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CRYSTALLIZATION AND MELTING OF β-NUCLEATED ISOTACTIC POLYPROPYLENE

J. Varga[1], *I. Mudra*[1] *and G. W. Ehrenstein*[2]

[1]Department of Plastics and Rubber Technology, Technical University of Budapest
H-1521 Budapest, Hungary
[2]Lehrstuhl für Kunststofftechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg
D-91058 Erlangen, Germany

Abstract

Ca salts of suberic (Ca-Sub) and pimelic acid (Ca-Pim) were synthesized and used as β-nucleating agents in different grades of isotactic polypropylene (IPP). Propylene homo-, random- and block-copolymers containing these additives crystallize principally in pure β-modification as demonstrated in isothermal and non-isothermal crystallization experiments. Ca-Sub proved the most effective β-nucleating agent known, so far. It broadens the upper crystallization temperature range of pure β-IPP formation up to 140°C. The effect of the additives on the crystallization and melting characteristics of the polymers was studied. The degree of crystallinity of the β-modification was found to be markedly higher than that of α-IPP. High temperature melting peak broadening was first observed and discussed in literary results regarding the same phenomenon for α-IPP.

Keywords: β-nucleating agent, β polypropylene, crystallization, degree of crystallinity, melt enthalpies, melting, recrystallization

Introduction

Admixing β-nucleating agents may lead to the preparation of pure or nearly pure β-modification of isotactic polypropylene [1–3]. For preparation of β-IPP products under processing conditions, β-nucleating agents with high activity and selectivity and with sufficient physical and chemical stability should be used. The most wide-spread highly active β-nucleating agent is γ-quinacridone red pigment [1, 4–5]. The drawback of β-quinacridone is its intense red colour and its polymorphism. The latter could lead to the modification transition and consequently to the decrease of the nucleating activity during processing. It has been observed in our laboratory that certain salts of aliphatic dicarboxylic acids are effective β-nucleating agents [1, 6]. The highest selectivity and activity were found for calcium salts of pimelic and suberic acids. In the present paper, preparation and characterization of these β-nucleating agents and their effects on crystallization and melting of isotactic polypropylene are covered.

Experimental

The β-nucleating agents were admixed at a concentration of 0.001–0.1 w% with commercial granulates of three polypropylene homopolymers of different melt flow

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index (Tipplen H384F, H543F, and H781), a random ethylene-polypropylene copolymer with ethylene content of 2.2 mol% (Tipplen R351F), and an ethylene-polypropylene block copolymer (Tipplen K392). Hereinafter the samples are referred as B-H3, B-H5, B-H7, B-R3, and B-K3, respectively, for the β-nucleated versions while A-H3, A-H5, A-H7, A-R3, and A-K3 for the nucleating agent-free grades used for comparison. The first and second letters represent the mode of nucleation and the type of the polymer (H for homopolymer, R for random copolymer, and K for block copolymer) while the number refers to the character of the melt flow feature in the trade name. MFI values [2.16 kg/230°C/10 min] for the homopolymers are 11, 3.9, and 0.7 for H3, H5 and H7 respectively, 11.0 for the random and 12.0 for the block copolymer. The β-nucleating agents were mixed with the pellets by powder sprinkling to the surface of granules followed by a homogenization in a Brabender plastograph at 200°C.

Thermal stability of the nucleating agents was characterized by thermo-gravimetric analyses (TG) and DSC measurements at V_h=20°C min^{-1}. For TG, DuPont 9900 (General V2.2A) apparatus was used in N_2 and in air.

Melting and crystallization of the samples were recorded by a Perkin Elmer DSC-7 instrument in N_2. The samples were heated up to 220°C and held for 5 min prior to crystallization to erase effects of the thermal-mechanical prehistory. During non-isothermal measurements, samples were crystallized at a cooling rate of V_c=10°C min^{-1}. In order to eliminate the tendency to βα-recrystallization during partial melting [1–3], the final temperature of cooling was T_R=100°C. During isothermal measurements, cooling to the crystallization temperature (T_c) occurred at 40°C min^{-1}. The samples were melted at 10°C min^{-1} heating rate beginning from T_R or T_c.

