

Application of Successive Self-nucleation and Annealing to Study the Stereo-defects Distribution of Biaxially Oriented Polypropylene^{*}

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Abstract The stereo-defects distribution of polypropylene of the two industry biaxially oriented polypropylene (BOPP) samples T28FE and F28SO with different processing properties was studied through successive self-nucleation and annealing (SSA) technique. It was found that there were more medium isotactic components in sample F28SO, and the isotactic sequence length of polypropylene of sample F28SO was shorter and the isotactic sequence length distribution of polypropylene of sample F28SO was broader, which could be processed well at high-speed orientation during the processing of BOPP films. This result indicates that the isotactic sequence length distribution of polypropylene is related to the processing speed during preparing BOPP films, and the stereo-defects distribution of polypropylene has an important influence on its processing ability.

Keywords: BOPP; Lamellar thickness; Isotactic sequence length; Successive self-nucleation and annealing.

INTRODUCTION

Biaxially oriented polypropylene (BOPP) is made of isotactic polypropylene, which is widely used in various applications such as packaging material and other industrial use because of its advantage of properties^[1–3]. Several millions tons BOPP resins per year are produced all of world. The orientation processing speed of BOPP is very important for its cost. Now, the processing speed is up to 500 meter per minute. The high-speed BOPP is not only related to the molecular weight distribution of polypropylene, but also related to the isotacticity distribution in the polypropylene chain.

Liu *et al.*^[4] fractionated two BOPP resins (resin A and resin B) by temperature rising elution fractionation (TREF), and found that there were more medium isotactic components of resin A which could be processed well at high-speed orientation during the processing of BOPP film while there were more higher isotactic components of resin B which tended to break at the same processing conditions, although BOPP resin A and resin B had similar average molecular weights and isotacticities, indicating that resin A possessing good processing properties during the processing of BOPP films had a lower isotacticity and more medium isotactic components than resin B. As the fractions eluted at the lower temperatures contained more stereo-defects, while the fractions eluted at higher elution temperatures had longer isotactic sequences, so the TREF results indicated that the processing properties of high-speed BOPP were related to the stereo-defects distribution^[5–8].

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The stereo-defects distribution of polypropylene prepared by Ziegler-Natta catalyst not only reflects the information of catalyst and polymerization mechanism, but also determines the processability and mechanical properties of polypropylene^[9, 10]. It is known that the methyl groups of its molecular chain for isotactic polypropylene are not all perfectly located on one side of polymer chain to form isotactic structure, as well as there is some syndiotactic or atactic structure in polypropylene caused by a small amount of "mistake inserted" monomers, which isn't usually good for the physical and mechanical properties of polypropylene^[11]. However, the presence of suitable amounts of stereo-defects in polypropylene chains will greatly influence its orientation behavior for BOPP, which can improve the performances and quality of the BOPP films^[12, 13]. In this case, a combination of low percentage of atactic fractions and moderate amounts of stereo-defects in the isotactic fractions will be the most favourable conditions. As the stereo-defects of polypropylene prepared by Ziegler-Natta catalyst are the stereo-defects of the arrangements of the side methyl groups of "mistake inserted" monomers, and the length between every two "mistake inserted" monomers is called isotactic sequence length of polypropylene, which can reflect stereo-defects distribution of polypropylene, as shown in Fig. 1.

