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Esterification Reactions on Syndiotactic Poly(methallylalcohol)

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Summary

Syndiotactic poly(methallyl alcohol) was esterified with selected carboxylic acids under complete conversion to the corresponding homopolymers. Reactions were carried out in HBr-acetic acid to yield acetate; with pivaloyl chloride or phthalic anhydride to obtain pivalate and acid phthalate, respectively, as well as with the N-protected amino acids, N-phthaloyl-glycine, N-phthaloyl-L-phenylalanine or N-carbobenzoxy-L-tryptophane in the presence of dicyclohexylcarbodiimide (DCC) or 1-ethoxycarbonyl-2-ethoxy-1.2-dihydroquinoline(EEDQ) to yield N-protected amino acid ester side chains. Conversion and structure of the polymers were confirmed by ^{1}H- and ^{13}C-NMR spectra.

Introduction

Only for selected cases may vinyl homopolymers, possessing a tactic purity of more than 95% of either syndiotactic or isotactic diads of monomer units, be obtained by polymerisation. One well known example are the tactic poly(methyl-methacrylates)(ABE et al 1968; TSURUTA et al 1966). For the preparation of highly tactic copolymers the possibilities are still more restricted. However, the range of the accessible tactic homo- and copolymers may be extended by carrying out polymer analogous reactions on tactic homopolymers, transforming them to other polymers which cannot be prepared directly by polymerisation. Previously the esterification and amidation of syndiotactic poly(methacrylic acid) by dicyclohexyl-carbodiimide (DCC) has been studied (KLESPER et al 1979 a, b; BERG-FELD, M.C. and KLESPER, E., 1981). The reactions possess on account of their cyclic anhydride intermediate a limiting conversion, leading to copolymers only. In contrast, no acrylic intermediate or limiting conversion may be expected for the esterification of syndiotactic poly(methallyl alcohol) (PMA) by means of DCC. Several carboxylic acids were chosen as examples, together with different esterification procedures. The reactions could be carried to complete conversion, even when bulky side chains were being formed. Three of the six carboxylic acids selected were N-protected L-amino acids, leading to tactic and chiral polymers. To our knowledge, none of the polymers have been prepared before.

Experimental

Syndiotactic poly(methallyl alcohol)(PMA) was prepared from syndiotactic poly(methyl methacrylate)(PMMA) of >92% syndiotactic triads and $\bar{M}_n$ = 200000 by a modified procedure of COHEN and

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MINSK (1959):
5 g (0.131 mole $LiAlH_4$ are dissolved in 250 ml hot N-methyl morpholine. While refluxing, 10.75 g(0.108 mole)PMMA dissolved in 150 ml N-methyl morpholine are added dropwise within 1 h. The mixture is kept stirring for another 4 h. Then a solution of 40g sodium-potassium tartrate in 175 ml H_2O is added dropwise to the refluxing mixture which is kept at reflux for another 90 min. The precipitate consists of an aluminium complex of the tartrate which is filtered off. Then the polymer is precipitated in acetic acid - H_2O(1:5). Reprecipitation is in DMSO solution by acetic acid-H_2O. After filtering and thorough washing with dilute aqeous NH_3, and finally H_2O, the PMA is dried at 100°C in vacuo.
The N-protected amino acids N-phthalylglycine (PHT-Gly-OH) and N-phthalyl-L-phenylalanine(PHT-Phe-OH) (HOUBEN-WEYL 1974) and N-carbobenzoxy-L-tryptophane (Z-Try-OH)(SMITH 1948) were prepared according to literature procedures.
Esterification in acetic acid - HBr : 300 mg PMA are dissolved at room temperature in 30 ml of a solution of 33% HBr in acetic acid. After reaction times of 4-40 h with stirring, complete conversion is obtained. The polymer is precipitated in 500 ml H_2O, filtered and dried. Reprecipitation is from $CHCl_3$/ether and drying at 50° in vacuo.
Esterification by pivaloyl chloride : 300 mg(4.17 mmole) PMA are dissolved in 30 ml pyridine and 0.3 ml triethyl amine added. With agitation, a solution of 0.85 g (7.05 mmole)pivaloyl chloride in 5 ml pyridine is added dropwise, and the mixture left reacting at 50°C for 95 h. The polymer is precipitated in 500ml H_2O, reprecipitated from $CHCl_3$/ether and dried at 50°C in vacuo.

