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PREPARATION AND CHARACTERIZATION OF MONOLAYERS AND MULTILAYERS OF PREFORMED POLYMERS*

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In an attempt to study which factors determine the transferability of monolayers of preformed polymers from the air–water interface onto substrates we investigated flexible polymers (poly(octadecylmethacrylates) (PODMAs)) and α -helical polymers (polyglutamates). Pressure–area isotherms show the formation of a liquid-analogous state which depends on temperature and side chain “impurity”. Y-mode Langmuir–Blodgett multilayers of these polymers can be formed with a constant transfer ratio under conditions at which a more or less liquid-analogous state exists. Polarized IR spectra suggest that the polyglutamate α helices in the multilayer are oriented with the main axis parallel to the transfer direction and that carbon side chains are practically randomly oriented around the α -helical cylinder. In PODMA multilayers the side chains are perpendicular to the film. In both cases the side chains seem to interdigitate.

1. INTRODUCTION

The preparation of multilayered ultrathin films by the Langmuir–Blodgett (LB) technique has been investigated by several researchers in the last decade because of the possible applications of these films in for example microelectronics¹. In most cases, however, the starting material was a low molecular weight amphiphilic molecule, whereas the preparation of multilayers starting with preformed polymer is rather unexplored^{2–5}. It appeared, however, that the transfer of monolayers of preformed polymers onto solid and planar substrates by the usual LB technique is not fully understood and is in some cases only possible when special techniques and precautions are introduced⁵.

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In this paper we try to elucidate some of the parameters which are important for a successful transfer and, further, present some structural information on the multilayers formed.

2. EXPERIMENTAL DETAILS

Octadecylmethacrylate was from Merck and 95% pure. It was purified by distillation or by crystallization from acetone at 0°C. Other solvents were of p.a. quality. Chloroform was of Uvasol quality. Atactic poly(octadecylmethacrylate) (a-PODMA) and copolymers with dodecylmethacrylate (a-PODMA-co-DMA) were obtained by polymerization in dilute solution in toluene at 80°C under nitrogen, using Azobisisobutyronitrile as initiator. Isotactic poly(octadecylmethacrylate) (i-PODMA) was obtained according to the method of Goode *et al.*⁶ The polymers were purified by repeated precipitation from filtered toluene solution into methanol and dried under vacuum at room temperature. The tacticity was characterized by ¹H nuclear magnetic resonance (NMR), ¹³C NMR and IR spectroscopy. Molecular weights were determined by gel permeation chromatography (GPC) using the K and a values of Fee *et al.*⁷

The methacrylate polymers shown in Table I were synthesized. Poly(γ -methyl-L-glutamate) was prepared by the *N*-carboxyanhydride method^{8,9}. Poly(γ -methyl-L-glutamate-co- γ -*n*-alkyl-L-glutamate) polymers were synthesized according to the method of Watanabe *et al.*¹⁰ using different *n*-alkyl alcohols. The degree of substitution was determined by elemental analysis. Molecular weights were determined with GPC in tetrahydrofuran using polystyrene standards. Table II shows the poly(γ -methyl-L-glutamate-co-*n*-alkyl-L-glutamate) polymers that were synthesized. The polymers were dissolved in chloroform at concentrations of about 0.1 wt. %.

Pressure-area isotherms were measured on a Lauda film balance at different temperatures with a compression speed of 42.16 cm² min⁻¹. Small angle X-ray

TABLE I
METHACRYLATE POLYMERS SYNTHESIZED

	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	Substitution of DMA (%)
a-PODMA	7.2	12	
a-PODMA-co-DMA	8	12	13
i-PODMA-1	8	12	
i-PODMA-2	7	51	

TABLE II
POLY(γ -METHYL-L-GLUTAMATE-CO-*n*-ALKYL-L-GLUTAMATE) POLYMERS SYNTHESIZED

<i>n</i> -alkyl group	Polymer abbreviation	Degree of substitution (mol.%)	$\bar{M}_n \times 10^{-3}$
<i>n</i> -dodecyl	PM-co-DdLG	32	≈ 12
<i>n</i> -octadecyl	PM-co-OLG	35	≈ 12
<i>n</i> -eicosyl	PM-co-ELG	25	≈ 12
<i>n</i> -docosyl	PM-co-DcLG	25	≈ 12

scattering (SAXS) patterns and Fourier transform (FT) IR transmission spectra were obtained from multilayers on silicon wafers. Grazing incidence reflection FTIR spectra of the multilayers were obtained from multilayers on gold substrates.

