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Miscibility of binary blends of poly[(*R*)-3-hydroxybutyric acid] and poly[(*S*)-lactic acid]

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The miscibility of binary blends of bacterial poly[(*R*)-3-hydroxybutyric acid] {P[(*R*)-3HB]} (M_w = 650 000) with poly[(*S*)-lactic acid] {P[(*S*)-LA]} of various molecular weights (M_w = 9900–530 000) have been studied by means of differential scanning calorimetry (d.s.c.). D.s.c. analysis revealed that the structure of P[(*R*)-3HB]/P[(*S*)-LA] blends was strongly dependent on the molecular weight of the P[(*S*)-LA] component. The blends of P[(*R*)-3HB] with P[(*S*)-LA] of high M_w values over 20 000 showed two phases in the melt at 200°C, while the blends of P[(*R*)-3HB] with P[(*S*)-LA] of low M_w values below 18 000 were miscible in the melt over the whole composition range. On the basis of the relationship between the miscibility of blends and the molecular weight of the P[(*S*)-LA] component, the difference in the solubility parameters δ_1 and δ_2 of the blend components in the Flory–Huggins equation was estimated to be 0.34 $(\mathrm{J\,cm^{-3}})^{1/2}$. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly[(*R*)-3-hydroxybutyric acid]; poly[(*S*)-lactic acid]; blends)

INTRODUCTION

A wide variety of bacteria synthesize an optically active polymer of (*R*)-3-hydroxybutyric acid as an intracellular storage material of carbon and energy source[1,2]. Poly[(*R*)]-3-hydroxybutyric acid] {P[(*R*)-3HB]} isolated from bacteria is a biodegradable and biocompatible thermoplastic with a melting temperature around 180°C[3,4]. The bacterial P[(*R*)-3HB] has attracted industrial attention as a possible candidate for large biotechnological products[5]. A remarkable characteristic of P[(*R*)-3HB] is its biodegradability in the environment. The films and fibres of P[(*R*)-3HB] are degraded by various microorganisms in soil, sludge or seawater, and the degradation rate is extremely fast under optimum conditions[2]. Various microorganisms excrete extracellular PHB depolymerase to degrade environmental P[(*R*)-3HB] and utilize the decomposed compounds as nutrients[6–8]. However, the rate of non-enzymic hydrolysis of P[(*R*)-3HB] chains is relatively slow in the aqueous environment without microorganisms[9,10].

Poly[(*S*)-lactic acid] {P[(*S*)-LA]} has been investigated as a material for medical devices such as controlled drug release matrixes, degradable sutures and implants for bone fixation[11]. Although it has been reported that some enzymes hydrolyse P[(*S*)-LA][12,13], the degradation of P[(*S*)-LA] in an aqueous environment is mainly due to non-enzymic hydrolysis of polymer chains catalysed by carboxyl end groups of polymers[14]. In a previous paper[15], we studied the miscibility, morphology and biodegradability of a blend of P[(*R*)-3HB] (M_n = 300 000, M_w = 650 000) with atactic P[(*R*,*S*)-LA] (M_n = 9000, M_w = 21 000) and reported that the P[(*R*)-3HB]/P[(*R*,*S*)-LA] blend was miscible in the amorphous state and that the non-enzymic hydrolysis of P[(*R*)-3HB] chains was accelerated by blending with P[(*R*, *S*)-LA]. Iannace *et al.*[16] showed that the blend of bacterial poly[(*R*)-3-hydroxybutyric acid-*co*-(*R*)-3-hydroxyvaleric acid] (PHBV) with P[(*S*)-LA] had two distinct phases in the melt and that the P[(*S*)-LA] component was partially dispersed in the PHBV phase. Blümm and Owen[17] studied the spherulitic structure and melting behaviour of P[(*R*)-3HB]/P[(*S*)-LA] blends and found that a low molecular weight P[(*S*)-LA] (M_n = 1759) was miscible with P[(*R*)-3HB] (M_n = 222 000) in the melt over the whole composition range, while a blend with high molecular weight P[(*S*)-LA] (M_n = 159 400) showed biphasic separation.