Esterification by phthalic acid anhydride : 500 mg(6.95 mmole) PMA are dissolved in 30 ml pyridine. With stirring,10.28 g (69.5 mmole) phthalic anhydride are added, dissolved and left reacting for 90 h at 50°C. The polymer is precipitated in 500 ml ether, redissolved in 5% aqueous NH_3, reprecipitated by 1 N HCl, repeatedly washed with H_2O and ether, and dried at 50°C in vacuo.
Esterification by N-phthaloylglycine (PHT-Gly-OH): 200 mg(2.78 mmole)PMA are dissolved in 30 ml pyridine. With agitation, 1,5g (7,27 mmole)DCC are added and left stirring for 1 h at 50°C. Consecutively, 1,5g (7.3 mmole) PHT-Gly-OH in 10 ml pyridine is added dropwise. The mixture is kept for 90 h at 50°C, whereby N.N'-dicyclohexylurea precipitates. It is cooled to 0°C and, after filtering off the urea, precipitated in 500 ml ether.Reprecipitation is in pyridine/ether, drying at 50°C in vacuo. Alternatively, 1-hydroxybenzotriazole (HOBT) may be added in half the molar amount of DCC, to increase the reaction rate.
Esterification by N-phthalyl-L-phenylalanine (PHT-Phe-OH): To 200 mg (2.78 mmole) PMA in 30 ml pyridine is added 1.13 g (8.31 mmole)HOBT and o.86 (4.15 mmole) DCC with stirring and left for 1 h. Then 3.27 g (11.08 mmole) PHT-Phe-OH in 10 ml pyridine is added dropwise. The mixture is stirred for 150 h at 50°C, whereby the urea precipitates. The isolation of the polymer is analogous to the reaction of PHT-Gly-OH.
Esterification by N-carbobenzoxy-L-tryptophane (Z-Try-OH): The reaction is carried out with 3.76 g (11.08 mole)Z-Try-OH in the same way as with PHT-Phe-OH, isolation is analogous to the

reaction product obtained with PHT-Gly-OH.
The ^{1}H-NMR spectra were recorded at 200 MHz and the ^{13}C-NMR spectra at 50.3 MHz on a Bruker CXP - 200 multinuclear FT - instrument. The concentration of the polymer was 5% and 10%, respectively, using TMS as internal standard. The molecular weight $\bar{M}_n$ of polymethylmethacrylate was determined on a Knauer membrane osmometer at 29°C in acetone.

