Melting behavior of nascent polyolefins synthesized at various polymerization conditions

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Summary

Linear and branched polyethene, isotactic polypropene and ethene-propene copolymers were synthesized. Solution, slurry, bulk and gasphase polymerizations were performed using homogeneous or supported metallocene and nickel-based catalysts. The thermal behavior of the nascent, as-polymerized polyolefins has been investigated in relation to the used polymerization conditions. The nascent polymer samples exhibit in general a notable thermal behavior: differential scanning calorimeter traces show in most first heating scans (nascent) higher melting temperatures and higher enthalpy of fusion than in the second heating scans of the same, but now melt-crystallized samples. A similar thermal behavior is well known for ultra-high molecular weight polyethene (UHMW-PE), but less or even not identified for polyethene with lower molar mass and other semi-crystalline homo- and copolymers. By varying systematically the polymerization conditions we could prove that mainly the local kinetics of polymer formation at the active catalysts, which is controlled by the polymerization conditions (e.g. synthesis process, polymerization temperature), and the subsequent crystallization determine the thermal properties and the morphology of the nascent state. This is in accordance with the kinetic principle of crystallization during polymerization introduced by Wunderlich in the late 70ties of the last century.

Introduction

Better understanding the nature of the nascent morphology of polyolefins, namely the formation and molecular organization of polymer particles initiated by supported or homogeneous catalyst systems in the reactor, and its related physical properties is an important research topic. The interaction between the polymerization process and the subsequent crystallization, and hence the development of the polymer morphology, results from continuous insertion of fresh monomer at the catalyst active site, creating new macromolecules which have to displace the already laid polymer. The chains

crystallize during polymerization, if the temperature is below the melting and/or the dissolution temperature of the polyolefin, or during subsequent steps such as cooling down, drying, filtering etc.

The development of the nascent state morphology of polyolefins in the reactor is understood reasonable well on the micrometer level, the overall particle morphology, as used in important industrial processes such as catalyst replication in the case of polypropene [1]. On the molecular scale, however, such events are only poorly understood and, so far, nascent polyolefins have rare and somewhat contradictory physical properties [2,3]. For example, the nascent ultra-high molecular weight polyethene (UHMW-PE) powder produced in a reactor exhibits an unusually high melting temperature, which is in general attributed to the formation of extended chain crystals during polymerization, more or less similar to the formation of cellulose fibrils in nature, and their superheating during the thermal investigation [4-6].

Hellmuth and Wunderlich have shown [7] that the melting of polymers with extended chain crystals was not instantaneous as found for chain-folded crystalline samples. With extended chain crystals, superheating occurs before fusion, thereby delaying melting. This delay, which can become very large with samples of high molar mass, also depends on crystal quality. Besides the ideal extended chain polyethene and polymethene crystals, superheating has also been detected for shear-crystallized [8,9] and for drawn polyethene [10]. Thus, in the instance of UHMW-PE reactor powder this model is adopted to explain the thermal behavior of the nascent, as-polymerized state. Other authors claim that the high melting temperature is related to the formation of metastable folded chain crystals during polymerization, which reorganize prior to melting [11,12].

The effect of high temperature melting of nascent UHMW-PE is generally known since more than three decades, but the thermal properties of other nascent polyolefins have been less investigated. In the present study we have synthesized numerous polyolefins, such as linear polyethene (PE), isotactic polypropene (iPP) and their copolymers (branched PEs and random propene-ethene copolymers), using various synthesis processes (e.g. bulk and gas phase polymerization). The polymerization conditions (e.g. polymerization temperature) were systematically varied to study their influence on the thermal behavior of nascent, as-polymerized polyolefins, and to identify general characteristics of the nascent state.

Experimental

All operations involving air- and moisture sensitive reagents were carried out in an argon atmosphere using Schlenk, syringe and glove box techniques. Methylaluminoxan (MAO) (10 wt.% in toluene, Witco) was stored as a solid after removal of all volatiles in vacuum. Toluene (p.a., Riedel-de-Häen), Ethene (99.8%, Linde) and Propene (99.9%, Gerling) were purified by passing through two columns: one filled with 4 Å molecular sieves and the other with a Cu catalyst (BASF R3-11). Metallocenes were used in toluenic solutions, while Ni-based catalysts were dissolved in fluorobenzene.