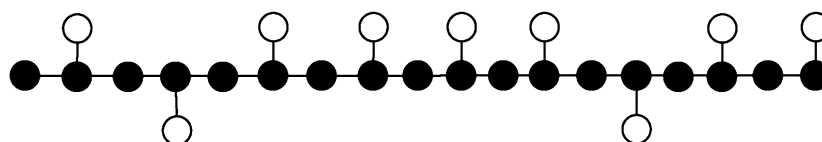


Fig. 1 Schematic diagrams for chain structure of PP

Successive self-nucleation and annealing (SSA) thermal fractionation technique is based on the self-nucleation and annealing steps sequentially used to a polymer sample, and has been widely used to analyze the chain structures of semi-crystallized polymers such as PE and PP^[14–30]. There is a good correspondence between the SSA and TREF techniques, and the results of SSA are coincident with the results of high resolution ¹³C-NMR, GPC, TREF, and xylene solvent (XS) fractionation^[10, 16, 20, 31–33]. With the increase of separation temperature, the component separated by TREF shows higher melting temperature and longer isotactic sequence length after SSA treatment, ¹³C-NMR result also shows that isotacticity of polypropylene and isotactic sequence length of polypropylene increase^[10, 34–36]. Compared with ¹³C-NMR and TREF fractionation, SSA fractionation is not only a more time-saving and practical technique in the characterization of the molecular structure of *i*PP, but also SSA can provide important quantitative information about the lamellar thickness and its distribution of polypropylene, which gives a more accurate characterization to the isotactic sequence length and its distribution of polypropylene.

In this paper, the stereo-defects distribution of polypropylene of the two industry BOPP samples T28FE and F28SO with different processing properties was studied through SSA technique, and it's found that the isotactic sequence length distribution of polypropylene was related to the processing speed in preparing BOPP films, indicating that the stereo-defects distribution of polypropylene has an important influence on its processing ability.

EXPERIMENTAL

Materials

The commercial BOPP samples T28FE and F28SO were provided respectively by PetroChina and SINOPEC Co. Ltd.

Differential Scanning Calorimetry (DSC)

All DSC measurements were performed with a Mettler 822e differential scanning calorimeter in a nitrogen atmosphere. Samples about 3.0 mg in aluminium pans were first melted by heating from 50 °C up to 200 °C at a rate of 50 K/min and were held at this temperature for 5 min in order to erase previous thermal history, then

cooled down to 50 °C, held at 50 °C for 2 min, and then finally heated again to 200 °C at a rate of 10 K/min.

The melting temperature T_m and the enthalpy of fusion ΔH_m were determined from the second melting. The degree of crystallinity was calculated according to the following equation^[37]:

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0}$$

where ΔH_m was the fusion enthalpy obtained from DSC curve, ΔH_m^0 was the fusion heat of a perfectly crystallization PP, *i.e.*, 209.0 J/g^[38].

Successive Self-nucleating and Annealing (SSA) Fractionation

SSA fractionation was performed as presented by Müller^[14]. The complete thermal treatment comprises the following steps: (a) Erasure of the crystalline thermal history by heating the sample to 200 °C and held for 5 min; (b) Cooling the sample at 20 K/min to 50 °C and held for 2 min; (c) The sample was heated at 20 K/min from 50 °C to a partial melting temperature denoted T_s ; (d) The sample was kept at T_s for 15 min; (e) DSC cooling scan at 20 K/min from T_s to 50 °C; (f) Repeat step (c) to (e) at a new lower T_s which is 5 °C lower than the previous T_s for a total six self-nucleation/ annealing steps; (g) finally, the sample was heated at 10 K/min from 50 °C to 200 °C, and a multiple melting endotherm was obtained.

In our previous research^[27], the effect of SSA parameters including the determination of the optimal annealing temperature T_s , the annealing time t_s , annealing temperature interval and heating and cooling rates on the crystallization properties of polypropylene were studied in detail, so the first optimal annealing temperature T_s used in step (c) in this study for BOPP samples was carefully chosen as 164 °C after the same self-nucleating step according to the procedure proposed in literatures^[14, 15, 19, 22, 39–41]. Pijpers *et al.*^[42] recently introduced the high-speed calorimetry concept that the increment of heating rate could be compensated by reducing the sample mass. So a higher scanning rate of 20 K/min was employed to reduce the fractionation time, and a smaller sample mass of 2.5 mg was used as compensation.

Nuclear Magnetic Resonance Spectroscopy (¹³C-NMR)

¹³C-NMR spectra of polymers were tested with a DMX 300M instrument (Bruker). Polymer solution was prepared with 80 mg of polymer in 0.5 mL of deuterated *o*-dichlorobenzene at 383 K. The *o*-dichlorobenzene solvent was used to provide the internal lock signal with its highest peak at $\delta = 132.700$ as the standard reference. Experimental conditions were: number of pulses more than 5000, pulse angle 30°, spectrum width 25000 Hz, and relaxation delay 7 s. All spectra were completely proton decoupled.