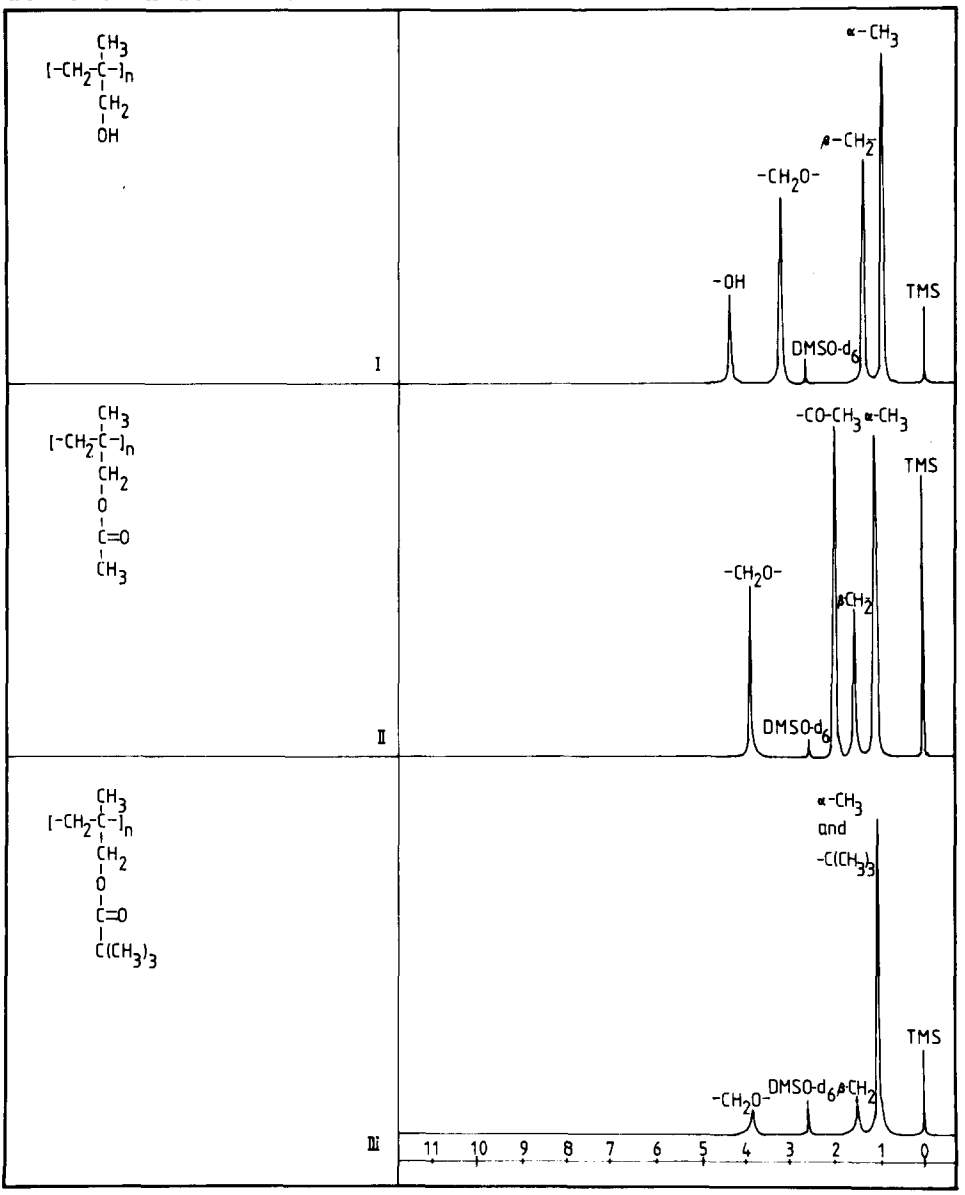

Fig. 1 ^{1}H-NMR spectra of syndiotactic poly(methallyl alcohol) (trace I), poly(methallyl acetate (trace II) and poly (methallyl pivalate)(trace III).

Results and Discussions

The ^{1}H-NMR spectra of PMA and its derived homopolymers obtained by esterification with acetic acid and pivaloyl chloride are shown in Fig. 1. As with all other NMR-spectra, they have been recorded from DMSO-d_6 at 100°C, i.e. under directly comparable conditions. Complete conversion to the two homopolymers is immediately verified by the disappearance of the β-CH_2-, -CH_2O-and α-CH_3 peaks from the original positions shown in the PMA spectrum. In addition, the expected new resonances appear, i.e. those for -$COCH_3$ and -$COC(CH_3)_3$.

In Fig. 2 the ^{1}H-NMR spectra of the homopolymers possessing the acid phthalate and the N-protected L-amino acid ester as side chains are seen. Here,complete conversion expresses itself by the disappearance of the -CH_2O- resonance at 3.2 ppm and the reappearance at a higher value. Newly appearing resonances are more numerous on account of the large side chains and are compatible with the expected polymer structure. The spectra of Figs. 1 and 2 allow also to foresee in which resonance region a sequence splitting may be expected for incomplete conversions. For instance,comparison of the -CH_2O- resonance in trace I of Fig. 1 and trace I in Fig. 2, shows a difference in chemical shift of appr. 0.8 ppm, this range being available, in principle, for splitting into compositional sequences in corresponding copolymers. The aromatic resonances are particulary useful for determining the conversion. Thus for the polymeric acid phthalate and N-phthalyl-glycinate

$$1)\quad P(A)=\frac{5 \cdot I_{\emptyset_1}}{4 \cdot \left[I_{\alpha\text{-}CH_3} + I_{\beta\text{-}CH_2\text{-}}\right]}$$

