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BLOCK COPOLYMERS POLY(8-OCTANELACTAM)-POLYSTYRENE-POLY(8-OCTANELACTAM) AND POLY(12-DODECANELACTAM)-POLYSTYRENE-POLY-(12-DODECANELACTAM) PREPARED BY THE ANIONIC POLYMERIZATION OF LACTAMS

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Abstract—Copolymers consisting of triblocks poly(8-octanelactam)-polystyrene-poly(8-octanelactam) and poly(12-dodecanelactam)-polystyrene-poly(12-dodecanelactam) were prepared by solution anionic polymerization of lactams with the appropriate polystyrene-*bis*-acyllactams at 120°. Both crosslinked and soluble products were formed with 8-octanelactam in toluene, while polymerization in dimethylacetamide gave rise to soluble copolymers. Thus, the solvent affects side condensation reactions leading to crosslinking.

INTRODUCTION

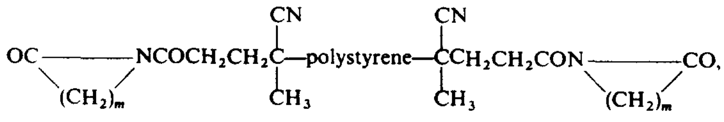
Up to now, only Owen and Thompson [1] have studied the preparation of block copolymers containing poly(12-dodecanelactam) segments, preparing AB and ABA copolymers in which block B was poly-(dimethylsiloxane).

We have described [2] the preparation of polystyrene-*bis*-acyllactams by radical polymerization initiated with appropriate bifunctional azo initiators. These polystyrene-*bis*-acyllactams were used as activators in the anionic polymerization of caprolactam; the polymeric products formed, viz. block copolymers ABA where B and A refer respectively to polystyrene and polycaprolactam, contained virtually none of the homopolymers. This fact was attributed to the chosen type of the polymeric activator and to the polymerization conditions. We now use the same procedure for preparation of block copolymers containing polystyrene and poly(8-octanelactam) or poly(12-dodecanelactam) segments.

EXPERIMENTAL

The preparation and characterization of polystyrene-*bis*-acyllactams and formation and isolation of copolymers have been described [2]. 8-Octanelactam (BASF, Ludwigshafen), m.p. 74.0–74.5°, was crystallized thrice from acetone and once from benzene; 12-dodecanelactam (Chemische Werke Hülls A.G.), m.p. 151.0–151.5°, was crystallized thrice from methanol and once from benzene. The purification of caprolactam, and preparations of sodium caprolactam, *N*-benzoylcaprolactam and *N,N'*-terephthaloyl-*bis*-caprolactam have been described [3]. Dimethylacetamide (Koch-Light), *N*-methylpyrrolidone (Fluka A.G.), dimethylformamide (Soyuzkhimexport) and *N*-methylcaprolactam [4] were purified by repeated rectification *in vacuo* with toluene added, stored at 0° under argon over molecular sieves 5A and dosed with syringes in a stream of inert gas; toluene was distilled with sodium hydride.

The gel–sol separation was carried out by swelling 0.1 g copolymer in 15 ml *m*-cresol (room temperature, 12 hr), by removal of gel by filtration and washing with 15 ml *m*-cresol and twice with 15 ml of the mixture *m*-cresol–toluene, 2:1. The sol was obtained by precipitation into 300 ml methanol; both fractions were washed with methanol and dried at 50° and 130 Pa for 24 hr. The NMR spectra of copolymers were recorded in the mixture trichloroacetic acid—1,1,2,2-tetrachloroethane (1:1 v/v) at 118–123° with a JEOL 100 apparatus. For crosslinked copolymers, the spectra were recorded after the copolymer–solvent mixture had been heated to 100–120° for 1 hr in a sealed measuring cell. DTA measurements were performed with a DuPont Thermal Analyzer 900 under argon at a heating rate 10° K min^{-1}; samples used in repeated melting were crystallized at a heating rate about 5° K min^{-1}. Penetrometric curves were obtained on discs, 5 mm dia., by means of a recording penetrometer [5] at the measuring needle pressure 0.8 MPa and at a heating rate 1.3° K min^{-1}. The discs were either moulded at room temperature from powdery copolymers in a hand-operated screw press, or stamped from plates prepared by copolymer pressing in a stainless mould at 210° and 25 MPa in a multistage press.