Electron diffraction patterns were obtained using a Philips EM 300 microscope. The pattern was recorded from a sample consisting of 13 monolayers of *i*-PODMA-1. The multilayer was deposited onto hydrophobic glass and was afterwards transferred onto electron microscope grids after floating off the film from the glass with dilute HF.

3. RESULTS AND DISCUSSION

3.1. Poly(octadecylmethacrylate)

Figures 1–4 show the pressure π –area A isotherms of different PODMAs at different temperatures.

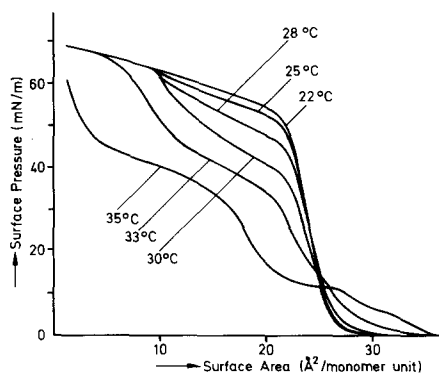


Fig. 1. π - A isotherms of *a*-PODMA at different temperatures.

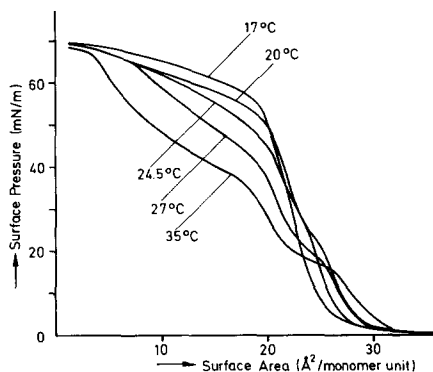


Fig. 2. π - A isotherms of *i*-PODMA-1 at different temperatures.

From a comparison of the isotherms of *i*-PODMA and *a*-PODMA (Figs. 1 and 2) it follows that apparently the atactic polymer forms a more stable monolayer at the water surface. (The isotherm of *a*-PODMA below 20 °C is completely analogous to that published previously^{4,11}.) An increase in the temperature of the subphase has two effects on all the isotherms shown: (i) from a certain temperature the collapse pressure decreases; (ii) a “liquid-analogous” state is formed.

However, the temperatures at which these phenomena occur differ. So, *a*-PODMA and *i*-PODMA-2 only show a liquid state at $T > 32$ °C, whereas *i*-PODMA-1 and *a*-PODMA-co-DMA are liquid at $T > 20$ °C. More or less parallel to the appearance of a liquid state is the decrease in the collapse pressures. For all polymers it can be seen that the area at which the liquid state occurs becomes larger with increasing temperatures. Comparing the results for the atactic and isotactic polymers, one can deduce that in this case the tacticity of the backbone chain does not play a dominant role and the origin of these effects has to be found in side-chain impurities. This is very clearly seen in Fig. 4, where “impurities” were deliberately introduced by copolymerization of an octadecylmethacrylate with a methacrylate monomer with a shorter alkyl chain.

The difference between the two isotactic samples originates from the different purification steps used for the monomer before polymerization: i-PODMA-1 was polymerized from a monomer, which was obtained by partially melting a stock bottle, followed by a distillation procedure, whereas i-PODMA-2 was obtained from a monomer, purified by melting the whole content of the stock bottle, followed by crystallization from acetone according to Fee *et al.*⁷

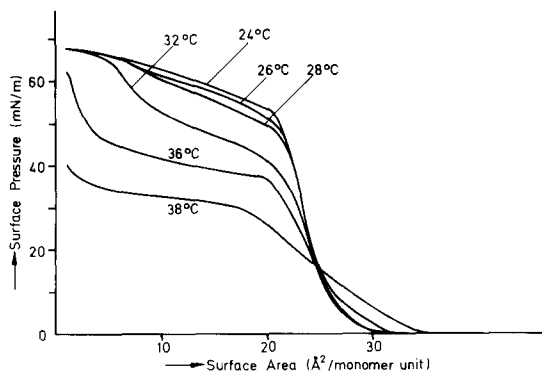


Fig. 3. π - A isotherms of i-PODMA-2 at different temperatures.