A = ester monomer unit
I = area of peak
$\emptyset_1$ = -C_6H_4-
$\emptyset_2$ = -C_6H_5-

For the N-phthalyl-L-phenylalanate

$$2)\quad P(A)=\frac{5 \cdot \left[I_{\emptyset_1} + I_{\emptyset_2}\right]}{9 \cdot \left[I_{\alpha\text{-}CH_3} + I_{\beta\text{-}CH_2\text{-}}\right]}$$

and for the N-carbobenzoxy-L-tryptophanate

$$3)\quad P(A)=\frac{I_{\emptyset_2} + I_{indole}}{2 \cdot \left[I_{\alpha\text{-}CH_3} + I_{\beta\text{-}CH_2\text{-}}\right]}$$

Using eqs. 1 to 3 the conversion was determined. It was found that by means of 1-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ) in the mole ratio 1.0 PMA : 2.0 EEDQ : 2.6 PHT-Gly-OH , and an otherwise similar procedure as for DCC,a conversion of 13% (P(A) = 0.13) was obtained. Using PHT-Phe-OH instead of PHT-Gly-OH resulted in 8% conversion.

The ^{13}C broad band decoupled Fourier transform spectra are given for the first three homopolymers in Fig. 3, and for the four homopolymers possessing the acid phthalate and the N-protected amino acid side groups in Fig. 4. As for the ^{1}H-spectra, the assignments given were based on the spectra of the educts as well as on spectral tables of low molecular weight substances. For groups of peaks close to each other, as shown in Fig.4

