

Crystallization of controlled rheology type polypropylene

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Investigation of the crystallization behaviour of polypropylene samples of various molecular weights prepared by peroxide melt degradation of commercial polymers has shown that the spherulite growth rate does not depend on a molecular weight. The degraded and initial PP materials were crystallized in the same manner in regimes II or III according to the crystallization temperature. The II–III regime transition took place at $T_c = 137^\circ\text{C}$.

The overall crystallization rate was controlled by the number of heterogeneous crystallization nuclei. The dependence of nuclei number on the molecular weight of the degraded samples exhibited a flat minimum in the range of medium molecular weights. It was proposed as an explanation of this minimum assuming two competing processes for the probability of attachment of the polymer chain to the solid surface of heterogeneity present in the polymer: decreasing probability for shorter chains and increased probability for more polar chains.

(Keywords: polypropylene; controlled rheology; growth rate; crystallization rate; heterogeneous nuclei)

INTRODUCTION

An important development in polypropylene (PP) grades are the so-called controlled rheology (CR) types¹, because PP obtained directly from the polymerization (reactor types) is not suitable for some applications (extrusion coating or fibre preparation) or is less suitable (injection moulding of complicated thin walled products) without modification of the molecular weight (MW).

CR types are prepared mostly from reactor types by melt degradation initiated by free radicals generated thermally from peroxides with suitable decomposition rate. CR types are characterized by narrower distribution of molecular weight (D). Due to the statistical character of degradation the higher molecular weight fractions are consumed first and the increase of the lower fractions is minimal². This markedly influences the rheological and mechanical properties of the product.

Most of the literature describes the production technology and the process of controlled degradation^{3,4}, but also compares the properties of CR and reactor types of PP⁵. In only one case⁶ has the morphology been studied as well.

This paper deals with the results of the crystallization of PP prepared by degradation of high or medium molecular weight material to medium or low molecular weight material. The aim was to elucidate the influence of the controlled degradation on the number of heterogeneous crystallization centres and to find the way of increasing the PP crystallization rate.

EXPERIMENTAL

Materials

Polymers. The medium or high molecular weight PP was melt degraded by organic peroxide in an extruder, the

usual additive (stabilizers) being added simultaneously. The resulting MW was controlled by the peroxide concentration. The dwell time in the extruder and melt temperature (200–220°C) were equal for all samples. The samples were characterized by g.p.c. and by melt flow index (MFI). The material characteristics are summarized in Tables 1 and 2.

Organic peroxide. 2,5-dimethyl-2,5-ditert-butylperoxyhexane was used for degradation.

Nucleation agent. In some cases the nucleation agent Siloyd 244 (Grace GmbH, W. Germany) was applied.

Crystallization. Linear spherulite growth rates G were measured on 0.03 mm–0.05 mm thick films with a polarized light microscope. The temperature dependences of rates were analysed according to the theory of Hoffman *et al.*^{7,14} in order to identify the growth regimes. The errors of the measured values were approximately 5%.

The overall crystallization rate was measured by an X-ray diffraction method and the rate was characterized by the crystallization half-time ($t_{1/2}$). The errors of the

Table 1 Characteristics of initial materials

Initial material	MFI (g/10 min)	\bar{M}_w	\bar{M}_n	II (%)
PH1	0.45	890 000	160 000	99.4
PH2	1.0	644 000	116 000	99.4
PH4	2.8	386 000	69 000	99.1
PH6	5.5	310 000	55 000	98.7
PH8	8.0	282 000	53 000	97.1

MFI, melt flow index (230°C; 21.16 N)

II, isotacticity index (by n-heptane extraction)

Source of initial materials: Chempetrol (Litvínov, Czechoslovakia)

