. The NMR lineshape, characteristic for the crystalline order in low temperature is transformed into the narrow line in the higher temperature. Between low (233 K) and high temperature one may observe two components of the line which indicate the coexistence of both faces, amorphous and crystalline. Based on the changes of the lineshape one may estimate the second moment which indicate the rigidity of the structure and of the thermally activated changes of mobility.

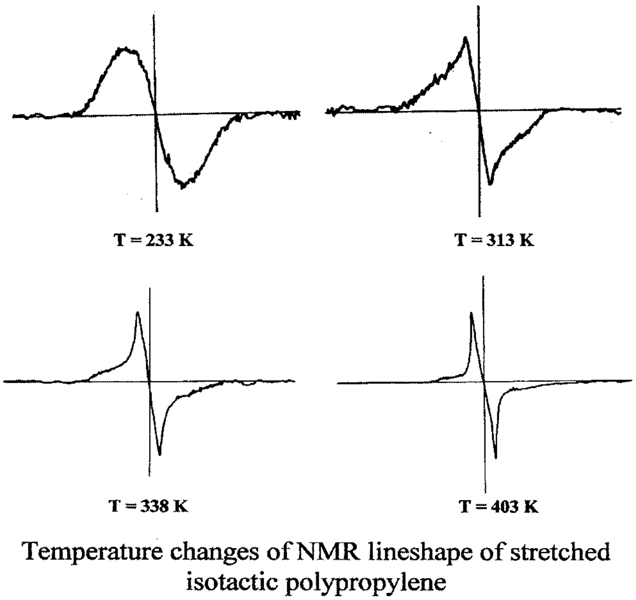

Fig. 4. The NMR line shape for stretched iPP measured by 233K, 313 K, 338 K and 403 K.

Temperature Dependent NMR Second Moment

The temperature dependent run of the NMR second moment for pure iPP samples as well for samples modified with 0.1 wt % of DMDBS and 0.1 wt. % of NJ may be seen on Figure 5.

A clear difference in the macromolecular mobility, represented by the separation of curves of the second NMR moment ΔH^2, for the temperatures below and above the glass transition T_g may be seen. Further, it follows that the temperature dependence of the ΔH^2 is strongly related to the crystalline structure of iPP. Always lower values of ΔH^2 for β - phase iPP indicates a lower chain mobility, what may be understand as a consequence of a different structure packing and organisation of the crystal structure.

An apparent distinction in second moment between α and β-iPP was observed above the T_g, with the exception of the temperature range of about 340 K. In the same temperature range the appearance of a maximum on the tan δ curves was observed, measurements below the T_g.

Such an effect observed in the region between the relaxation and melting temperature, signify a first step from order to disorder transformation in the crystalline phase of the iPP. As effects described above are not observed by WAXS, either by DSC, it may indicate that the changes in the macromolecular mobility, observed in the isotactic polypropylene, independent on the specific crystallographic form, leads to higher disordered without changes of the form and dimensions of the elementary unit.

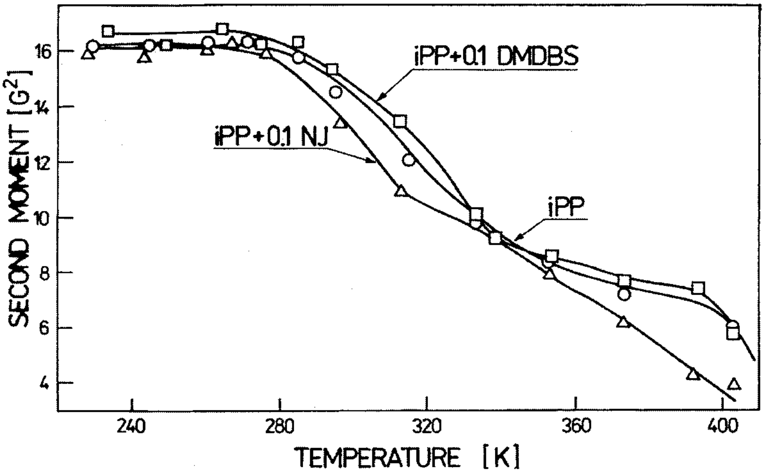

Fig. 5. The second moment as a function of temperature for pure iPP and iPP nucleated with 0.1 wt. % of DMDBS and NJ.