Results and discussion

Preparation and characterization of the new β-nucleating agents

The β-nucleating agents were synthetized according to [6]. Ca salts contained one mole of water of crystallization which had to be removed before use by thermal treatment at 220°C. Finally, the crystals were milled to fine powder. According to DSC and TG measurements in nitrogen atmosphere, these Ca salts have excellent thermal stability. It can be established from the mass loss in the TG traces that, Ca-Pim, before annealing, looses 1 mole of water of crystallization in the range between 110 to 170°C. TG traces of the thermally treated Ca-Pim and Ca-Sub revealed a mass loss process between 390 and 530°C where the organic part decomposes and $CaCO_3$ is formed, which then transforms to CaO above 550°C (Fig. 1). The experimental mass losses are practically identical to the theoretically calculated ones. No endothermic peak indicating melting of Ca-Pim and Ca-Sub is observed in the corresponding DSC record before 390°C; presumably, melting point of the Ca-salts is above the temperature range of their decomposition. Comparing the different additives, Ca-Sub is a little bit more stable, up to almost 450°C. The decomposition characteristics of the nucleating agents were similar in air, though the decomposition steps started 20–30°C lower.

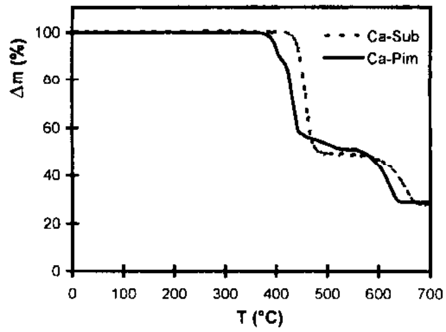

Fig. 1 TG traces of thermally treated nucleating agents (V_h=20°C min^{-1})

Crystallization and melting characteristics of β nucleated samples

Melting and crystallization characteristics of nucleated samples were studied under isothermal and non-isothermal conditions by DSC. β-Nucleated homopolymers and copolymers containing 0.1 w% Ca-Pim crystallized principally in β-modification as indicated by the high β-melting peaks in Figs 2–3. Only a small peak pertaining to the presence of the α-modification appeared in the melting curves. In homopolymers and in the block copolymer, peak temperatures of α- and β-melting are practically identical. However, crystallinity of the block copolymer is somewhat lower than that of the homopolymers. Due to the less regular chain structure, both α- and β-modifications of the random copolymer have 10°C lower melting temperatures, lower crystallinity, and higher ability to be super-cooled than those of the cor-

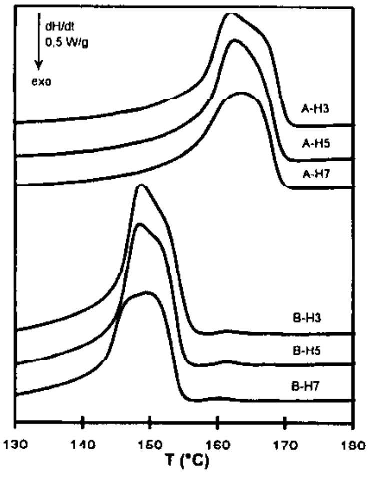

Fig. 2 Melting curves of β-nucleated and non-nucleated homopolymers; (0.1 w% Ca-Pim; V_c=V_h=10°C min^{-1})

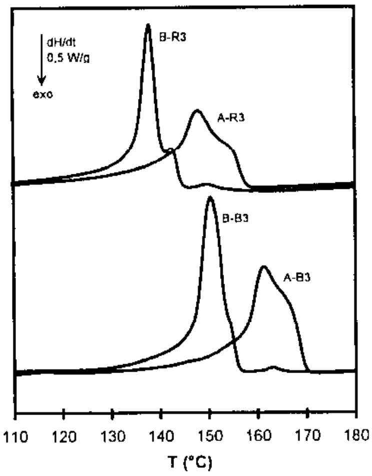

Fig. 3 Melting curves of β-nucleated and non-nucleated random and block copolymers (V_c=V_h=10°C min^{-1}; 0.1 w% Ca-Pim)

responding modifications of the homopolymers or block copolymers (Table 1). Comparing the effectiveness of the different β-nucleating agents, the salt of suberic acid proved more active than Ca-Pim. In the presence of Ca-Sub the crystallization temperature range is higher and the portion of α-IPP is lower. The difference is enhanced with decreasing additive concentration. With decreasing nucleator concentration, the α-content increases up to 5–8% at the lowest additive concentration (Figs 4–5 and Tables 1–2). Due to the lower β-nuclei density and the lower crystallization temperature at such a low concentration, the spontaneous α-nucleator, which was originally present in the sample, can grow to a larger size, which leads to the increase in α-IPP content. The shoulder or the duplication appearing on the higher-temperature side of the β-melting peak resulted from ββ′recrystallization [1–3]. This is a structure perfection process within the β-phase, which is superimposed on the melting of the original crystals. It becomes more pronounced at low nucleating agent concentration (Figs 4–5), at which the crystallization temperature range is lower and less perfect crystals are formed.