Immobilization of metallocenes on MAO/SiO_2 and the polymerization procedure in solution, slurry, bulk and in gas phase are described elsewhere [13-16].

Analytics

The molar masses M_η were determined using an Ubbelohde viscosimeter (capillary 0a, K = 0,005). The samples were prepared by dissolving 50 mg of polymer in 50 ml of decahydronaphthalene (stabilized with 1 g/l 2,6-di-*tert*bu-4-methylphenol) and

measured at 135 °C. The Mark-Houwink constants were taken from literature. Molar mass distributions were determined by gel permeation chromatography on a Waters high temperature 150-C-ALC/GPC instrument in 1,2,4-trichlorobenzene at 135 °C using a PL-EMD-960 evaporation light scattering detector.

The tacticity of polypropenes as well as the incorporation rates and branching of the copolymers were determined by ^{13}C-NMR-spectroscopy at 100°C on a Bruker MSL 300 spectrometer at 75 MHz. Samples were prepared by dissolving the polymers (10 mass%) in a mixture of perchlorobutadiene (PCB) and 1,1,2,2-tetrachloro-1,2-dideuteroethane (TCE-d_2).

Thermal properties of polyolefin reactor powders or flakes were studied in their nascent, as-polymerized state and after melt-crystallization by differential scanning calorimetry (DSC), using a Mettler-Toledo DSC 821^e equipped with a mechanical intercooler, purged with nitrogen and calibrated with dodecane and indium. Typically the samples were cooled from room temperature to -50°C, than heated to 200°C using a heat rate of 20°C/min (1. heating scan), kept at 200°C (iPP) for 2 minutes and than cooled to -50°C with 20°C/min, respectively, before heating again to 200°C with 20°C/min (2. heating scan). Maximum melting peak temperature and enthalpy of fusion of the nascent and the melt-crystallized states were determined using the first and second heating scan. Baseline correction and enthalpy of fusion calculation were performed using standard DSC software. The crystallinity χ was calculated from enthalpy of fusion by the following equation:

$$\chi = \Delta H_f / \Delta H^*_f \text{ x } 100 \qquad (1)$$

using the reliable value $\Delta H^*_f = 4.1$ kJ/mol for 100%-crystalline polyethene and 8.7 kJ/mol for 100% crystalline polypropene [17]. Melting temperatures were not corrected for zero heat rate and for differences of heat of fusion in first and second heat scan (ΔH_f β correction), and the heat of fusion was not determined by establishing a very accurate solid-melt baseline, e.g. by iterative techniques, which turn out to be, in the present case, not an inconvenience, because the main aim of the present study is the identification of general features and trends in the behavior of nascent polyolefins.

Results

From previous DSC studies of UHMW-PE samples [11,18,19] it is known that nascent reactor powders exhibit a higher melting temperature and crystallinity than identical, but melt-crystallized samples. In order to check if this feature is typical only for UHMW-PE we have studied more than 100 samples of nascent, as-polymerized linear and branched polyethenes, ethene-propene copolymers (EP), and isotactic polypropenes (iPP). All polyolefins were synthesized using metallocene- and nickel-based homogeneous and immobilized, heterogeneous catalysts at polymerization temperatures below the melting points of the polymers. Most of the samples show prominent differences in the thermal properties of the nascent and the melt-crystallized state.