$$\underbrace{\mathrm{OC{-}N}}_{(\mathrm{CH_2})_m}\mathrm{COCH_2CH_2}\overset{\mathrm{CN}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{—polystyrene—}\overset{\mathrm{CN}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2CH_2CO}\underbrace{\mathrm{N{-}CO}}_{(\mathrm{CH_2})_m},$$

RESULTS AND DISCUSSION

Formation of insoluble polymers

Products formed by the polymerization in toluene of the nine-membered 8-octanelactam (L9) ring and of the thirteen-membered 12-dodecanelactam (L13) ring were predominantly insoluble in cresol and in a cresol–toluene mixture. On the other hand, the polymerization of seven-membered caprolactam (L7) in toluene under similar conditions gave rise always to polymers soluble in cresol [2]. This fact suggests that side reactions of the growth centres occur during the polymerization of higher lactams to a greater extent than for L7. With block copolymers of L9, the higher reactivity of the monomer allowed longer polyamide segments than with copolymers of L13. From the results in Table 1, it may be inferred that both the crosslinked fraction and the viscosity of completely soluble copolymers increase with increasing polymerization time (or with the length of the polyamide segment) and also with decreasing length of the polystyrene segment $\bar{P}_B$. Polymerization carried out for short times and with $\bar{P}_B$ above 100 yielded soluble copolymers. On the other hand, it was impossible to trace similar dependences in the polymerization of L13 (Table 2) as with L9.

Effect of solvent on the course of polymerization

The observed special features for L13, compared with the preparation of block copolymers L7, i.e. formation of insoluble products and difficult control of copolymer composition, stimulated investigation of the effect of polarity of the polymerization medium. Only aprotic polar solvents, particularly dialkylamides, can be considered for the anionic polymerization. The low-temperature polymerization (120°) does not greatly restrict their choice with respect to thermal stability, but traces of reactive impurities (water, amines, etc.), and also possible side reactions of solvent in the alkaline medium are critical. Comparison of yields in the polymerization of L7 under the same conditions in *N*-methylpyrrolidone, *N*-methylcaprolactam and *N*,*N*-dimethylacetamide (DMA) and in their mixtures with toluene (Table 3) has revealed that, with the employed procedure of purification and storage of solvents under investigation, DMA is the best solvent. *N*-Methylcaprolactam could not be freed from traces of O-methylcaprolactam, which evidently inhibits the polymerization proportionally to the amount of solvent. In pure *N*-methylpyrrolidone, side reactions seem to be preferred, giving an intense orange–yellow colour of the reaction mixture; the polymerization occurred only in mixtures of this solvent with toluene. Polymerization in DMA proceeds at 120° about three times faster and is slowed down in extended reaction periods at higher conversions than in toluene. These facts can be explained, on the one hand, by the acceleration of the propagation and,

Table 1. Anionic polymerization of L9 with polystyrene-*bis*-acyllactams. (L9 3 g, sodium caprolactam initiator 0.106 mmol, 120°C, 10 ml of solvent.)

No.	$\bar{P}_B$	I, mmol	t, hr	p, %	$\bar{P}_A$			η_{sp}‡ (gel, %)
					wt.*	NMR	N†	
Solvent Toluene								
C13§	40.5	0.117	1	91.8	197	169	—	(87.2)
C14§	40.5	0.116	0.25	54.3	118	130	163	(52.8)
C15	40.5	0.093	0.15	14.9	32.2	36	40	(32.8)
C16	71	0.097	1	76.8	160	—	201	(80.9)
C17	71	0.098	0.15	28.4	59.0	58	69	(51.0)
C18	102	0.100	1	78.2	158	158	160	(69.7)
C19	102	0.100	0.15	34.3	70.6	46	68	6.07
C20	150	0.100	0.15	17.5	35.9	25	29	3.372
C21	346	0.053	1	4.3	17.8	10	—	1.290
C22	‖	0.106	1	50.5				5.23
C23	‖	0.106	0.15	9.7				—
C24	**	0.053	1	18.5				insol.
Solvent Toluene—DMA (1 : 1 v/v)								
C25	71	0.105	0.15	69.2	131	127	128	(45.6)
Solvent DMA								
C26	40.5	0.094	0.15	81.8	173	133	155	7.13
C27††	40.5	0.105	0.15	23.3	46.2	67	62	2.341
C28‡‡	40.5	0.105	1	4.9	10.5	13	10	1.303
C29	371	0.103	0.12	80.7	161	144	139	4.57
C30	**	0.053	1	13.2				1.087