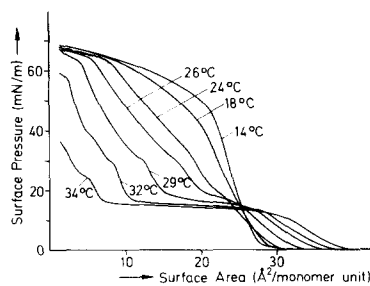


Fig. 4. π - A isotherms of a-PODMA-co-DMA at different temperatures.

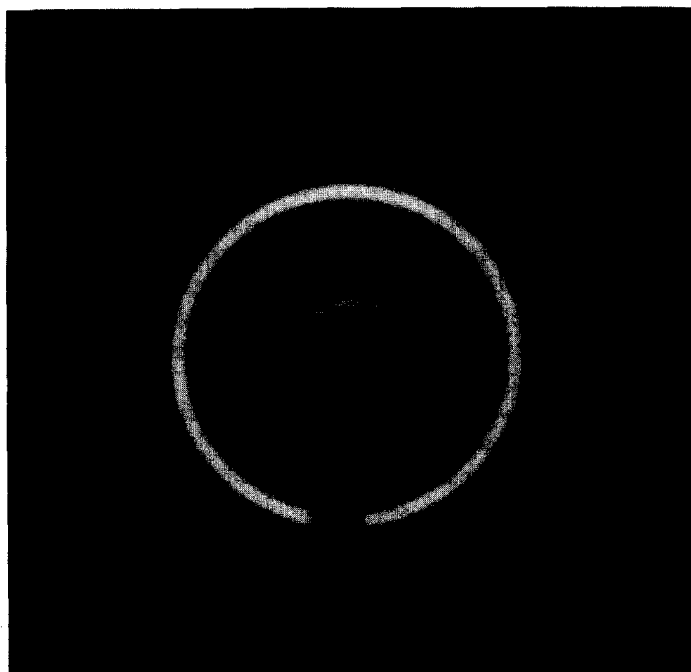


Fig. 5. Electron diffraction pattern of a multilayer (13 layers of i-PODMA-1) with the beam perpendicular to the film.

3.2. Multilayers

Formation of multilayers by the LB technique could be achieved only under conditions at which the polymer or copolymer existed to some extent in the liquid state. So, for i-PODMA-1 at $T = 28^\circ\text{C}$ and $\pi \approx 10 \text{ mN m}^{-1}$ transfer ratios onto quartz substrates were constant at least up to 50 layers. However, under the same conditions it was not possible to transfer the monolayer of i-PODMA-2: only at high pressures (about 30 mN m^{-1}) and $T > 32^\circ\text{C}$ did some transfer take place.

Electron diffraction (Figs. 5 and 6) with the beam normal to the layers results in a set of Bragg reflections, the intensities of which are isotropically distributed around the side chain axes. The rings can be indexed as $h,k,0$ values of a metrically hexagonal lattice of the side chains. In other words, the alkyl chains are packed in a hexagonal fashion with the stems extending normal to the layer plane with some orientational disorder. Tilting of the specimen by approximately 60° results in a diffraction pattern which exhibits a meridional reflection corresponding to the repeating distance of a zigzag polyethylene chain (2.5 \AA).

SAXS experiments give a value of 30 \AA for the layer spacing with several orders of SAXS peaks being visible. The same spacing is also derived from a set of meridional reflections visible in the electron diffraction pattern of the tilted specimen. Together with the observation that transfer of the monolayers of i-