Table 2 Characteristics of the CR type materials

Sample	Initial material	IT (g/10 min)	II (%)	\bar{M}_w	\bar{M}_n
DPP3011	PH1	3.3	97.6	309 000	117 000
DPP3009	PH1	27	97.7	201 000	88 000
DPP3010	PH1	41	97.7	181 000	80 000
DPP3015 ^a	PH1	23	—	211 000	90 000
13/87 ^c	PH2	1.3	—	—	—
229/86 ^c	PH2	1.2	—	—	—
DPP3006	PH2	6.3	98.3	246 000	73 000
DPP3007	PH2	14	—	218 000	66 000
DPP3019	PH2	21	—	209 000	64 000
DPP3018	PH2	43	—	172 000	63 000
185/86	PH2	55	—	—	—
14/87	PH2	73	—	—	—
DPP3022 ^a	PH2	9.6	—	211 000	70 000
DPP3021 ^a	PH2	23	—	200 000	73 000
DPP3023 ^a	PH2	30	—	192 000	71 000
186/86 ^a	PH2	53	—	—	—
15/87 ^a	PH2	71	—	—	—
212/86 ^b	PH2	25	—	—	—
DPP3026	PH4	2.5	97.6	373 000	67 000
DPP2097	PH4	21	97.5	258 000	65 000
DPP2099 ^a	PH4	19	—	272 000	66 000
178/84	PH6	13	—	241 000	55 000
180/84	PH6	21	—	203 000	48 000
196/84	PH6	39	—	145 000	46 000
345/85 ^c	PH8	9.4	—	259 000	52 000
347/85	PH8	20	—	—	—
344/85	PH8	42	—	—	—

^a Nucleated by 0.1% Siloyd 244^b Nucleated by 0.2% Siloyd 244^c Reactor type PPTable 3 The spherulite growth rate G at various crystallization temperatures T_c for samples prepared by degradation of initial material PH2

Sample	G ($\mu\text{m}/\text{min}$)							
	T_c (°C):	123	126	129	132	135	139	142
13/87 ^c	18.8	9.52	6.18	3.32	1.68	0.70	0.46	0.28
229/87 ^c	18.7	10.2	6.27	3.26	1.72	0.75	0.45	0.29
DPP3006	15.6	9.53	5.82	3.51	1.75	0.80	0.45	0.22
DPP3007	15.3	10.4	5.91	3.20	1.74	0.74	0.46	0.27
DPP3019	18.1	12.3	5.22	3.50	1.87	0.72	0.45	0.28
DPP3018	17.2	11.2	4.91	3.49	1.93	0.79	0.46	0.28
185/86	16.2	10.7	5.12	3.27	1.70	0.77	0.46	0.28
14/87	18.6	11.7	6.38	3.14	1.72	0.78	0.45	0.28
DPP3022 ^a	14.9	10.2	5.71	3.09	1.83	0.77		
DPP3021 ^a	15.4	11.0	5.23	3.17	1.92	0.75		
DPP3023 ^a	14.9	9.69	5.33	3.20	1.79	0.79		
186/86 ^a	16.3	11.1	5.51	3.32	1.85	0.80		
15/87 ^a	16.5	10.8	5.63	3.27	1.76	0.78		
212/86 ^b	15.7	10.9	5.27	3.13	1.88	0.78		

^a Nucleated by 0.1% Siloyd 244^b Nucleated by 0.2% Siloyd 244^c Reactor type

measured values were approximately 0.5 min. The heterogeneous nuclei number N was calculated from the equation:

$$N = (3 \ln 2)/(4G^3 t_{1/2}^3) \quad (1)$$

RESULTS

The spherulite growth rate, G , data of the CR types of PP, measured over a wide range of crystallization

temperature T_c (for MFI values see Table 2) are shown in Table 3. G increased with decreasing T_c for all nucleated and unnucleated samples by two orders of magnitude. MFI did not influence the spherulite growth rate. To a lesser extent the effect of the starting material was also followed (Table 4).

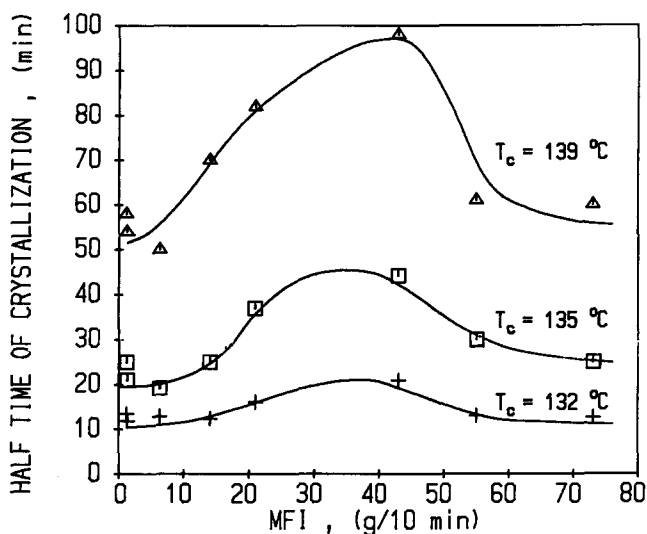
The overall crystallization rate was investigated as a function of T_c , MFI and concentration of the nucleation agent. Table 5 shows the typical effect of T_c on