In this paper, we investigate the miscibility of binary blends of P[(*R*)-3HB] (M_w = 650 000) with P[(*S*)-LA] of various molecular weights (M_w = 9900–530 000) by means of differential scanning calorimetry (d.s.c.). The effect of the molecular weight of the P[(*S*)-LA] component on the miscibility of the blends is discussed.

EXPERIMENTAL

Materials

The bacterial P[(*R*)-3HB] sample (M_n = 300 000, M_w = 650 000) was purchased from Aldrich Chemicals, The P[(*R*)-3HB] sample was purified by precipitation in hexane from chloroform solution at room temperature and dried *in vacuo* for two days. The P[(*S*)-LA] sample (M_w = 300 000, M_w = 530 000) was purchased from Polysciences and used as received without further

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purification. P[(*S*)-LA] samples of low molecular weights were prepared by methanolysis[18]. The P[(*S*)-LA] (1 g) of $M_w = 530\,000$ was dissolved in chloroform (30 ml) in a 50 ml screw-cap bottle, and 10 ml of 3 vol% sulfuric acid in methanol was added. The bottle was kept at 35°C for a given time. The reaction solution was neutralized by addition of 5 wt% of sodium bicarbonate solution. The organic layer was dried over anhydrous magnesium sulfate, precipitated 10 times in methanol, recovered, and dried under reduced pressure at room temperature. Eight P[(*S*)-LA] samples of various molecular weights ($M_w = 9900$–$80\,000$) were prepared and used as a blending component.

Preparation of blend films

Blend films were prepared by conventional solvent-casting techniques from chloroform solution of P[(*R*)-3HB] and P[(*S*)-LA], using glass Petri dishes as casting surfaces. The films were then aged for at least three weeks at room temperature to reach equilibrium crystallinity prior to analysis.

Analytical procedures

All molecular weight data were obtained by gel-permeation chromatography (g.p.c.) at 40°C, using a Shimadzu 6A GPC system and 6A refractive index detector with Shodex K-80M and K-802 columns. Chloroform was used as eluent at a flow rate of 0.8 ml min^{-1}, and a sample concentration of 1.0 mg ml^{-1} was applied. Polystyrene standards with a low polydispersity were used to prepare a calibration curve.

The d.s.c. data for samples were recorded in the temperature range −100–200°C under a nitrogen flow rate of 30 ml min^{-1} on a Shimadzu DSC-50Q instrument equipped with a cooling accessory. The sample films (3 mg) were encapsulated in aluminium pans and heated from 0 to 200°C at a heating rate of 10°C min^{-1} (first scan). The peak melting temperature (T_m) and enthalpy of fusion (ΔH_m) were determined from the d.s.c. endotherms. For measurement of the glass transition temperature (T_g), the melt samples were maintained at 200°C for 1 min and then rapidly quenched at −100°C. They were then heated from −100 to 200°C at a heating rate of 20°C min^{-1} (second scan). The T_g was taken as the midpoint of the heat capacity change. The cold crystallization peak temperature (T_{cc}) was determined from the d.s.c. exotherm.

RESULTS AND DISCUSSION

The glass transition temperature (T_g), cold crystallization peak temperature (T_{cc}), melting temperature (T_m) and enthalpy of fusion (ΔH_m) of binary blends of P[(*R*)-3HB] ($M_w = 650\,000$) with P[(*S*)-LA] of various molecular weights ($M_w = 9900$–$530\,000$) were determined from d.s.c. thermograms. The results are summarized in *Table 1*. *Figure 1* shows typical d.s.c. thermograms (second scan) of miscible and immiscible blends. In this experiment all blend samples were melted at 200°C for 1 min and then rapidly quenched at −100°C. The T_g value of P[(*R*)-3HB] ($M_w = 650\,000$) was 4°C, and those of P[(*S*)-LA] samples increased from 45 to 62°C as the M_w value increased from 9900 to 530 000.