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[1] J. Varga, in: *"Polypropylene: Structure, Blends and Composites",* J. Karger-Kocsis, Ed., Chapman & Hall, London 1995, p.56.
[2] A. Gałęski, in: *"Polypropylene: An A-Z Reference"*, J. Karger – Kocsis, Ed., Kluwer Publishers, Dordrecht 1999, p. 543.
[3] B. Fillon, Lotz, A.Thierry, J. C. Wittmann, *J.Polym. Sci.,* **1993**, *31*, 1395.
[4] P. Jacoby, B. H. Bersted, W. J. Kissel, C. E. Smith, *J. Polym. Sci. Polym. Phys.*, **1986**, *24*, 461.
[5] B. Fillon, J. C. Wittmann, B. Lotz, A. Thierry, *J. Polym. Sci. Polym. Phys.,***1993**, *31,* 1407.
[6] J. Varga, *J. Macromol. Sci., Phys. B*, **2002**, *41,* 1121.
[7] T. Sterzynski, *Polimery*, **2000**, *45,* 786.
[8] F. L. Binsbergen, B. G. M. De Lange., *Polymer*, **1968**, *9,* 23.
[9] T. Sterzynski, H. Oysaed, *Polym. Eng. Sci.,* **2003,** *43*,
[10] G. Shi, J. Zhang, Z. Qiu, *Macromol. Chem.,***1992**, *193,* 583.
[11] X. Zhang i G. Shi, *Polymer*, **1994**, *35,* 5067.
[12] B. Lotz, J. C. Wittmann, A. J. Lovinger, *Polymer*, **1996**, *37,* 4979.
[13] J. X. Li, W. L. Cheung, *Polymer,* **1999**, *40,* 2085.
[14] T. Sterzyński, P. Calo, M. Lambla, M. Thomas, *Polym. Eng. Sci.*, **1997**, *37 (12)*, 1917.
[15] J. Karger-Kocsis, P. P. Shang, *J. Thermal. Anal. Cal.*, **1998**, *51,* 237.
[16] T. Sterzyński, M. Lambla, F. Georgi, M. Thomas, *Intern. Polymer Processing*, **1997**, *XII, 1*, 64.
[17] T. Sterzyński, M. Lambla, H. Crozier, M. Thomas, *Adv. Polymer Tech.*, **1994**, *13,* 25.
[18] M. Aboulfaraj. B. Ulrich, A. Dahoun, C. G'sell, *Polymer*, **1993**, *34,* 4817.
[19] T. Sterzynski, in: *"Performance of Plastics"*, W. Brostow, Ed., Hanser Verlag, Munich 2000, p. 254.
[20] J.Murin, *Czech.J.Phys.* **1981**, *B 31*, 62.
[21] J.Murin and D.Olčák, *Czech. J. Phys.* **1984**, *B34*,247.
[22] D. Olčák, L.Ševčovič, L.Mucha, O.Ďurčová, *Polymer,* **1996**, *28,* 232.
[23] M.A.Gomez, H.Tanaka, A.E.Tonelli, *Polymer*, **1987**, *28,* 2227.
[24] D.Olčák, J.Murin, J.Uhrin, M.Rákoš, W.Schenk, *Polymer*, **1985**, *26,*1455.
[25] D.Olčák, A Stančáková, Špaldonová, O.Katreniaková, *Polymer*, **1995**, *36*, 487.
[26] U.Kienzle, F.Noack, J.von Schütz, *Kolloid Z.-Z. Polym.*, **1970**, *326*, 129.
[27] J.Murin, D.Geschke, P.Holstein, D.Olčák, L.Ševčovič, L.Mucha, *Acta Polymerica*, **1988**, *39*, 389.
[28] J.M. Crissman, *J.Polym.Sci., A2*, **1969**, **7**, 389.
[29] J.Varga, A. Breining, G.W.Ehrenstein, G.Bodor, *Intern. Polymer Processing*, **1999**, *14,* 358.
[30] J. Varga, I.Mudra, G.W.Ehrenstein, *SPE,Inc. Technical Papers,* **1998**, *XLIV*, 3492.
[31] A.Romankiewicz, *PhD Thesis*, Poznan University of Technology, 2002, Poznan, Poland
[32] J.Jurga, *Scientific Instrumentation* **1988**, *4,* 67.
[33] T. Labour, C. Gauthier, R. Seguela, G. Viger, Y. Bomal, G. Orange, *Polymer*, **2001**, *42,* 7127.
[34] A. Romankiewicz, T. Sterzynski, G. Broza, K. Schulte, *„Nucleation and processing induced modification of an isotactic polypropylene (dynamic investigation of specific nucleated iPP)"* in: Polymerwerkstoffe P'2002, Halle (Saale) 2002.
[35] A.Romankiewicz, T.Sterzynski, *in preparation*
[36] A. Romankiewicz, T.Sterzynski, *Macromol. Symp.*, **2002**, *180,* 241.