Table 4 The spherulite growth rate G as a function of the crystallization temperature T_c , melt flow index MFI and the initial material

Sample	Initial material	IT (g/10 min)	G ($\mu\text{m}/\text{min}$)		
			T_c ($^{\circ}\text{C}$):		
			129	132	135
DPP3011	PH1	3.3	5.43	3.31	1.73
DPP3009	PH1	27	4.58	3.30	1.62
DPP3010	PH1	41	4.97	3.20	1.71
DPP3015 ^a	PH1	23	5.70	3.66	1.78
DPP3026 ^b	PH4	2.5	4.91	2.97	1.55
DPP2097	PH4	21	5.56	3.04	1.78
DPP2099 ^b	PH4	19			
178/84	PH6	13	6.03	4.07	2.04
180/84	PH6	21	6.61	3.90	2.18
196/84	PH6	39	6.48	4.50	2.22
345/85 ^b	PH8	9.4	6.35	4.50	1.85
347/85	PH8	20	7.48	3.73	1.90
344/85	PH8	42	6.74	4.26	1.99

^a Nucleated by 0.1% Siloyd 244^b Reactor type**Table 5** Half time of crystallization $t_{1/2}$ as a function of crystallization temperature T_c for CR samples from initial material PH2

Sample	$t_{1/2}$ (min)		
	T_c ($^{\circ}\text{C}$):		
	132	135	139
13/87	11.8	21.0	54.0
229/86	13.4	25.0	58.0
DPP3006	12.8	19.2	50.0
DPP3007	12.3	25.0	70.0
DPP3019	16.1	37.0	82.0
DPP3018	20.9	44.2	98.0
185/86	13.0	30.0	61.0
14/87	12.6	25.0	60.0

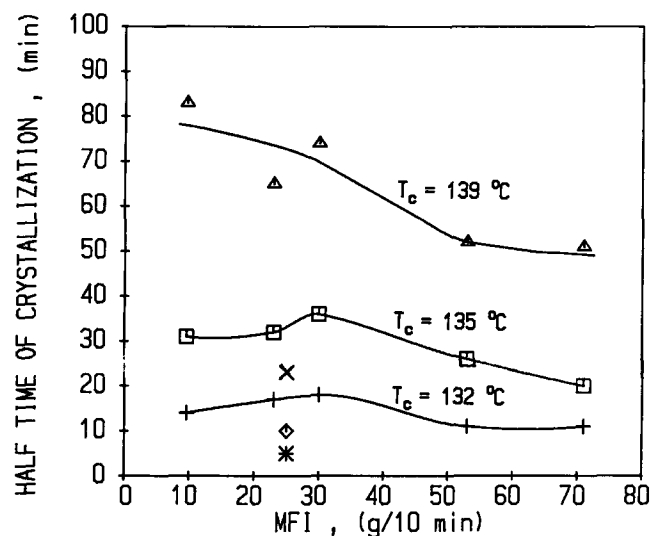
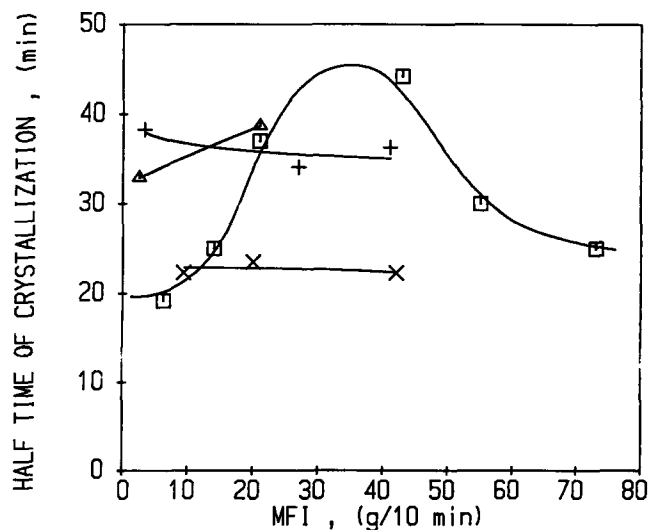
**Figure 1** The dependence of the crystallization half time $t_{1/2}$ on the melt flow index MFI for the CR samples prepared from the initial material PH2, measured at various crystallization temperatures