As it can be seen from *Table 1* and *Figure 1a*, the blends of P[(*R*)-3HB] with P[(*S*)-LA] of low M_w values below 18 000 showed a single T_g, and the T_g value increased from 4 to 55°C with an increase in the fraction of the P[(*S*)-LA] component. The relationship between T_g value and blend composition is shown in *Figure 2*. The T_g values are in good agreement with the curves calculated by Wood's equation[19] [equation (1)] with k values of 0.44, 0.50, 0.56 and 0.51 for P[(*S*)-LA] with M_w values of 18 000, 16 000, 13 000 and 9900, respectively.

$$T_g = (w_1 T_{g_1} + k w_2 T_{g_2})/(w_1 + k w_2) \qquad (1)$$

where w_1 and w_2 are the weight fractions, T_{g_1} and T_{g_2} are, respectively, the glass transition temperatures of P[(*R*)-3HB] and P[(*S*)-LA] components, T_g is the glass transition temperature of the blend, and k is an empirical adjustable parameter. This result indicates that a bacterial P[(*R*)-3HB] ($M_w = 650\,000$) is miscible with P[(*S*)-LA] of low molecular weights ($M_w = 9900$–$18\,000$) in the melt over the whole composition range.

As *Table 1* and *Figure 1b* show, the blends of P[(*R*)-3HB] with P[(*S*)-LA] of high M_w values over 20 000 exhibited two T_g values, suggesting a biphasic separation in the melt. A low T_g value corresponds to the glass transition of the P[(*R*)-3HB]-rich phase, while a high T_g value corresponds to the relaxation of the P[(*S*)-LA]-rich phase. In the blends with P[(*S*)-LA] of M_w values from 20 000 to 39 000, a low T_g value slightly increased with increasing P[(*S*)-LA] content, indicating the partial dispersion of P[(*S*)-LA] in the P[(*R*)-3HB] phase. The T_g values of the P[(*S*)-LA] phase were not detected for several blends due to the crystallization of the P[(*R*)-3HB] component (see *Figure 1b*).

The cold crystallization peak temperatures (T_{cc}) of P[(*R*)-3HB] and P[(*S*)-LA] components were determined from d.s.c. curves (second scan). The result is given in *Table 1*. The blends of P[(*R*)-3HB] with P[(*S*)-LA] of low M_w values below 18 000 showed a single T_{cc}, while the blends with P[(*S*)-LA] of high M_w values over 20 000 exhibited two T_{cc} values. The result for T_{cc} was closely related to the result for T_g. In the immiscible blends of P[(*R*)-3HB] with P[(*S*)-LA] of M_w values from 80 000 to 530 000, the T_{cc} values for P[(*R*)-3HB] and P[(*S*)-LA] components were 51–61°C and 112–126°C, respectively, independent of blend composition. The T_{cc} values for P[(*R*)-3HB] component in the blends with P[(*S*)-LA] of M_w values from 20 000 to 39 000 increased from 51 to 79°C with an increase in the P[(*S*)-LA] component, and the T_{cc} values for P[(*S*)-LA] decreased slightly with an increase in the P[(*R*)-3HB] content. The crystallization behaviour of P[(*R*)-3HB] and P[(*S*)-LA] components suggests that the blends with P[(*S*)-LA] of M_w values from 20 000 to 39 000 form two phases in the melt, and that a small amount of the P[(*S*)-LA] component disperses in the P[(*R*)-3HB] phase. In contrast, in the miscible blends of P[(*R*)-3HB] with P[(*S*)-LA] of M_w values from 9900 to 18 000, a single T_{cc} was observed and the value increased from 51 to 91–113°C, with an increase in the P[(*S*)-LA] content. The increase of the cold crystallization temperature observed for the blends of P[(*R*)-3HB] with P[(*S*)-LA] of low molecular weights can be explained, considering that the crystallization process takes place from a single homogeneous phase[20].