$\bar{P}_A$ and $\bar{P}_B$—number average degrees of polymerization of polystyrene and polyamide segments, respectively; I—amount of acyllactam groups in the polymerization mixture; t—polymerization time; p—copolymerization yield (conversion of lactam into polymer).

* Calculated from weight increase in copolymerization.

† Calculated from nitrogen content in the copolymer.

‡ Tricresol, 25°C, 0.4 g dl^{-1} ($dl\,g^{-1}$).

§ 8.1 ml toluene.

‖ *N*-benzoylcaprolactam as activator.

** *N*,*N*′-terephthaloyl-*bis*-caprolactam as activator.

†† 20 ml DMA.

‡‡ Polymerized at 80°C.

Table 2. Anionic polymerization of L13 with polystyrene-*bis*-acyllactams. (L13 3 g, sodium caprolactam initiator 0.076 mmol, 120°C, 5 ml of solvent)

No.	$\bar{P}_B$	*I*, mmol	*t*, hr	*p*, %	$\bar{P}_A$ wt.*	NMR	N†	η_{sp}‡ (gel, %)
Solvent Toluene								
C31§	96	0.075	6	7.4	16.0	14	17	(0.5)
C32§	96	0.075	24	25.0	51.6	52	53	(62.1)
C33	150	0.072	6	28.2	59.2	61	31	(52.3)
C34	346	0.037	24	0.5	2.9			
C35	96	0.073	6	43.0	89	—	96	(62.3)
C36	69	0.069	6	23.0	50.6	46	58	(24.4)
C37	38.2	0.066	6	33.5	77	76	75	(38.9)
C38	‖	0.076	6	19.1				
Solvent Toluene—DMA (4:1 v/v)								
C39	102	0.074	6	12.8	26.9	27	19	0.987
C40	82	0.078	6	8.0	16.3	17	12	0.614
C41	38.2	0.074	6	13.9	28.9	27	22	1.303
C42	‖	0.076	6	4.6				

Symbols cf. Table 1.

* Calculated from the weight increase in copolymerization.

† Calculated from nitrogen content in the copolymer.

‡ Tricresol, 25°C, 0.4 g dl^{-1} (dl g^{-1}).

§ 10 ml toluene.

‖ *N*-benzoylcaprolactam as activator.

on the other, by increased solubility of the forming polymer in the amide solvent, which maintains the growth centres for a longer period in a phase readily accessible to the lactam anions. The reproducibility of polymerization depends on the storage time of the solvent, in which traces of dimethylamine inhibiting the low-temperature polymerization are formed even under dry inert gas at about 0°. The polymerization yields varied from 20.1 to 28.4%, if the solvent had been stored up to 27 days over molecular sieves 5A, or up to 22 days without sieves (Table 3). The polymerization in pure DMF proceeds similarly but the possibility of storing this solvent is restricted due to its lower stability.

The preparation of block copolymers L9 by solution polymerization in DMA gave soluble products, but gel fraction was formed again in a DMA–toluene mixture 1:1. The fact that side reactions of the growth centers [6] are influenced in this case is confirmed by the polymerization of L9 with bifunctional acyllactam (terephthaloyl-*bis*-caprolactam) which similarly yields a crosslinked polymer in toluene and a soluble polymer in DMA (cf. Table 1). Like the polymerizations of L7, L9 also polymerizes in DMA more rapidly than in toluene, although the difference is not so large owing to its higher polymerization rates.

A different situation arises on passing from toluene to DMA in the polymerization of L13. The yields under comparable conditions rapidly decrease with increasing DMA content in the polymerization solvent (cf. Fig. 1). Only the mixed solvent toluene–DMA 4:1 (v/v) was used in the preparation of block copolymers. Soluble polymers were obtained, but they contained shorter polyamide segments, and no valid comparison with products prepared in toluene was possible.