the crystallization half-time $t_{1/2}$. The plots for individual samples are similar, a decrease of T_c by 3°C roughly corresponds to a 50% reduction of the $t_{1/2}$ value. The influence of MFI on the $t_{1/2}$ measured at various T_c values is shown in Figure 1. In the MFI range 10–50, especially at higher T_c , a marked decrease of the

crystallization rate takes place, forming a broad maximum in the $t_{1/2}$ -MFI plots.

The effect of the nucleation agent is illustrated in Figure 2. Although 0.1% of the nucleating agent influenced the crystallization rate, a much higher concentration of the agent is necessary for a substantial effect. The presence of the nucleation agent increases not only the crystallization rate, but also suppresses the maximum of the $t_{1/2}$ -MFI plots. At higher T_c values the effect of the initial material was also followed (Figure 3). The least influence of MFI on $t_{1/2}$ was found with the low MW starting material (PH8) which gives products with the highest crystallization rate.

The analysis of the crystallization kinetics according to the Avrami equation is summarized in Table 6. The data in Table 6 show that the value of the exponent n from the Avrami equation is close to 3, mainly at higher values of T_c and slower crystallization rates where the measurements could be done with a higher precision. The

**Figure 2** The dependence of the crystallization half time $t_{1/2}$ on the melt flow index MFI for CR samples prepared from the initial material PH2 containing 0.1% of nucleating agent**Figure 3** The dependence of the crystallization half time $t_{1/2}$ on the melt flow index MFI for CR samples prepared from various initial materials. Crystallization temperature = 135°C . Initial materials: +, PH1; \square , PH2; \triangle , PH4; \times , PH8

value $n=3$, together with microscopic observation, confirms the heterogeneous character of the nucleation process in our PP samples. The influence of MFI on n was not observed.

DISCUSSION

Spherulite growth rate

As with other authors⁸⁻¹¹ we have not observed any important dependence of G on MW. The comparison of our data for CR types of PP with those of reactor types of PP with comparable isotacticity, taken from the literature^{10,12,13}, proves that they are very similar.

We have analysed the G data according to general growth rate equation⁷ and the results are shown in Tables 7 and 8. From this it was found that at about $T_c = 137^\circ\text{C}$ there is a change from crystallization regime III to II. The ratio $K_g(\text{III})/K_g(\text{II})$ lies in the range 1.81–2.18 which is close to the theoretical value of 2 (see refs. 7, 14). Regime I was not reached.

Crystallization kinetics

The comparison (Figure 4) of the overall crystallization rate of our CR type samples with literature data for the reactor type PP discloses significant differences. From the discussion above it is clear that the differences in the crystallization rate are due to various amounts of heterogeneous crystallization nuclei and not to the growth process. The same follows from the results of Martuscelli *et al.*¹². The main source of heterogeneous crystallization nuclei in polyolefins is the residue of the initiation system. It is clear that only a very small fraction of the heterogeneities present in the polymer are nucleation active and therefore there is no simple correlation between the nuclei number and, for example, ash content. The nucleation activity of heterogeneities is closely

Table 6 The analysis of overall crystallization data according to Avrami equation for CR samples from initial material PH2

Sample	$T_c = 132^\circ\text{C}$		$T_c = 135^\circ\text{C}$		$T_c = 139^\circ\text{C}$	
	n	$K \times 10^4$	n	$K \times 10^5$	n	$K \times 10^6$
13/87 ^a	2.3	15.9	2.6	66.6	2.6	22.7
229/86 ^a	2.9	3.3	2.3	15.7	2.8	6.2
DPP3006	2.5	10.2	2.9	10.0	3.1	5.4
DPP3007	2.3	3.9	3.0	4.5	3.2	1.1
DPP3019	2.5	5.3	3.1	1.1	3.1	0.7
DPP3018	2.6	2.5	2.9	1.2	2.9	1.2
185/86	2.4	11.8	2.9	4.6	2.7	11.6
14/87	2.6	8.9	2.8	9.1	2.8	7.0

^a Initial material (reactor type)

Table 7 The analysis of spherulite growth data for CR samples prepared from initial material PH2