Gel Permeation Chromatography (GPC)

The molecular weights (M_n and M_w) and the molecular weight distribution (MWD) of polypropylene were determined by a PL-GPC 220 high-temperature gel permeation chromatography (Polymer Laboratories Ltd) at 413.15 K, using 1,2,4-trichlorobenzene as solvent, the injection volume was 100 mL, and the flow rate was 1.0 mL/min. Calibration was made by using polystyrene as the standard sample.

RESULTS AND DISCUSSION

Preliminary Characterization of BOPP Samples F28SO and T28FE

All of the BOPP samples were characterized preliminarily, and the results are listed in Table 1. The DSC melting curves and crystallization curves of BOPP samples T28FE and F28SO are shown as Fig. 2 and Fig. 3, respectively.

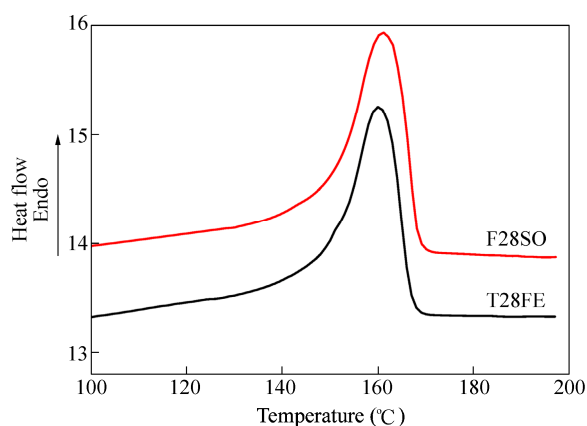


Fig. 2 The DSC melting curves of BOPP samples T28FE and F28SO

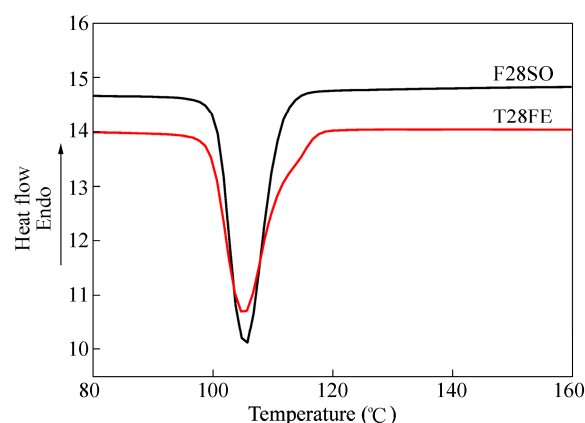


Fig. 3 The DSC crystallization curves of BOPP samples T28FE and F28SO

Table 1. Preliminary characterization of all BOPP samples

Samples	I.I. ^a (%)	$M_n \times 10^{-4}$	M_w/M_n	T_m^b (°C)	ΔH_m^c (J/g)	T_c^d (°C)	ΔH_c^e (J/g)	X_c^f (%)
T28FE	96.3	7.2	5.5	160.8	89.3	105.4	-98.6	42.7
F28SO	96.2	6.3	5.8	160.1	88.3	105.3	-89.3	42.2

^a The isotactic index (I.I.) tested by extraction with boiling *n*-heptane for 6 h;

^b Melting temperature determined from the endothermic curves of DSC;

^c The value of the endothermic enthalpy determined from DSC;

^d Crystallization temperature determined from the exothermic curves of DSC;

^e The value of the exothermic enthalpy determined from DSC;

^f The degree of crystallization calculated from the value of the endothermic enthalpy

F28SO and T28FE samples are two typical high-speed BOPP in china market. While, the processing speed of the former is about 50 meter per minute higher than that of the latter. As is known, the high-speed BOPP is not only related to the molecular weight distribution of polypropylene, but also related to the isotacticity distribution in the polypropylene chain. The BOPP resin processed well at high-speed orientation has a lower isotacticity and a more homogeneous isotacticity distribution, which are related to the stereo-defects in the polypropylene chain. Preliminary characterization of BOPP samples in Table 1 shows that the isotacticity, the melting temperature, the enthalpy of fusion ΔH_m , the crystallization temperature, the crystallization enthalpy and the degree of crystallinity of sample of T28FE are a little higher than those of F28SO while the molecular weight distribution (MWD) of F28SO is broader than that of T28FE, which can't reveal the key reason for the different processing properties clearly.