Figure 1 introduces typical DSC traces of some synthesized polymers. Their melting behavior significantly differs comparing traces of the first (nascent) and the second (melt-crystallized) heating run. In the nascent state the samples exhibit a high peak melting temperature, which is observed e.g. at 141°C for linear PE (Fig. 1a), at 164°C for iPP (Fig. 1c) and in a broad temperature range around 80°C to 130°C for branched PE and EP copolymers (Fig. 1e,g), respectively. Melting of the same but melt-crystallized samples occurs at lower peak temperatures (Fig. 1b,d,f,h). Moreover, the enthalpy of fusion (area between DSC trace and baseline), therefore the crystallinity

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of the nascent state is higher than that of the melt-crystallized samples. It has to be pointed out that some DSC traces show a somewhat complex melting behavior of the nascent state polymers indicated by a second melting peak or shoulder at lower temperatures, which is absent or less pronounced after melt-crystallization.
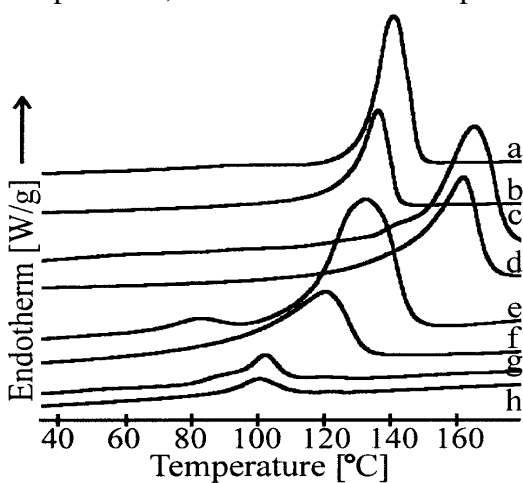
Peak melting temperatures of linear and branched PEs, EPs and iPPs in the nascent state and after melt-crystallization are visualized in Figure 2. With only a few exceptions, all investigated polyolefins have a higher melting temperature in their nascent state, whereas the absolute difference between first and second peak melting temperature can reach values up to more than 10°C for some polyethene and polypropene samples. Even highly branched PE and random EP with high ethene concentration have similar thermal characteristics. Because of short sequence lengths of these polymers (average distance between two branches) they form small crystallites. Thus, the peak melting temperatures of these samples are low. However, the melting temperature difference between first and second heating scan is pronounced.
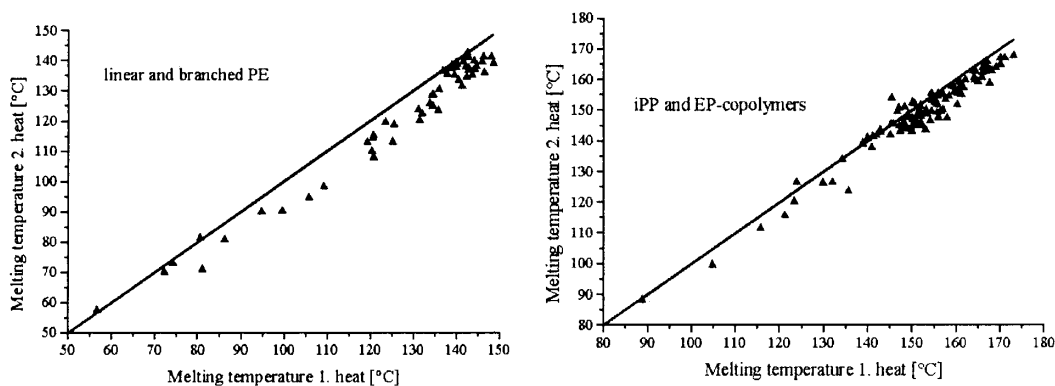

Figure 1: Typical DSC traces of nascent and melt-crystallized samples of linear and branched PE, iPP and EP-copolymer. a,b) linear PE; c,d) iPP; e,f) branched PE; g,h) EP-copolymer, respectively.

Figure 2: Melting temperatures of melt-crystallized vs. nascent linear and branched PE (left) and iPP and EP-copolymers (right). The diagonal lines indicate identical temperature values.