P[(*R*)-3HB] is a semi-crystalline polymer with a melting temperature (T_m) at 177°C. P[(*S*)-LA] is also a semi-crystalline polymer, and the T_m value increased from 143 to 175°C with an increase in the M_w value (see *Table 1*). The solution-cast films of P[(*R*)-3HB]/P[(*S*)-LA]

Table 1 Thermal properties of P[(*R*)-3HB]/P[(*S*)-LA] blends

Sample	Composition (wt ratio)	T_g[a] (°C)		T_{cc}[b] (°C)		T_m[c] (°C)	ΔH_m[d] ($J\ g^{-1}$)
1. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4		51		177	95
$M_w = 9900$	75/25	11		75		153,172	93
$M_w/M_n = 2.2$	50/50	19		94		145,167	82
	25/75	27		107		141,162	69
	0/100	45		113		143	40
2. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4		51		177	95
$M_w = 13\,000$	75/25	10		63		153,174	83
$M_w/M_n = 1.7$	50/50	21		78		157,172	82
	25/75	35		79		156,170	53
	0/100	52		91		158	75
3. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4		51		177	95
$M_w = 16\,000$	75/25	12		64		159.173	69
$M_w/M_n = 1.8$	50/50	20		79		157,172	76
	25/75	35		80		159,170	68
	0/100	55		94		162	60
4. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4		51		177	95
$M_w = 18\,000$	75/25	11		66		173	88
$M_w/M_n = 1.5$	50/50	21		71		161,172	77
	25/75	35		79		162,170	83
	0/100	55		–		164	70
5. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4	–	51	–	177	95
$M_w = 20\,000$	75/25	9	n.d.[e]	63	92	162,175	80
$M_w/M_n = 1.4$	50/50	9	n.d.	71	92	168,175	76
	25/75	13	50	79	95	168,174	72
	0/100	–	58	–	94	167	59
6. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4	–	51	–	177	95
$M_w = 34\,000$	75/25	9	n.d.	63	95	163,176	86
$M_w/M_n = 1.8$	50/50	10	n.d.	71	94	175	79
	25/75	12	57	79	100	168	78
	0/100	–	60	–	98	170	64
7. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4	–	51	–	177	95
$M_w = 39\,000$	75/25	7	n.d.	62	95	161,175	69
$M_w/M_n = 1.7$	50/50	8	41	67	95	161,175	76
	25/75	8	44	72	97	170	68
	0/100	–	59	–	105	170	60
8. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4	–	51	–	177	95
$M_w = 80\,000$	75/25	5	n.d.	55	105	178	83
$M_w/M_n = 1.6$	50/50	6	n.d.	57	108	178	82
	25/75	n.d.	n.d.	54	112	178	53
	0/100	–	62	–	119	171	76
9. P[(*R*)-3HB]/P[(*S*)-LA]	100/0	4	–	51	–	177	95
$M_w = 530\,000$	75/25	4	n.d.	58	118	177	93
$M_w/M_n = 1.8$	50/50	5	n.d.	61	126	177	82
	25/75	4	n.d.	51	124	177	69
	0/100	–	62	–	116	175	40

[a] Glass transition temperature: measured by d.s.c. (second scan) from −100 to −200°C at a rate of 20°C min^{-1}

[b] Cold crystallization peak temperature measured by d.s.c. (second scan)

[c] Melting temperature measured by d.s.c. (first scan) from 0 to 200°C at a rate of 10°C min^{-1}

[d] Enthalpy of fusion measured by d.s.c. (first scan)

[e] Not detected

blends exhibited two endotherm peaks at temperatures of 141–178°C. The T_m values of the endotherm peaks are given in *Table 1*. The T_m data were not correlated with the miscibility of the blend.

As described above, the miscibility of P[(*R*)-3HB]/P[(*S*)-LA] blends is strongly dependent on the molecular weight of the P[(*S*)-LA] component. The effect of the molecular weight of the P[(*S*)-LA] component on