SSA Thermal Fractionation Characterization of BOPP Samples F28SO and T28FE

In order to study the distribution of stereo-defects in the polypropylene chain, the BOPP samples were studied and fractionated by SSA, and the SSA melting curves of the BOPP samples T28FE and F28SO are shown in Fig. 4, and each peak of the melting point and the enthalpy of fusion ΔH_m of each sample are listed in Table 2.

Table 2. The SSA results of BOPP samples T28FE and F28SO

Samples	I.I. (%)	T_s (°C)	ΔH_m (J/g)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	T_{m4} (°C)	T_{m5} (°C)
T28FE	96.3	164	121.0	177.5	169.8	158.3	152.8	147.4
F28SO	96.2	164	116.2	177.1	169.4	158.1	152.5	147.4

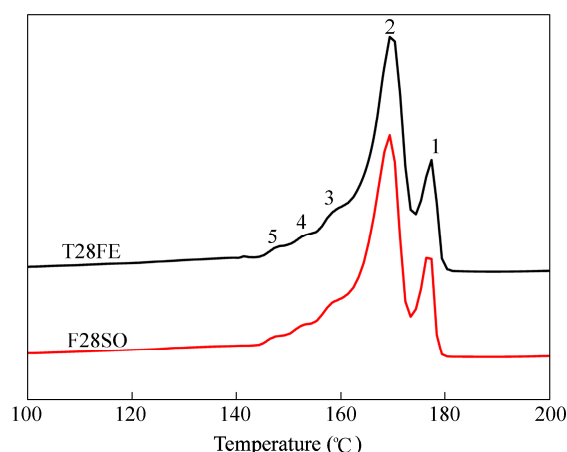


Fig. 4 The SSA melting curves of BOPP samples T28FE and F28SO

It's known that higher melting temperature on the SSA final melting curve is corresponding to higher isotacticity and longer isotactic sequence length in the molecular chains^[10]. As can be seen clearly from Fig. 4 and Table 2, there are five melting peaks on the melting curves after SSA fractionation for BOPP samples, and the melt peaks of sample T28FE are a little higher than those of F28SO, indicating the sample T28FE has higher regularity of the polypropylene chain and a longer isotactic sequence length than F28SO and is more likely to crystallize. The DSC data in Table 1 show that the melting temperature, the enthalpy of fusion ΔH_m , the crystallization temperature, the crystallization enthalpy and the degree of crystallinity of sample T28FE are a little higher than those of sample F28SO, and the sample T28FE has higher molecular weights and narrower molecular weight distribution, although the isotacticities of the two BOPP samples are almost the same, which are also indicating that there are more isotactic components in polypropylene chain of sample F28SO.

In order to quantitatively evaluate the variations of all melting peaks, the relative contents (the integral area percentages on the SSA melting curve) of each peak are calculated using Peakfit 4.12 software, and the relative contents of all peaks are shown in Table 3. Figure 5 shows plots of SSA melting curve and its fitted curves of BOPP sample T28FE after using Peakfit 4.12 software. Figure 6 shows the fitted peaks of SSA melting curves of two BOPP samples after using Peakfit 4.12 software.

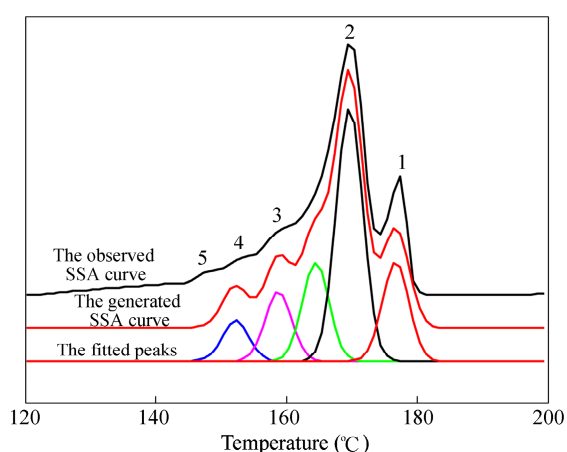


Fig. 5 Plots of SSA melting curve and its fitted curves of BOPP sample T28FE by using Peakfit 4.12 software (The peakfit variance r^2 of the fitted peaks is 0.976.)