A similar trend is found comparing the crystallinities of the nascent and the melt-crystallized polymers. Figure 3a shows the crystallinities of linear and branched PEs calculated from the enthalpies of fusion of the first and the second heating scan. In almost all cases the crystallinity of the nascent state is higher than that of the melt-crystallized samples and reaches values up to 85% for the nascent state and up to 70% for melt-crystallized samples, respectively. Again, even highly branched PE exhibits the same trend. In case of polypropenes and EPs no clear trend can be worked out. The majority of samples has higher crystallinity in the nascent than in the melt-crystallized state, but several samples show an contradictory behavior having increased crystallinity of the melt-crystallized state.
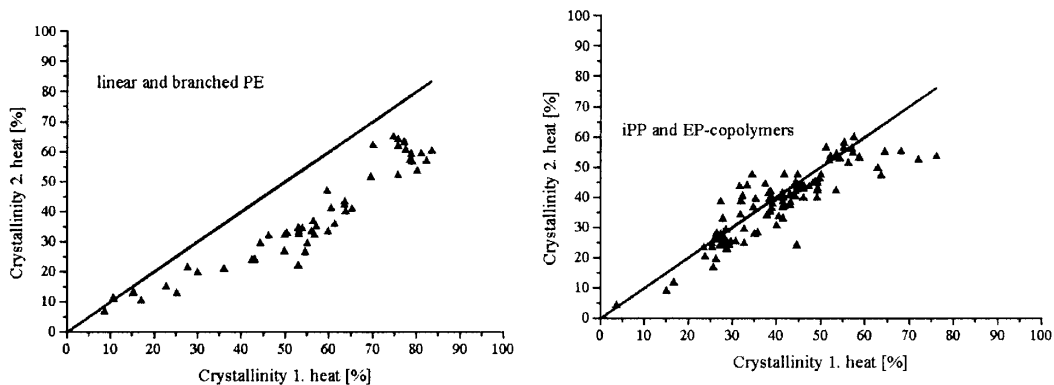
Figure 3: Crystallinities of melt-crystallized vs. nascent linear and branched PE (left) and iPP and EP-copolymers (right). The diagonal lines indicate equal crystallinity values.

Table 1: Melting temperatures (top) and crystallinities (bottom) of nascent and melt-crystallized isotactic polypropene homopolymers prepared using comparable synthesis conditions changing only polymerization temperature (columns) and/or the polymerization process (rows).

T_{pol} [°C]	solution T_m [°C] 1. heat	solution T_m [°C] 2. heat	bulk T_m [°C] 1. heat	bulk T_m [°C] 2. heat	slurry T_m [°C] 1. heat	slurry T_m [°C] 2. heat	slurry bulk T_m [°C] 1. heat	slurry bulk T_m [°C] 2. heat	gas phase $_{NaCl}$ T_m [°C] 1. heat	gas phase $_{NaCl}$ T_m [°C] 2. heat
0	166	163	167	163	157	156	156	155	148	146
15	167	163	166	161	157	155	145	154	152	150
30	166	164	167	163	154	155	147	151	145	146
45	164	163	164	161	151	152	147	150	142	142
60	161	160	161	158	150	153	148	151	143	144

T_{pol} [°C]	solution χ [%] 1. heat	solution χ [%] 2. heat	bulk χ [%] 1. heat	bulk χ [%] 2. heat	slurry χ [%] 1. heat	slurry χ [%] 2. heat	slurry bulk χ [%] 1. heat	slurry bulk χ [%] 2. heat	gas phase $_{NaCl}$ χ [%]] 1. heat	gas phase $_{NaCl}$ χ [%] 2. heat
0	56	51	50	48	27	24	29	29	24	23
15	53	42	64	55	33	30	32	41	26	28
30	59	53	68	55	32	34	32	39	28	33
45	63	50	76	54	37	44	27	39	33	44
60	64	47	72	54	34	48	32	44	42	48

The influence of the polymerization temperature and the polymerization process on the thermal behavior of isotactic polypropene homopolymers is shown in Table 1. A whole set of samples was prepared using comparable synthesis conditions (catalyst, cocatalyst, catalyst concentration etc.) changing only the polymerization temperature (columns) and/or the polymerization process (rows). In case of polymerization in solution or bulk the melting temperature of the nascent state samples (1. heat) is always higher than for melt-crystallized samples (2. heat), while the temperature difference decreases mainly with increasing synthesis temperature.