Heats of fusion for the nucleating agent-free and β-nucleated samples fall in the range of 80 to 90 J g^{-1} (Tables 1 and 2), while the respective values for the latter are somewhat higher. The degree of crystallinity (x) can be determined from the calorimetric data with the knowledge of the melting enthalpy (ΔH_f^o) of completely crystalline α- and β-IPP. Although the literary values vary in a wide range [1], a comparison between $\Delta H_f^o(\alpha)$ and $\Delta H_f^o(\beta)$, determined by identical methods, always reveals higher values for α-IPP than for β-IPP. Degrees of crystallinity in Tables 1 and 2 were calculated from $\Delta H_f^o(\alpha)$=146 J g^{-1} [7] and $\Delta H_f^o(\beta)$=113 J g^{-1} [8], both determined by linear extrapolation of the heats of fusion plotted against the temperature of crystallization (T_c) up to the equilibrium melting temperature (T_m^o). It is clear from

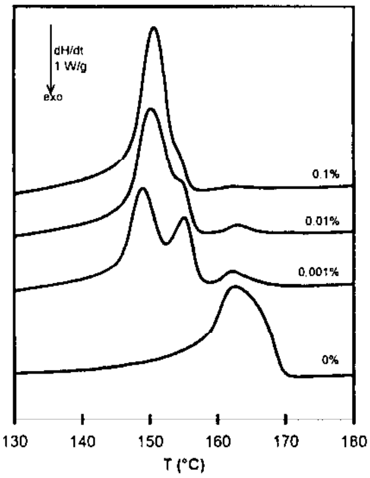

Fig. 4 Effect of the concentration of Ca-Pim on the melting curves of H5 homopolymer (V_c=V_h=10°C min^{-1})

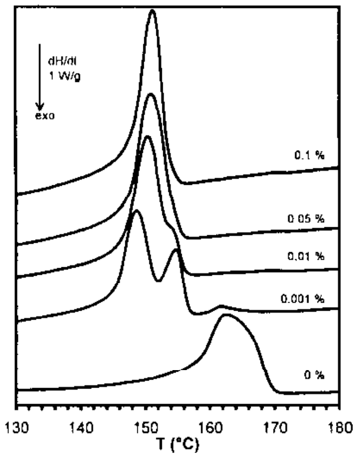

Fig. 5 Effect of the concentration of Ca-Sub on the melting curves of H5 homopolymer (V_c=V_h=10°C min^{-1})

the data of Tables 1 and 2 that the crystallinity of β-nucleated samples, crystallized at constant cooling rate, is higher than those of α-IPP. This fact might be explained by thermodynamic cause. The most important thermodynamic parameter of the crystallization is the undercooling (ΔT defined as T_m^o–T_c), which shows how far the polymer crystallizes from its melt-crystal equilibrium-state. The lower the undercooling, the more perfect crystals are formed and hence, the higher crystallinity. Due to the

Table 1 Crystallization and melting characteristics of IPP samples nucleated by Ca salt of pimelic acid based on DSC curves recorded at cooling and heating rate $V_c=V_h=10°C\ min^{-1}$ (T_{co} and T_{cp} are the initial and peak temperatures of crystallization, respectively; $T_{mp}(\alpha)$ and $T_{mp}(\beta)$ are the peak temperatures of melting of the α- and β-modifications, respectively; $\Delta H_f(\alpha)$ and $\Delta H_f(\beta)$ are the melt enthalpies of α- and β-modifications, respectively; $x(\alpha)$ and $x(\beta)$ are the degrees of crystallinity of α- and β-modifications, respectively)

Samples	β-nucleant/%	T_{co}/	T_{cp}/	$T_{mp}(\alpha)$/	$T_{mp}(\beta)$/	$\Delta H_f(\alpha)$/	$\Delta H_f(\beta)$/	$x(\alpha)$	$x(\beta)$
		°C				J g^{-1}		%	
A-H3	–	115	103	162	–	89.3	–	61.1	–
A-H5	–	113	105	162.8	–	86.2	–	59.0	–
A-H7	–	110	100.5	163.5	–	80.7	–	55.3	–
B-H3	0.1	119.8	116.2	–		1.0	92.0	–	81.4
B-H5	0.1	119	115.7	–	148.2	1.1	89.3	–	79.0
B-H5	0.01	120.1	116.7	162	150.1	3.9	83.6	–	74.0
B-H5	0.001	117.8	113.3	162	150.1	6.3	80.0		70.8
B-H7	0.1	116.6	112.3	–	149.4	1.1	81.0		71.7
A-K3	–	118	108	161.5	–	78.4	–	53.7	–
B-K3	0.1	121.7	118.4	–	150.5	0.8	80.0		70.8
A-R3	–	104	98	148	–	64.7	–	44.3	–
B-R3	0.1	111.2	108.9	–	138.0	2.2	62.9		55.7