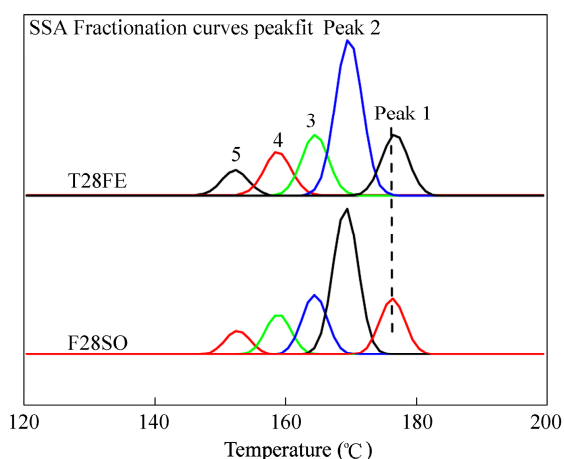


Fig. 6 The fitted curves using Peakfit 4.12 software of SSA melting curves of BOPP samples T28FE and F28SO

Table 3. The relative contents of all peaks on the SSA curve of polypropylene

Samples	I.I. (%)	T_s (°C)	ΔH_m (J/g)	n_1^a (%)	n_2 (%)	n_3 (%)	n_4 (%)	n_5 (%)
T28FE	96.3	164	121.0	17.45	45.22	17.42	12.43	7.47
F28SO	96.2	164	116.2	17.12	44.85	18.26	12.42	7.35

^a The relative content of peak 1 on the SSA curve of polypropylene calculated using Peakfit 4.12 software.

As can be seen from Table 3 and Fig. 6, the relative contents of peak 1 and peak 2 for higher isotactic components in sample T28FE molecular chain are higher than those of sample F28SO, showing the sample F28SO which can be processed well at high-speed orientation during the processing of BOPP films has lower relative content of the higher isotactic components of polypropylene. Meanwhile, the total relative content of peak 3 of sample F28SO is higher than that of sample T28FE, indicating that there are more medium isotactic components in sample F28SO. The relative contents of peak 4 and peak 5 for lower isotactic components of T28FE are a little higher than those of sample F28SO, also showing that the sample F28SO which can be processed well at high-speed orientation during the processing of BOPP films has lower relative contents of lower isotactic component of polypropylene. The above results suggest that the variations of the relative contents of different isotactic components in the polypropylene chain can have important effects on the processing of BOPP films, and the polypropylene having lower high isotactic component and more medium isotactic component in molecular chains can be processed well at high-speed orientation during the processing of BOPP films.

The stereo-regular sequences with different lengths of polypropylene can crystallize independently and form the microcrystals with different sizes when polypropylene is fractionated through thermal techniques such as SSA, so the stereo-regular sequence length of polypropylene is related to the lamellar thickness, and the multiplex melting peaks on the SSA melting curves in fact are the melting peaks of the microcrystals with different sizes formed and annealed at each self-nucleation temperature employed^[17, 20]. The lamellar thickness could be estimated from the SSA results with the following Thomson-Gibbs equation^[39, 43]:

$$T_m = T_m^0 \left(1 - \frac{2\sigma}{\Delta H_0 L_i} \right)$$

where the equilibrium melting temperature $T_m^0 = 460$ K (estimated values between 459 – 467 K)^[44, 45], $\Delta H^0 = 184 \times 106$ J/m³, the surface energy $\sigma = 0.0496$ J/m² and L_i is the lamellar thickness^[46]. Moreover, for further analysis, the statistical parameters describing the lamellar thickness, the arithmetic average L_n , weighted average L_w , and the broadness index I , are calculated using the following equations^[47]:

$$L_n = \frac{n_1 L_1 + n_2 L_2 + n_3 L_3 + n_4 L_4 + \cdots n_j L_j}{n_1 + n_2 + n_3 + n_4 + \cdots n_j} = \sum f_i L_i$$

$$L_n = \frac{n_1 L_1^2 + n_2 L_2^2 + n_3 L_3^2 + n_4 L_4^2 + \cdots n_j L_j^2}{n_1 L_1 + n_2 L_2 + n_3 L_3 + n_4 L_4 + \cdots n_j L_j} = \frac{\sum f_i L_i^2}{\sum f_i L_i}$$

$$I = \frac{L_w}{L_n}$$

where n_i is the normalized peak area, and the L_i is the lamellar thickness for each fraction. The results of all samples are listed in Table 4.