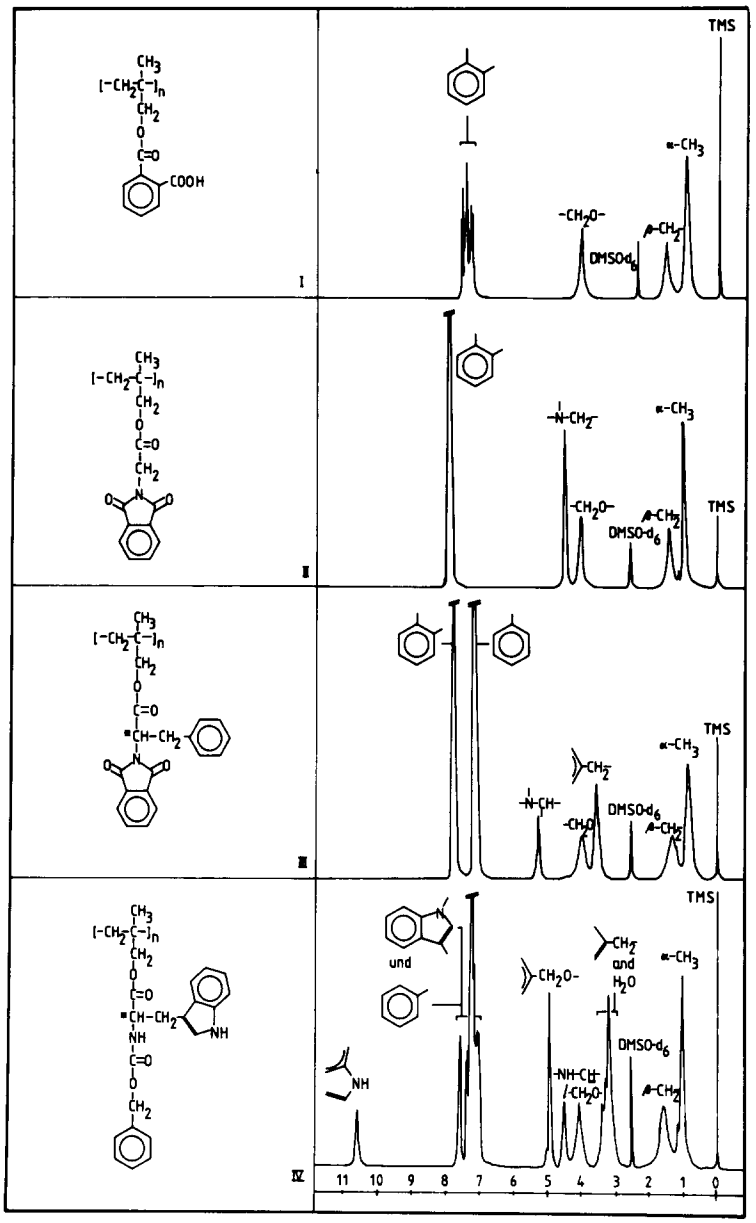

Fig.2 ^{1}H-NMR spectra of syndiotactic poly(methallyl acid phthalate)(trace I), poly(methallyl-N-phthalyl-glycinate) (trace II), poly(methallyl-N-phthalyl-L-phenylalanate) (trace III), and poly(methallyl-N-carbobenzoxy-L-tryptophanate)(trace IV).