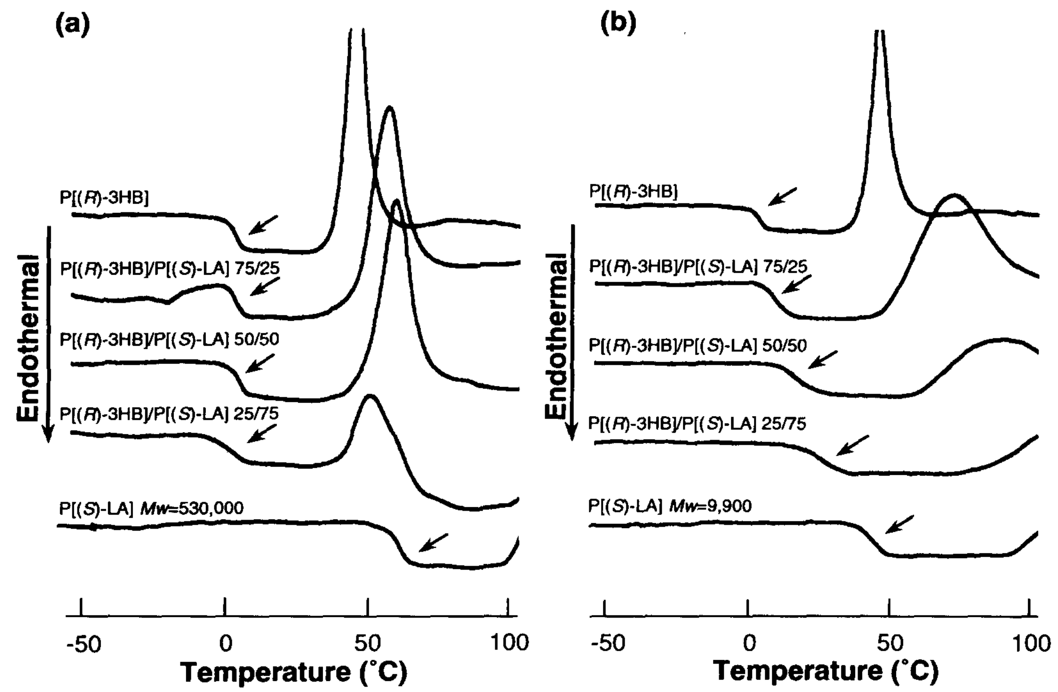

Figure 1 D.s.c. thermograms (second scan) of P[(*R*)-3HB]/P[(*S*)-LA] blends at a rate of 20°C min^{-1}: (a) blend of P[(*R*)-3HB] with a low molecular weight P[(*S*)-LA] (M_w = 9900); (b) blend of P[(*R*)-3HB] with a high molecular weight P[(*S*)-LA] (M_w = 530 000)

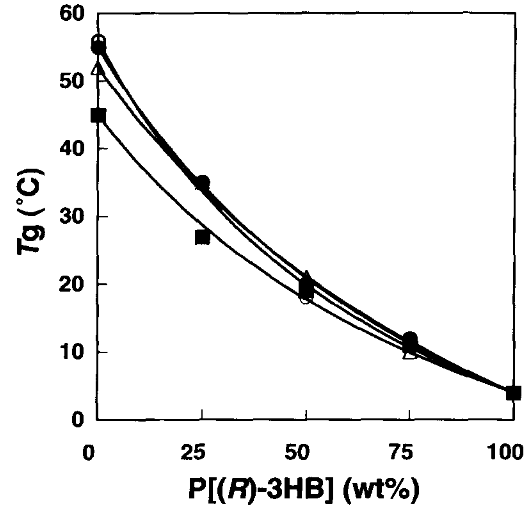

Figure 2 Glass transition temperature (T_g) of the blends of P[(*R*)-3HB] with P[(*S*)-LA] of various molecular weights: (■) M_w = 9900; (△) M_w = 13 000; (●) M_w = 16 000; (○) M_w = 18 000

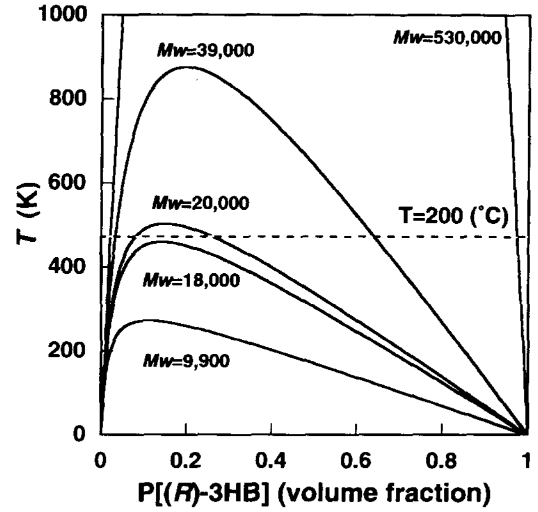

Figure 3 Spinodal curves for the blends of P[(*R*)-3HB] with P[(*S*)-LA] of various molecular weights calculated using the Flory–Huggins equation [equation (2)] with the difference in solubility parameters ($\delta_1 - \delta_2$) of 0.34 (J cm^{-3})$^{1/2}$