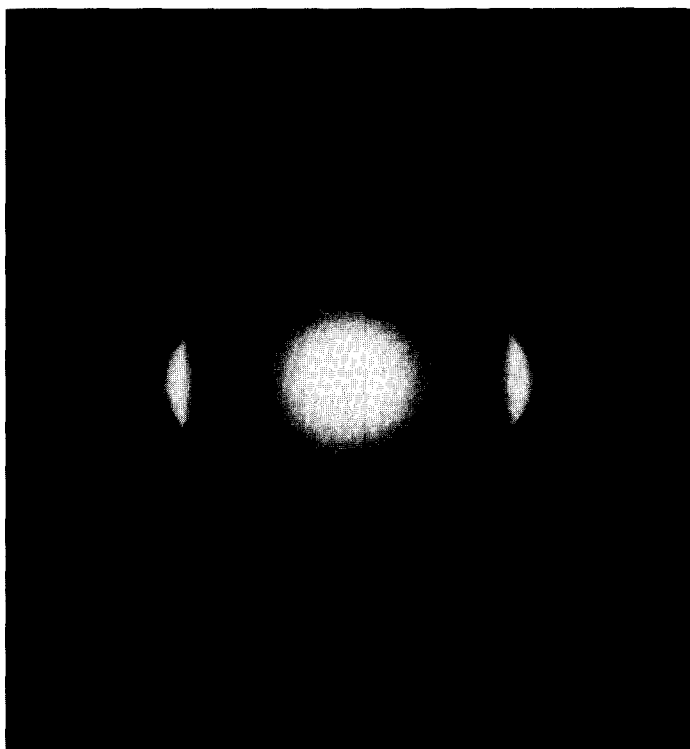


Fig. 6. Electron diffraction pattern of a multilayer (13 layers of i-PODMA-1) with the beam at an angle of about 60° to the film.

PODMA was of the Y mode, this leads to the conclusion that the side chains have to interdigitate, forming a new type of layered structure where part of the side-chain ordering was presumably obtained by compression on the water surface and part was due to subsequent crystallization on transfer.

3.3. Polyglutamates

Figure 7 shows pressure–area isotherms of PM–co-OLG monolayers at different temperatures. For 30 °C we observe a plateau region at *ca.* 30 mN m⁻¹ similar to the plateaux reported by other researchers^{12–15}. At lower temperatures the length of the plateau decreases, whereas a second linear rise in the surface pressure on further compression is observed. Extrapolating the first linear rise in pressure to zero pressure, we obtain the same value of the occupied area (24 Å group⁻¹) per zero unit of the copolymer at different temperatures.

Differences in monolayer behaviour from copolymers with different side chain lengths at 20 °C are shown in Fig. 8. The area per repeat unit increases with increasing side-chain length: PM–co-DdLG, 23.0 Å; PM–co-OLG, 24 Å; PM–co-ELG, 24.9 Å; PM–co-DcLG, 25.7 Å. For longer side chains the second rise is shifted to higher pressures and lower areas. PM–co-DdLG shows only the plateau and no second rise was found. It is evident from these observations that within the measured temperature interval copolymers containing longer side chains were able to form a condensed phase, whereas the copolymers with the shorter side chains cannot.

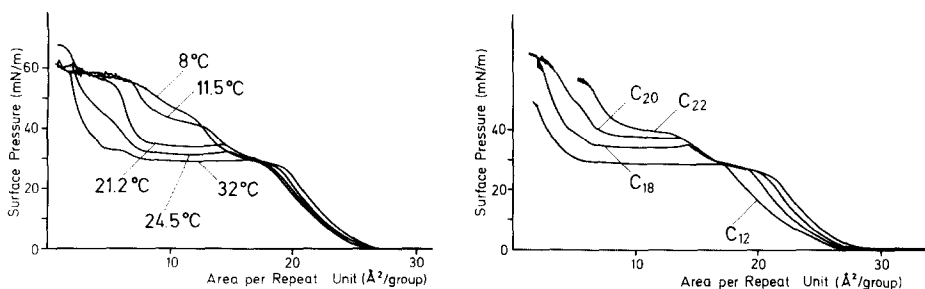


Fig. 7. π - A isotherms of PM–co-OLG on water surface as a function of temperature.

Fig. 8. π - A isotherms of copolyglutamate monolayers with different side-chain lengths at 20 °C: C₁₂, PM–co-DdLG; C₁₈, PM–co-OLG; C₂₀, PM–co-ELG; C₂₂, PM–co-DcLG.

3.4. Multilayers

All the described copolyglutamates could be transferred onto hydrophobic substrates at 20–25 mN m⁻¹ as Y-type LB multilayers. A constant transfer up to *ca.* 200 layers was possible with this kind of material as can be seen from Fig. 9, where the IR absorption in the NH stretch region is plotted as a function of the number of LB layers of PM–co-OLG.