Table 2 Crystallization and melting characteristics of homopolymer H5 nucleated by Ca-Sub based on DSC curves recorded at cooling and heating rate $V_c=V_h=10°C\ min^{-1}$ (notations as in Table 1)

Samples	β-nucleant/%	T_{co}/	T_{cp}/	$T_{mp}(\alpha)$/	$T_{mp}(\beta)$/	$\Delta H_f(\alpha)$/	$\Delta H_f(\beta)$/	$x(\alpha)$	$x(\beta)$
		°C				J g^{-1}		%	
A-H5	0	115	103	162	–	89.3	–	60.9	–
B-H5	0.1	123.6	120.5	–	151.2	–	87.8	–	77.7
B-H5	0.05	123.0	119.5	–	151.3	–	89.9		79.6
B-H5	0.01	121.7	117.8	–	150.8*	0.6	89.2		78.9
B-H5	0.001	119.1	114.7	162	148.6*	3.7	84.1		74.4

*– double melting peaks

presence of β-nucleating agent, β-IPP crystallizes in a temperature range of 10–15°C higher than its non-nucleated counterpart. On the other hand, $T_m^o(\alpha)$ was found to be always higher than that of β-IPP [1]. Therefore the β-nucleated samples crystallize under much lower undercooling, which might explain their higher crystallinity.

Isothermal crystallization experiments were carried out between 110 and 145°C in the case of H-5 with 0.1 w% additive concentration. The crystallization exotherms are characterized by the time of the highest crystallization rate (t_{max}). Similarly to the non-isothermal experiments, Ca-Sub is definitely more effective than Ca-Pim, indicated by the lower t_{max} values at each temperature compared (Fig. 6). DSC melting traces reveal the β-IPP content of the crystallized samples in Figs 7–8. The lowest temperature of the experiments are limited by the crystallization rate of the samples, which increases with decreasing T_c. Under T_c=120°C, the samples start to crystallize before T_c is reached, therefore the crystallization is not purely isothermal. Including the lowest T_c, the samples crystallize practically in β-form up to a certain temperature, above which appreciable α-IPP content appears and increases monotonously with T_c. The degree of crystallinity of β-nucleated samples crystallized isothermally, was found to be higher than that of α-IPP, though the difference, compared to non-isothermal crystallization, decreased ($x(\alpha)_{125°C}=62.5\%$; $x(\beta)_{125°C}=79.0\%$). The samples with Ca-Pim crystallize nearly in pure β-IPP up to 135°C, above which significant α-IPP content is obtained. In the presence of Ca-Sub, pure β-modification are formed up to 140°C, which was referred as the theoretical upper temperature limit for β-IPP formation, $T(\beta\alpha)$ ~140°C [1, 9]. Above this temperature, α-nuclei are formed by secondary βα-nucleation on the surface of the growing β-spherulites. These α-nuclei can transform into α-spherulite segments, which can reach smaller or greater size, depending on the time of growing. If the crystallization time is long enough, these α-segments can finally encompass the original β-spherulite, resulting in a mixed polymorphic composition [9]. The experimental results achieved here on β-IPP are essentially in accord with our earlier observations [1–3]. However, the earlier statement [1–3] of the meaning of $T(\beta\alpha)$ should be revised. Based on the high-temperature isothermal crystallization experiments, $T(\beta\alpha)$ refers the upper temperature limit of the formation of pure β-IPP. It can be established from these results that,

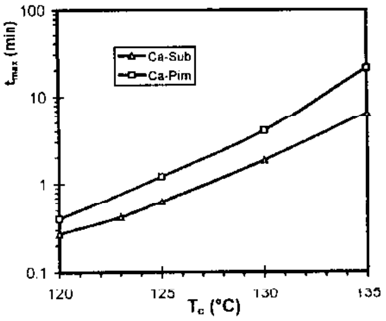

Fig. 6 Crystallization peak time (t_{max}) of H5 samples nucleated with 0.1 w% Ca-Sub and Ca-Pim and crystallized isothermally at different T_c