the miscibility of blends is interpreted on the basis of the Flory–Huggins equation[21]:

$$\frac{\Delta G}{RTV} = \left(\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \chi_{12}\phi_1\phi_2\right) \qquad (2)$$

where ΔG is the change of free energy by mixing of two polymers, R is the gas constant, V is the volume of the mixing system, ϕ_1 and ϕ_2 are, respectively, volume fractions of P[(*R*)-3HB] and P[(*S*)-LA], N_1 and N_2 are, respectively, molar volumes of P[(*R*)-3HB] and P[(*S*)-LA], and χ_{12} is the Flory interaction parameter. Molecular interactions, such as hydrogen bonding and dipole–dipole interactions, between P[(*R*)-3HB] and polymers [e.g. poly(epichlorohydrin) and poly(vinyl alcohol)] containing chlorine and hydroxyl groups have been reported[22,23]. In the blends of P[(*R*)-3HB] with P[(*S*)-LA], it seems that there is no specific interactions between P[(*R*)-3HB] and P[(*S*)-LA] molecules. Therefore, the interaction parameter χ_{12} may be expressed by equation (3) using the solubility parameters δ_1 and δ_2 of two-blend components:

$$\chi_{12} = \frac{(\delta_1 - \delta_2)^2}{RT} > 0 \qquad (3)$$

The temperature (473 K) of the melting blends should be present between the upper critical solution temperature (UCST) for the blend of P[(*R*)-3HB] with P[(*S*)-LA] (M_w = 18 000) and the UCST for the blend of P[(*R*)-

3HB] with P[(*S*)-LA] ($M_{\mathrm{w}} = 20\,000$). Thus, the difference in the solubility parameter ($\delta_1 - \delta_2$) can be estimated from the spinodal ($\partial^2 \Delta G / \partial \phi^2 = 0$) on the basis of the relationship between the miscibility of P[(*R*)-3HB]/P[(*S*)-LA] blends and the molecular weight of the P[(*S*)-LA] component. The molar volumes were calculated from the weight-average molecular weights of polymer components. As a result, the difference in the solubility parameters ($\delta_1 - \delta_2$) was determined to be $0.34\,(\mathrm{J\,cm^{-3}})^{1/2}$.

Figure 3 shows the spinodal curves for the blends of P[(*R*)-3HB] ($M_{\mathrm{w}} = 650\,000$) with P[(*S*)-LA] components of various M_{w} values (9900–530 000), which were calculated with the ($\delta_1 - \delta_2$) value of $0.34\,(\mathrm{J\,cm^{-3}})^{1/2}$. The UCST for the blend of P[(*R*)-3HB] with P[(*S*)-LA] of a high molecular weight ($M_{\mathrm{w}} = 530\,000$) was calculated as about 5100 K, indicating that the blend exhibits phase separation in the melt at 473 K over the whole range of blend composition. In contrast, the UCST for the blend of P[(*R*)-3HB] and P[(*S*)-LA] of a low molecular weight ($M_{\mathrm{w}} = 9900$) was about 270 K, which was less than the temperature of the melting blend, suggesting that the blend is a single homogeneous phase in the melt at 473 K. In addition, the UCST (500 K) for the blend of P[(*R*)-3HB] with P[(*S*)-LA] of medium molecular weight ($M_{\mathrm{w}} = 20\,000$) was a little higher than the melting temperature (473 K), suggesting that the blend forms a single phase or two phases depending on the blend composition in the melt at 473 K. The calculated results in *Figure 3* are in good agreement with the T_{g} behaviour of P[(*R*)-3HB]/P[(*S*)-LA] blends presented in *Table 1*.

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