Figures 10(a) and 10(b) show measurements of polarized transmission IR spectra of built-up LB films of PM–co-OLG with the electric vectors parallel and perpendicular respectively to the transfer direction. Figures 10(c) and 10(d) represent transmission IR spectra of LB layers and of a film cast from a chloroform solution of PM–co-OLG respectively. Figure 10(e) is a grazing incidence reflection IR spectrum

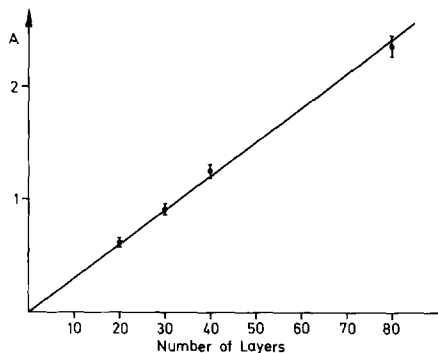


Fig. 9. NH stretching band absorption *A* as a function of the number of transferred LB multilayers of PM-co-OLG.

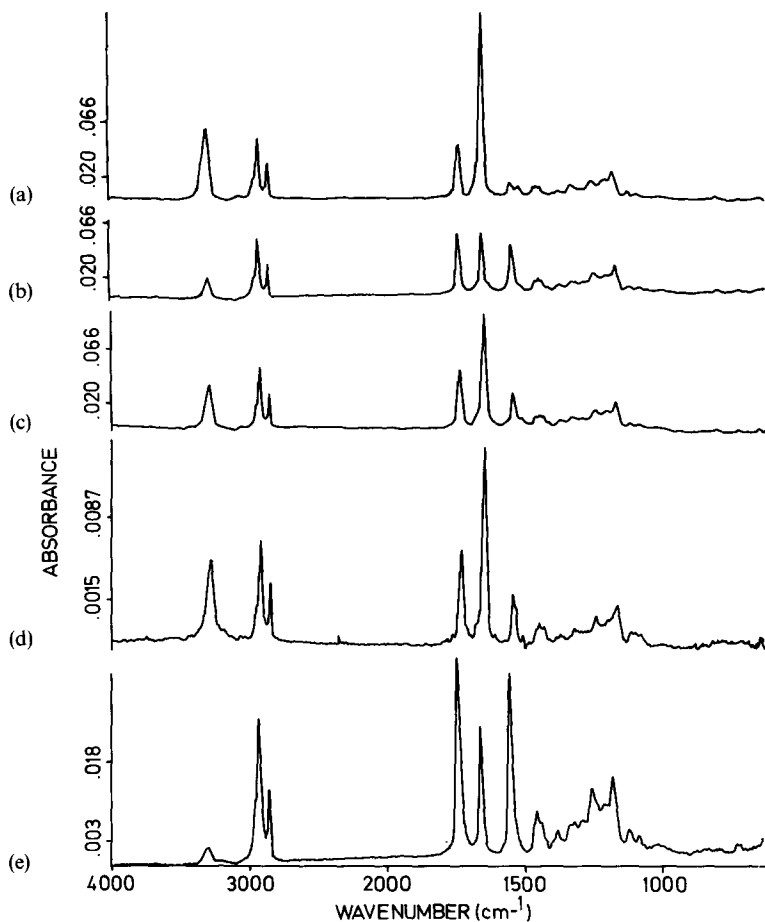


Fig. 10. Transmission IR spectra of LB layers of PM-co-OLG: (a) with polarized light parallel to the dipping direction; (b) with polarized light perpendicular to the dipping direction; (c) without a polarization filter; (d) transmission IR spectrum of a cast film; (e) grazing incidence reflection IR spectrum from LB layers on gold.

of a built-up LB film of PM-co-OLG. These spectra, which exhibit the typical NH stretching band at 3290 cm^{-1} , amide I band at 1653 cm^{-1} and amide II band at 1550 cm^{-1} , reveal that the main conformation of the molecules in the LB layer as well as in the cast film from CHCl_3 is α helical. Analysis of these three absorptions (Figs. 10(a)–10(c)), normalized to the carbonyl band of the ester group in the side chain at 1737 cm^{-1} , which is randomly distributed, shows that the polypeptide α helices are oriented with the main axis parallel to the transfer direction (Table III).