For all five synthesis processes using low polymerization temperatures (0°C) the melting temperature of the nascent state is above the melting temperature of melt-crystallized samples. In contrast polymerization at elevated temperatures, especially when carried out in slurry bulk or gas phase process, features nascent state samples melting at significant lower temperatures than melt-crystallized ones. Moreover, the melting temperatures of both the nascent and the melt-crystallized samples are higher using a solution or bulk

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process, while in slurry, slurry bulk and particularly in gas phase polymerization both the melting temperatures of the nascent and melt-crystallized samples are considerable low. For gas phase polymerization this characteristic may be attributed to the low monomer concentration utilized in this process leading to more defects in the polymer chain [16].
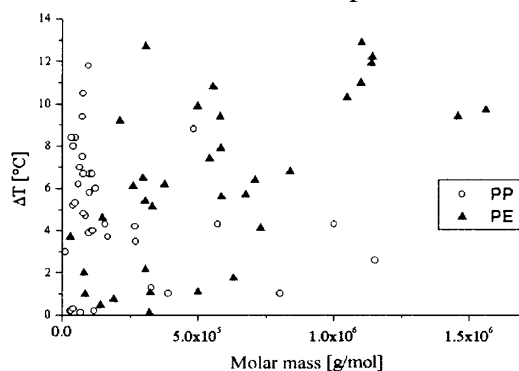

Figure 4: Melting temperature differences between nascent and melt-crystallized samples vs. molar mass.

Similar trends as described for the relation between melting temperature and used polymerization conditions are found for the crystallinity of the nascent and melt-crystallized polypropenes. Ethene polymerization experiments varying systematically the process conditions have shown analogue tendencies for the thermal behavior of nascent and melt-crystallized polyethene. Fig. 4 visualizes that there is no influence of the molar mass on the temperature differences of first and second heating scan for linear and branched PEs, PPs and EPs. Polyethene with very-high molar mass illustrates the well-known superheating feature. In addition, one can find for the whole investigated molar mass range from ~30 kg/mol to 1.600 kg/mol PE samples having high temperature difference of the first and second heating scan. Moreover, nascent and melt-crystallized iPPs and EPs show analogue characteristics.

Discussion

UHMW-PE is a polymer of industrial interest because of its improved mechanical properties and excellent wear resistance. Due to the high molar mass standard pelletization is skipped and the material is available in its nascent, as-polymerized state. This may explain why studies of nascent state polyolefins are mainly focused on UHMW-PE. However, it is shown in the present study that nascent, as-polymerized polyolefins in general have a similar thermal behavior: for "standard" polymerization conditions the melting temperature and the crystallinity of the nascent state usually is higher than that of the same, but melt-crystallized sample.

On the other hand, the results of the present study have shown a distinct influence of the used synthesis process and the polymerization temperature on thermal features of nascent polymers, which could be explained by the kinetic principle of crystallization during polymerization stated by Wunderlich [20]. Accordingly, an increase or decrease in polymerization temperature changes the relative rates of molecule formation and crystallization. While at low temperatures just formed molecules or molecule parts (stems) spontaneously crystallize, above a certain polymerization temperature molecule creation and crystallization proceed separately. For high polymerization temperatures (e.g. 60°C) the rate of molecule formation should be much higher than the rate of crystallization. Consequently, the high amount of formed molecules per localized volume and their high mobility on, at least, nanometer scale (in the surrounding polymerization medium, except for gas phase process) determines the crystal formation and the entanglement density, and therefore the molecular organization of the nascent state.