Table 4. The lamellar thicknesses of polypropylene samples after SSA thermal fractionation

Samples	L_1 (nm)	L_2 (nm)	L_3 (nm)	L_4 (nm)	L_5 (nm)	L_w (nm)	L_n (nm)	$I = L_w/L_n$
T28FE	26.52	14.55	8.69	7.28	6.29	19.63	15.65	1.255
F28SO	25.44	14.21	8.63	7.22	6.29	20.39	15.88	1.284

The lamellar thicknesses of the two BOPP samples T28FE and F28SO after SSA thermal fractionation are calculated and listed in Table 4. L_1 is the lamellar thickness of peak 1 of the highest isotactic composition of polypropylene after SSA treatment. As can be seen clearly from Table 4, the lamellar thicknesses of the isotactic component of peak 1 to peak 4 of sample T28FE are higher than those of sample F28SO, while their difference in L_5 is little, showing that the isotactic sequence lengths of sample T28FE are longer than those of sample F28SO. Table 4 also shows the broadness index I of the lamellar thickness distribution of sample F28SO ($I = 1.284$) is higher than that of sample T28FE ($I = 1.255$), indicating the isotactic sequence length distribution of sample F28SO is broader than that of sample T28FE.

¹³C-NMR Characterization of BOPP Samples F28SO and T28FE

In order to better understand the information of chain structure of BOPP samples F28SO and T28FE from SSA measurements, ¹³C-NMR is used for the measurement of the stereo-regularity of polypropylene. The methyl regions results of the 300 MHz ¹³C-NMR spectra of the polypropylene samples are listed in Table 5.

Table 5. The ¹³C-NMR results of the stereo-sequence distribution of BOPP samples

Samples	mm				mr				rr			
	mm	mmmm	mmmr	rmmr	mr	mmrr	mrmm+rmrr	mrmmr	rr	rrrr	rrrm	mrmm
T28FE	96.74	94.94	0.52	1.28	2.09	0.75	0.32	1.02	1.17	0.81	0.11	0.25
F28SO	96.60	94.88	0.82	0.90	2.38	0.82	0.79	1.07	1.02	0.52	0.16	0.34

It was known that there was in good correspondence between SSA and ¹³C-NMR methods when they were used to study polymer samples with large different stereo-regular defects^[20]. Our previous studies also showed that there was a good consistency between SSA and ¹³C-NMR techniques when the isotactic sequence length and its distribution of polypropylene with quite different isotacticity were studied by SSA and ¹³C-NMR techniques^[21, 36]. As can be seen from Table 5, the ¹³C-NMR results indicate that there are not obvious differences in the isotactic triad [mm], syndiotactic triad [mr], and atactic triad [rr] for sample T28FE and F28SO. Because the stereo-regularity and the isotacticity of the two BOPP samples are very similar, so there is no obvious consistency between SSA and ¹³C-NMR, revealing that SSA has a good advantage in studying the molecular chain structure of the polymer with similar stereo-regular defects compared with ¹³C-NMR.

As is studied previously for the BOPP samples, the small difference in the stereo-defects of polypropylene samples would have an important influence on their high-speed bi-orientation processing. The SSA fractionation results clearly suggest that there are more medium isotactic components in sample F28SO, which can be processed well at high-speed orientation during the processing of BOPP films, and the broader isotactic sequence length distribution and the shorter isotactic sequence length of polypropylene contribute to the high-speed processing of BOPP films.

CONCLUSIONS

In this study, the stereo-defects distribution of polypropylene of the two industry BOPP samples T28FE and F28SO with different processing properties was studied through SSA technique. Compared with sample T28FE, the sample F28SO which can be processed well at high-speed orientation during the processing of BOPP film has more medium isotactic components in molecular chains, and the isotactic sequence length is shorter and the isotactic sequence length distribution is broader, which may contribute to the high-speed processing of BOPP films. The results of two BOPP samples T28FE and F28SO indicate that the small difference in stereo-defects distribution of polypropylene has an important influence on the high-speed processing ability of bi-orientation polypropylene films.

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