Differences in the ratio of the growth reaction and of the side reactions of acyllactam terminal groups found between the individual lactams and between various polymerization solvents, leading to soluble or variously crosslinked products, are probably due to different interactions of the growing polymer chain with the solvent. In the case of a larger distance between reactive chain ends in a good solvent for the forming polymer, e.g. in the polymerization of L9 in DMA, the growth reaction is preferred because the

Table 3. Polymerization of L7 in dialkyl amides and toluene. (L7 3 g, sodium caprolactam and *N*-benzoylcaprolactam 0.132 mmol, 120°C)

	Yields of polymer, %			
	Solvent, ml		(Polymerization time, hr)	
Solvent	5 (1)	10 (6)	2.5 + 2.5 ml toluene (1)	5 + 5 ml toluene (6)
Toluene	9.97	6.50	—	—
N-Methylpyrrolidone	0.55	0.03	13.47	9.42
N-Methylcaprolactam	4.59	0	8.75	3.81
Dimethylacetamide	28.35*	36.67	21.81	15.27
Dimethylformamide	26.69	—	—	—

* Reproducibility within 20.1–28.4% according to the conditions and time of the solvent storage (cf. text).

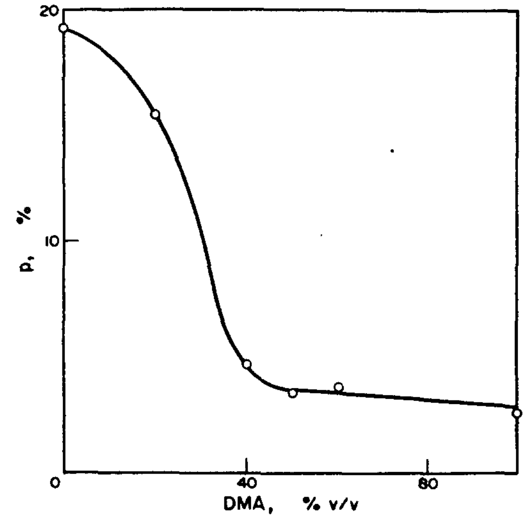


Fig. 1. Yield of solution polymerization (p, %) of L13 in the mixtures toluene–dimethylacetamide (DMA); 3 g lactam in 5 ml solvent, 0.076 mmol sodium caprolactam and *N*-benzoylcaprolactam, 120°, 6 hr.

end acyllactam groups of one chain or of neighbouring chains (in concentrated solutions) are less likely to react with each other and will rather react with the lactam anion. In a poor solvent, e.g. toluene, it is the other way round: aggregates of polymer chains are less swollen and the endgroups can more frequently react with each other and enter into condensation reactions. After the forming polymer has precipitated, an important role may be played by the solvation of the polar acyllactam group with the solvent, which may facilitate the growth reaction and impede the condensation. The different character of the polymerization of L13 is due to the predominant hydrocarbon character of the resulting polymer.

Composition of block copolymers

What has been said about the block copolymers prepared from L7 [2] also holds about the solubility of uncrosslinked copolymers prepared from L9. On the other hand, block copolymers from L13 are soluble in mixtures phenol–toluene or o-cresol–toluene up to the ratio 1:2. The crosslinked copolymers become soluble if heated to 100–120° in a mixture of trichloroacetic acid and 1,1,2,2-tetrachloroethane (1:1) so that the compositions of these polymers could be determined from the NMR spectra after partial acidolysis. Besides the more labile groups of the network knot points, some amide bonds of the polyamide segments probably also undergo acidolysis. Below 110° the solution of the copolymer–homopolymers mixture separates into two immiscible phases. Even though the spectra were recorded at 118 or 123° in a rotating cell, perfect coalescence of both phases could not be guaranteed, and the agreement with the gravimetric determination of the length of the polyamide segments, $\bar{P}_A$, is therefore poorer than with copolymers of L7 [2]. The τ values of bands in NMR spectra corresponding to individual ^1H types

$$[\mathrm{NH{-}\underset{(b)}{CH_2}\underset{(d)}{(CH_2)_n}\underset{(c)}{CH_2}{-}CO}][\mathrm{\underset{(d)}{CH_2}{-}\underset{(d)}{CH}\underset{(a)}{(C_6H_5)}}]$$

were for L9 copolymers ($n = 5$): (a) 3.25–3.78, (b) 6.92–7.08, (c) 7.84–7.98, and (d) 8.70–9.00 ppm and for L13 copolymers ($n = 9$): (a) 3.35–3.78, (b) 6.92–7.08, (c) 7.84–7.99, and (d) 8.30–9.08 ppm. In previous calculations [2], we used the peak areas of aromatic ^1H and ^1H of the ω-carbon atom of the amino acid, i.e. the multiplet *a* and the triplet *b*.