Based on the kinetic principle (e.g. in case of heterogeneous and therefore industrial important catalyst systems) we may predict the degree of molecular organization of the
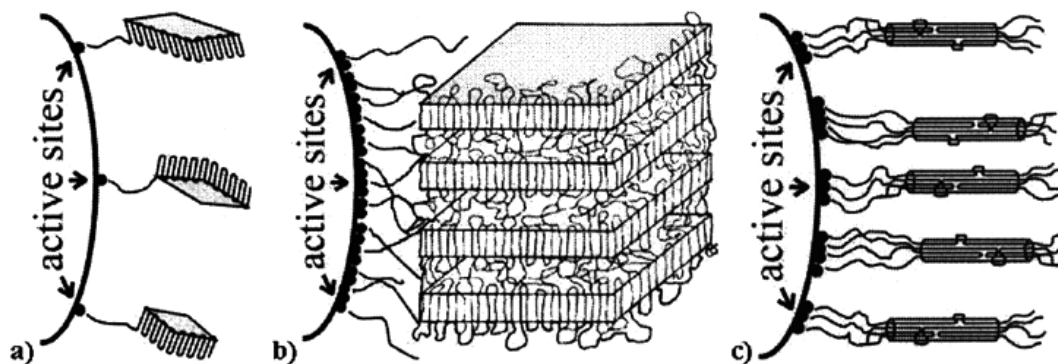
Figure 6: Sketch of the local synthesis environment, which determines the formation of molecules and their crystallization: **a)** low density of active catalyst sites and no interaction between molecules may result in (single-molecule?) tiny, metastable chain folded crystals; **b)** high density of active catalyst sites, very high rate of molecule formation and low rate of crystallization may result in highly entangled molecules and folded chain crystals; **c)** intermediate density active catalyst sites and equal rate of molecule and crystal formation may result in less entangled molecules and extended chain crystals.

nascent state. If the number of catalytically active sites is very low and/or the polymerization temperature is far below the melting and/or dissolution temperature the formed polymer chains can be considered as separated from each other. Therefore, the molecules may crystallize as folded chain lamellae without entanglements in the amorphous phase, which is illustrated in Figure 6a. These metastable crystals may reorganize prior to melting during the thermal scans [11,12], resulting in high melting temperature. After melting and recrystallization the entanglement density of the polymer may be increased. Therefore, the chain mobility will be reduced [21], which hinders crystallization and lamellar thickening [22], resulting in a differently organized morphology having lower melting temperature and crystallinity.

On the other hand, higher polymerization temperatures (still below melting and/or dissolution temperature of the polymer) and a high number of catalyst active sites may result in a morphology consisting of highly entangled molecules and disordered folded chain crystals. For this case the rate of polymerization should be higher than the rate of crystallization, causing entanglement and disorder of molecules before crystallization (Fig. 6b), so that the melting behavior of the nascent state should be similar to a sample isothermally crystallized, or even quenched from the melt. Finally, only when the number of active sites is low, and/or molecule formation and crystallization rates are equal, nascent morphology with low entanglement density and extended chain crystals should be favorable, even without any external shear or elongation forces (Fig. 6c).

An additional result of the present study is that the nascent morphology, and therefore the typical superheating behavior of the nascent state is independent of the molar mass of the formed polyolefins. This characteristic is contrary to the standard model, which explains the thermal behavior of the nascent state of e.g. UHMW-PE by the formation of extended chain crystals, as described in the introduction part.

Conclusion

Thermal studies are useful to characterize differences in nascent and melt-crystallized polyolefins synthesized under variety of conditions. For the investigated synthesis

conditions, such as different polymerization temperatures, polymerization processes and catalysts, main results are as follow: an increased melting temperature and crystallinity of the nascent state is found for almost all investigated polyolefins, namely linear and branched polyethene, isotactic polypropene and ethene-propene copolymers; and the used polymerization conditions control the overall thermal behavior of nascent and melt-crystallized polyolefins. In particular, the polymerization temperature and the synthesis process have striking influence on the melting of nascent polyolefins, e.g. decreasing the polymerization temperature results in higher melting temperatures of the nascent state for almost all investigated polyolefins.

Besides the *chemical* aspects related to the molecule formation at the catalyst during polymerization one major *physical* aspect may determine the organization of the nascent state morphology, and therefore its thermal behavior: the kinetic principle, the relation between the rates of molecule formation and rate of crystallization, which has been introduced by Wunderlich and which is supported by the results of the present study.

Further insights into the relation between chemical and physical aspects related to the organization of the nascent state will be gained only by control of the local kinetics during molecule and crystal formation. Main parameters are activity of the used catalyst, its concentration, polymerization pressure, polymerization and crystallization temperature, and type of support. In current projects we try to identify the relations of the process conditions with the formed polymer morphology using standard polymerization setups, micro reactor techniques and new model catalyst systems.

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