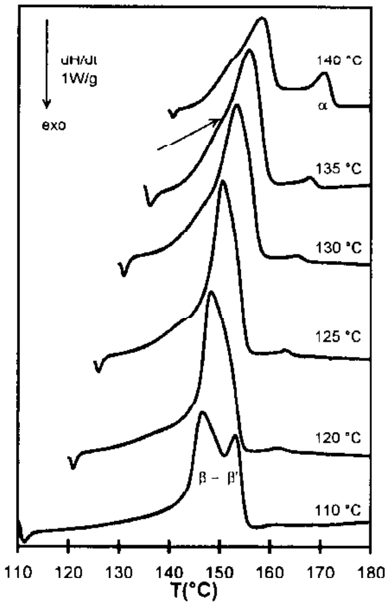

Fig. 7 Melting curves of B-H5 samples crystallized isothermally (V_h=10°C min^{-1}; 0.1 w% Ca-Pim)

with the help of Ca-Sub, pure β-IPP can be prepared at much higher temperatures than supposed in the earlier studies with different β-nucleating agents [1–3].

The temperature of the melting peaks depends only on the crystallization temperature and is practically independent of the type of β-nucleator. The melting curves of samples crystallized at low T_c<125°C show double β-peaks (β-β′ in Fig. 7) due to the tendency to recrystallization whithin the β-phase caused by high structural instability. In heating runs, the originally, thin lamella are melted partially and coincidentally go under lamella thickening process. In this range T_m is independent of T_c, while the high temperature peak refers to the recrystallized part of the sample. Melting curves recorded after crystallization at medium T_c (125–135°C) comprise a single and sharp peak. T_m increases monotonously with T_c and no appreciable recrystallization occurs. Above T_c=135°C, widening of melting peak occurs again (mark 1 in Figs 7–8.), but T_{mp} and T_m increases monotonously with T_c. This phenomenon has not been observed in the literature before for β-IPP. Due to the high β-nucleating activity of Ca-Sub, this high temperature melting peak-broadening can be studied up to a high T_c=145°C. The intensity of the shoulder of the melting peak seem to increase up to 142°C. In the case of the highest T_c, 145°C, it is rather hard to say that duplication is less intense, at least it does not increases further. Unfortunately, samples crystallized at higher T_c could not be utilized in the investigation because only a small part of the sample crystallized in β-form.

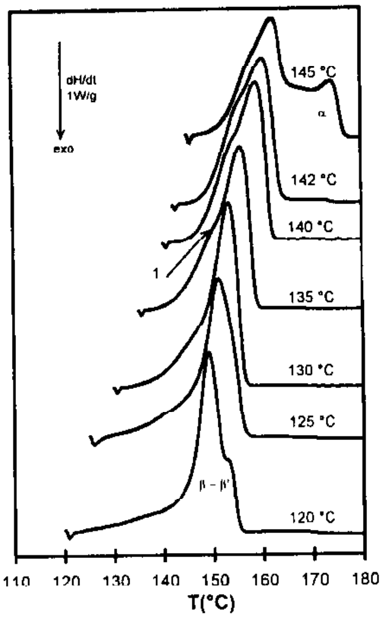

Fig. 8 Melting curves of B-H5 samples crystallized isothermally (V_h=10°C min^{-1}; 0.1 w% Ca-Sub)

It should be noted, that a similar melting behaviour was found and intensively studied in the case of α-IPP [1, 10–16]. Based on the results of several researcher groups, four T_c ranges resulting in different melting profiles can be distinguished for α-IPP [1]. The samples crystallized isothermally at low temperature (T_c<112°C) showed strong peak duplication. Increasing the T_c, between 112–132°C single melting peak was observed at even low heating rate. Above T_c=132°C high temperature peak duplication was found, which disappeared at T_c=152°C. The samples crystallized above 152°C with the help of self-nucleation lead to a high temperature single melting peak again. This latter T_c region is probably missing for β-IPP due to limited temperature range of β-IPP formation. The high temperature peak duplication of α-IPP has been explained in several, sometimes controversial way [1]. In order to give a satisfactory interpretation for the phenomenon in the case of β-IPP, systematically designed X-ray and MDSC measurements were carried out. The results of this latter effort is underway, to be published elsewhere.

Conclusions

Ca salts of pimelic and suberic acids are highly active thermally stable β-nucleating agents. In their presence, homopolymers, random and block copolymers of isotactic propylene crystallize almost purely in β-modification even at a low concentration. Ca-Sub proved the most effective β-nucleating agent ever found in the literature. In its presence IPP crystallized in pure β-form up to ~140°C. The additives cause significant changes in crystallization and melting characteristics of the polymers. The degree of crystallinity of the β-nucleated samples was markedly higher than that of the α-modification. Similar features were found between the melting behaviour of α- and β-IPP. The high temperature melting peak broadening of β-IPP was first found here in a wide crystallization temperature range.

* * *

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