Sample	$-\log G + U^*/2.303RT(T - T_\infty)$								
	T_c ($^\circ\text{C}$):	123	126	129	132	135	139	142	145
DPP3006		2.598	2.849	3.090	3.348	3.682	4.063	4.344	4.563
DPP3007		2.606	2.809	3.089	3.388	3.865	4.097	4.332	4.590
DPP3019		2.533	2.737	3.145	3.350	3.653	4.109	4.340	4.576
DPP3018		2.555	2.777	3.170	3.350	3.640	4.069	4.319	4.582
185/86		2.581	2.797	3.151	3.379	3.695	4.080	4.322	4.579

U^* , T_∞ , T_g according to ref. 16 ($U^* = 6279 \text{ J/mol}$, $T_\infty = 231.2 \text{ K}$, $T_g = 261.2 \text{ K}$)

connected with the interaction at the interface between polymer and the heterogeneity.

We have shown that the nucleation efficiency of various heterogeneities could be markedly changed by the presence of low molecular weight substances. Generally we have established that the treatment of polyolefins with substances which deactivate initiators of the coordination polymerization decreases the active nuclei number and vice versa, the treatment which increases the wetting of the solid surface increases the nuclei number. From this, we may deduce that the maximum in our $t_{1/2}$ -MFI plots reflects two competing processes. The process connected with the increase of nuclei number with decreasing MW is most probably due to the formation of polar groups on chain ends during the degradation process. The higher polarity enables better wetting of a larger amount of heterogeneities in the system. This process of 'activated

Table 8 The analysis of growth regimes for samples in Table 7

Sample	$K_g(\text{III})$ (K^2)	$K_g(\text{II})$ (K^2)	$K_g(\text{III})/K_g(\text{II})$
DPP3006	5.928	3.199	1.852
DPP3007	5.725	2.954	1.938
DPP3019	5.979	2.924	2.045
DPP3018	5.738	3.168	1.812
185/86	5.895	3.010	1.959

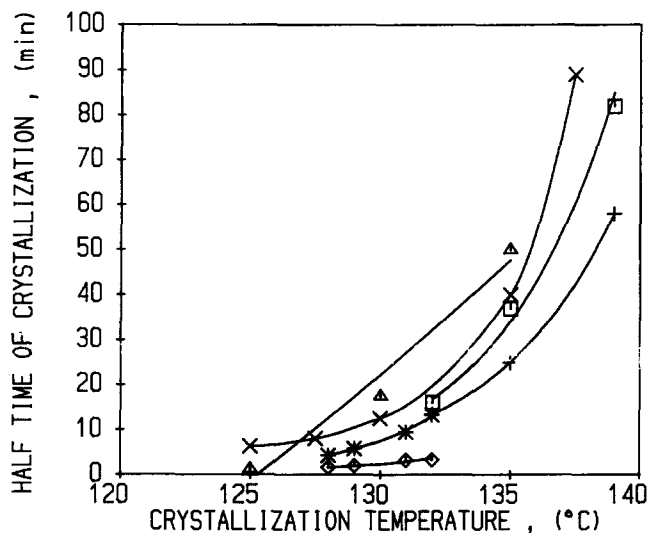


Figure 4 The comparison of the crystallization half time $t_{1/2}$ for our CR samples ((229/86), DPP 3019) and reactor types of PP (taken from the literature). Symbols, +, 229/86; \square , DPP 3019; \times , according to ref. 16 (calorimetric data); \triangle , according to ref. 17; \diamond , LY(97.5), $*$, HY(97.5) according to ref. 12

heterogeneous nucleation' will be further studied in another paper¹⁵.

The explanation of the initial decrease of crystallization nuclei with decreasing MW is not so straightforward. The idea that this effect is due to the presence of the peroxide or its degradation products used for PP degradation cannot be valid because the same type of behaviour was also observed with neat PP degraded by gamma irradiation¹³. There are two possibilities which come into consideration. The first is changes in configuration of the initiator particles acting as active nucleation centres. However, more probably the explanation is as follows. The formation of heterogeneous nuclei depends on the probability of attachment of a polymer chain segment on the polar solid surface of the heterogeneity. This probability is higher either for a longer polymer molecule or a more polar one. For less degraded samples the effect of decreased chain length, for lower MW samples predominates over the effect of a higher polarity.

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