A similar error appears in the calculation of $\bar{P}_A$ from the nitrogen content determined by elemental analysis according to

$$\bar{P}_A = (56.032 - N\bar{M}_B)/(2M_AN - 28.016),$$

where N is the weight fraction of nitrogen in the copolymer, $\bar{M}_B$ is the number average molecular weight of the polystyrene activator including incorporated residues of the azo initiator, and M_A is the molecular weight of the monomer unit (lactam) of the polyamide segments. We therefore believe that, as for copolymers of L7, the copolymer composition is best expressed by $\bar{P}_A$ calculated from the weight increase during the polymerization, Δg with assumptions given pre-

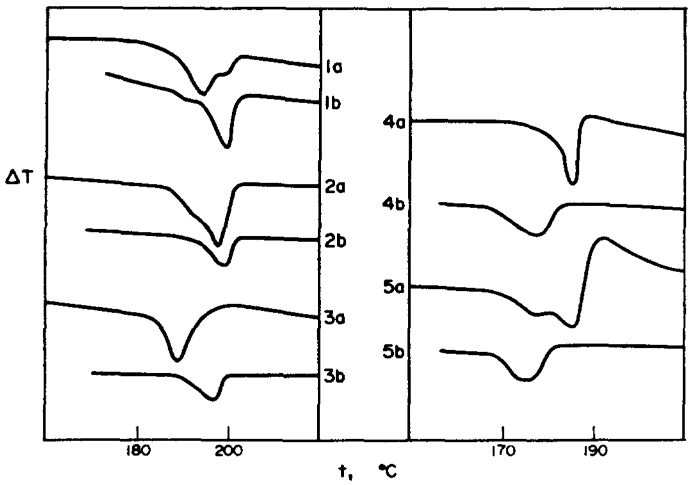


Fig. 2. DTA of block copolymers L9 (1–3) and L13 (4,5) crystallized during polymerization (a) and subjected to re-melting; (b) 1–C14, 2–C23, 3–C24, 4–C36, 5–C40; heating rate 10°K min^{-1}.

viously [2] according to

$$\bar{P} = (\Delta g/M_A I) + 1,$$

where I refers to moles of the end acyllactam groups of the telechelic polystyrene activator used.

The compositions of the soluble and crosslinked fractions of copolymers L9, determined from the NMR spectra of the whole copolymer and of its sol fraction, showed that only in few cases (copolymers C13, C14 and C18) is the soluble fraction slightly richer in polystyrene than the gel fraction. The composition of the main part of this fraction or of the whole sol corresponds to that of a gel formed from it during the polymerization via known condensation reactions of acyllactam groups [6]. This result indicates that the sol cannot exclusively consist of the copolymer AB formed from the polystyrene activators containing only one terminal active group.

Properties of block copolymers

Softening and melting of block copolymers were investigated by differential thermal analysis and penetrometrically without attempts to interpret the observed effects. The degree of ordering of crystallites formed by the segments A is strongly affected by the conditions of crystallization, which in the case of precipitation polymerization are completely different from those of the equilibrium crystallization from the melt. If the polymers were not subjected to further thermal treatment, the shape and position of endotherms in the DTA of block copolymers and of homopolymers may depend on the crystallization temperature (i.e. on the polymerization temperature), on the type of solvent (i.e. of the basic solvent), on the concentrations of dissolved components (monomer, polystyrene activator), and on the length and concentration of polyamide segments (i.e. on the polymerization rate). In the repeated melting carried out after defined crystallization, factors characterizing the polymer as such, i.e. participation and length of the crystallizing blocks, should become operative. Figure 2 shows the DTA curves of melting of chosen copolymers crystallized during polymerization and after re-melting. For copolymers L9 prepared in toluene the maximum of the endotherm was raised on re-melting (from 191–194° to 198–200°) probably owing to better ordering of the crystalline domains. In further cycles of crystallization-melting, the position of the maximum did not change. The copolymers prepared in DMA exhibit an endotherm at a higher temperature even during the first melting (197–199°). Some indications of a second maximum may be assigned to partial recrystallization even during the first heating or to artefacts of earlier structures in repeated melting. On the other hand, the maximum of endotherm of copolymers L13 is lowered by melting (from 175–177° to 167–170°) and becomes broader, probably due to the partial dissolution of the polystyrene phase in the polyamide phase, which in this case is less polar (plastification) or also due to the thermal degradation of the copolymer.