TABLE III
IR ABSORPTION DATA FOR POLY(γ -METHYL-L-GLUTAMATE-CO-*n*-OCTADECYL-L-GLUTAMATE)

Sample	$A_{\text{NH}}/A_{\text{ester}}$	$A_{\text{CH}}/A_{\text{ester}}$	$A_{\text{amide I}}/A_{\text{ester}}$	$A_{\text{amide II}}/A_{\text{ester}}$
LB film (polarized transmission, E_{\parallel})	3.93	2.63	3.04	0.48
LB film (polarized transmission, E_{\perp})	1.05	2.48	0.91	0.93
LB film (transmission without a polarization filter)	2.25	2.65	1.79	0.72
Cast film	2.43	2.82	1.98	0.72
LB film (grazing incidence reflection)	0.25	2.04	0.49	0.97

Polarized IR spectra analysis also shows that carbon side chains are practically randomly oriented around the α -helical cylinder. SAXS data of the different copolymers are listed in Table IV. The long spacing depends on the carbon side-chain length. Calculations of the diameter of the α helix including the ester groups gave a value of 14 \AA (ref. 16). Adding the calculated length of the extended carbon chain, we obtained maximum diameters for the whole cylinder including the side chain. These values, listed in Table IV, are much higher than the long spacings as measured by SAXS. However, assuming complete interdigitation of the side chains, we obtain the same values. Only PM-co-DdLG shows some discrepancy. Figure 11 shows a proposed model for these long chain polyglutamates in LB multilayers.

TABLE IV
SAXS DATA FOR LANGMUIR-BLODGETT MULTILAYERS OF THE DIFFERENT POLYGLUTAMATES

Copolymer	Measured spacing (\AA)	Calculated maximum spacing (\AA)	Calculated spacing with interdigitation (\AA)
PM-co-DdLG	32.7	41.50	27.75
PM-co-OLG	35.0	56.50	35.25
PM-co-ELG	37.0	61.50	37.75
PM-co-DcLG	41.0	66.50	40.25

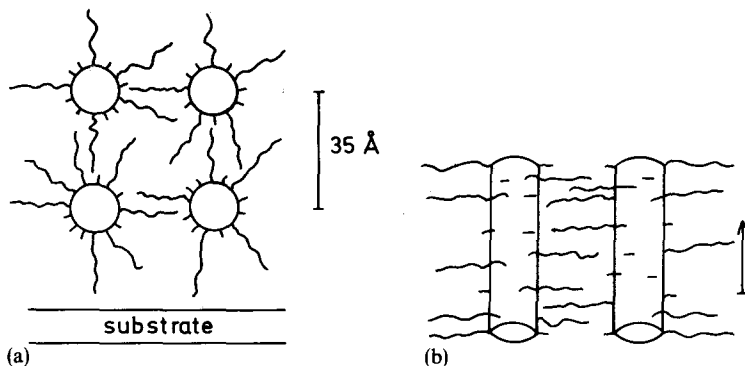


Fig. 11. Proposed model for α -helical copolyglutamates with long side chains in LB multilayers: (a) side view and (b) top view.

4. CONCLUSIONS

The appearance of a liquid-analogous state in the pressure–area isotherms of poly(octadecylmethacrylates) at higher temperatures can be induced by the copolymerization of shorter alkyl-chain-containing methacrylates. Furthermore, it appeared that transfer of monolayers from the water surface onto substrates was especially successful at those conditions when this liquid state exists.

The multilayers formed exhibited a layer spacing of 30 \AA and electron diffraction patterns showed the side chains to be perpendicular to the layers, indicating interpenetration of side chains of successive monolayers. Non-complete substitution of the γ -methyl-ester groups by long-chain alkyl groups in poly(γ -methyl-L-glutamates) also resulted in transferable monolayers. The multilayers of this polymer also showed interdigitation of the side chains, so that the layer spacings agreed very well with the calculated dimensions of an α helix with stretched side chains. Moreover, these α helices were oriented with the helix axis in the flow direction on the substrate.

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