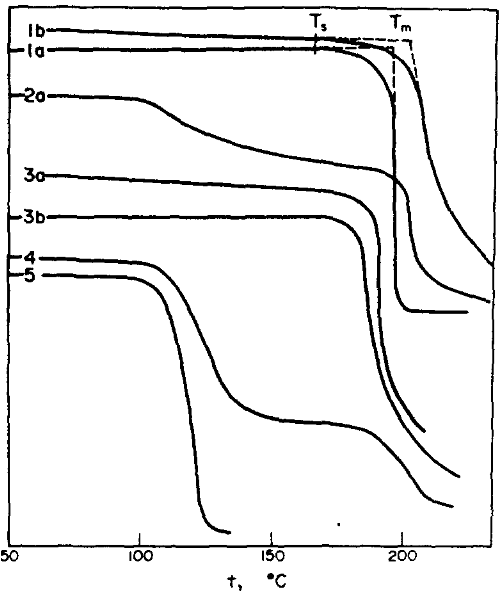


Fig. 3. Penetrometric curves of block copolymers of L9 (1,2) and L13 (3) and of the mixtures polyhexanelactam–polystyrene 1:1 (4) and 1:2 (5); a—samples moulded (without re-melting), b—samples moulded from melt; 1—C14, 2—C20, 3—C36; heating rate 1.3 K min^{-1}, needle pressure 0.8 MPa; T_s, T_m—softening and melting temperatures.

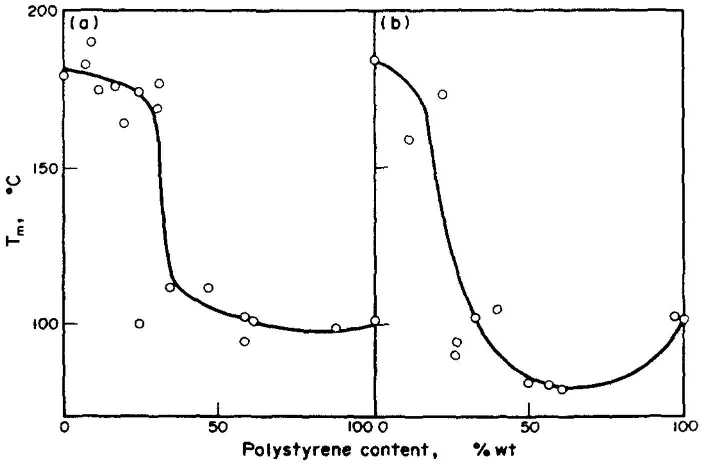


Fig. 4. Dependence of the softening temperature T_m on the weight content of polystyrene segments in copolymers of L9 (a) and L13 (b).

Similar regularities have been observed for melting points determined penetrometrically with tablets prepared by both methods. The copolymers L9, which were not subjected to re-melting, melted at 193–202°; on re-melting, they melted at somewhat higher temperatures (201–207°). The melting temperatures of copolymers of L13 on re-melting decreased from 180–191° to 178–184°.

The penetrometric temperature-deformation curves of block copolymers differ in their shape from those of the respective homopolymers and of their physical mixture (Fig. 3). In addition to the melting region of the crystalline component, they also exhibit small deformation of the amorphous component. The softening temperatures, i.e. where deformation sets in, can be correlated with the concentration of polystyrene blocks in the copolymers. With copolymers containing both types of the segments A, one can observe a pronounced change in the above plastification effect at 20–30 wt.% of the polystyrene component (Fig. 4).

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