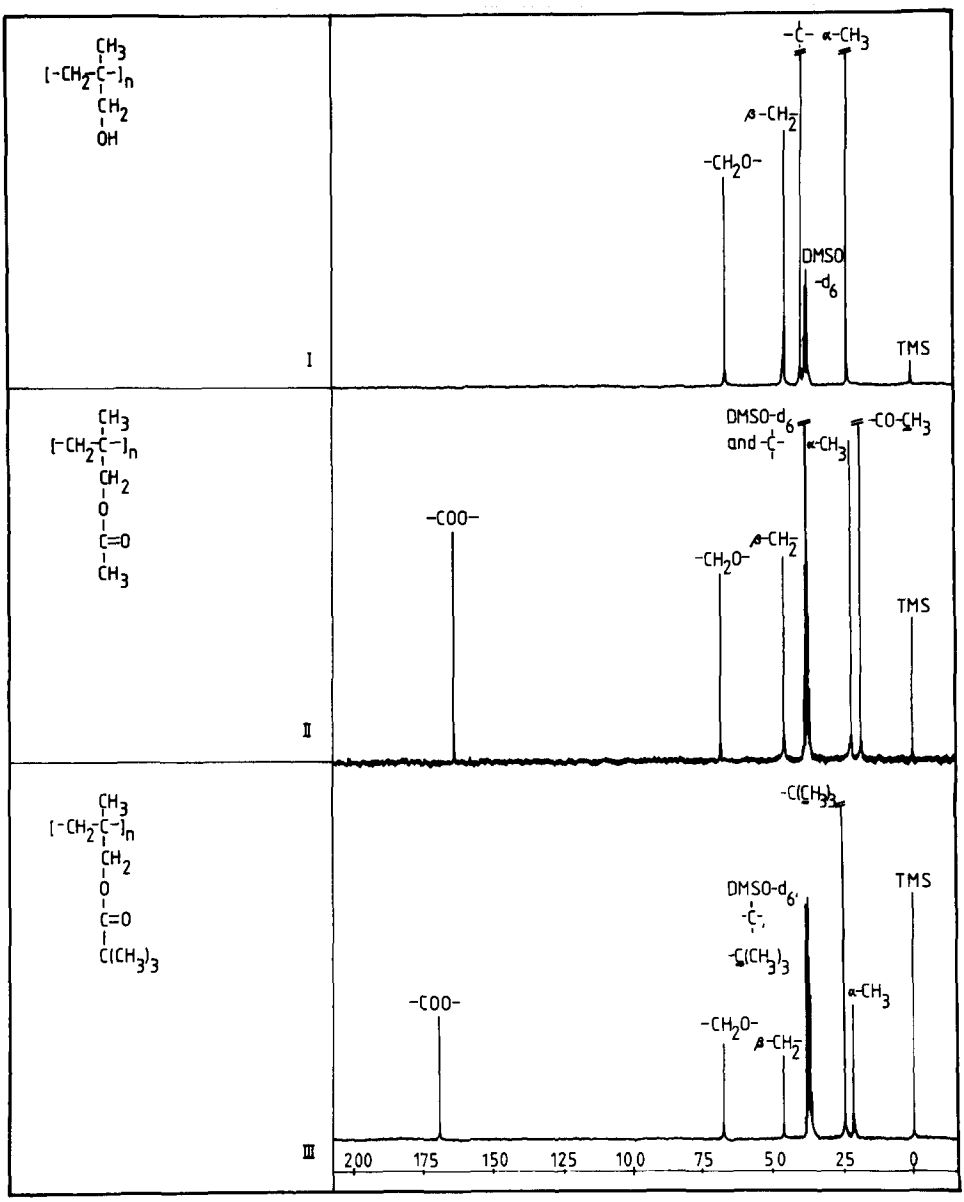

Fig. 3 ^{13}C-NMR spectra of syndiotactic poly(methallyl alcohol)(trace I), poly(methallyl acetate)(trace II),and poly(methallyl pivalate)(trace III)

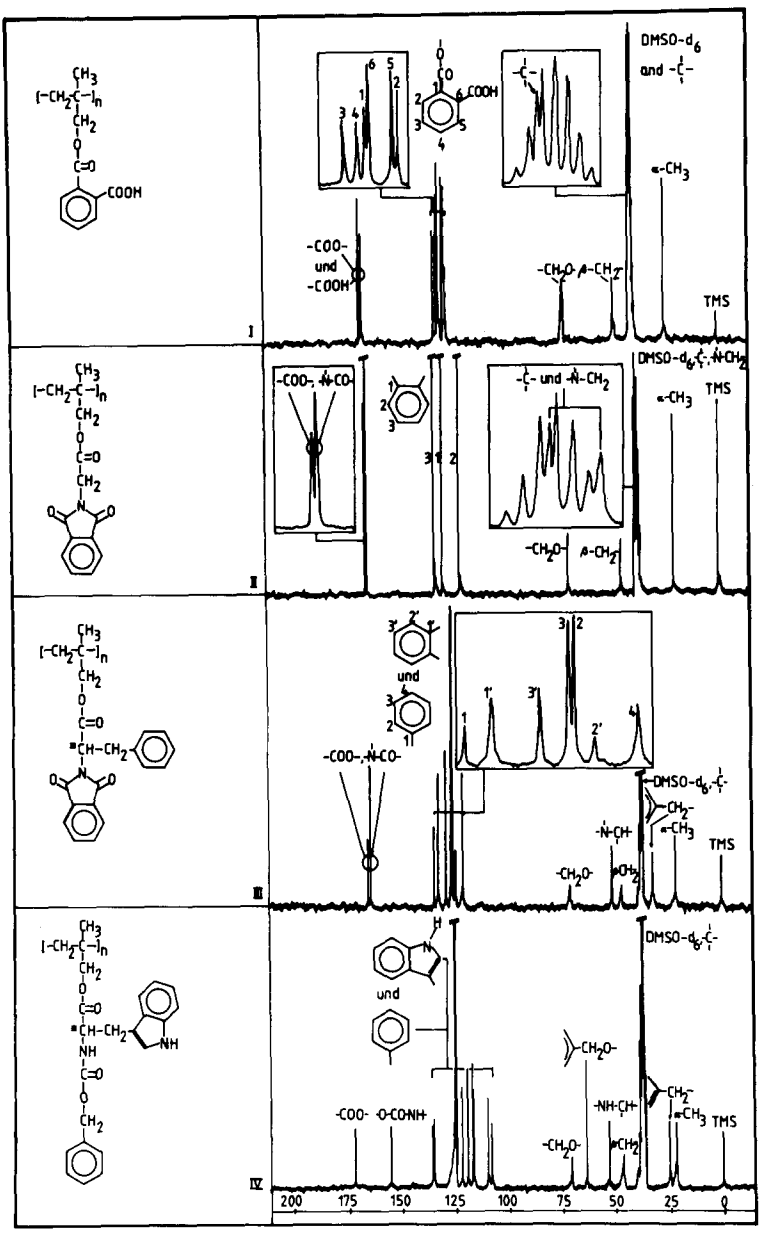

Fig. 4 ^{13}C-NMR spectra of syndiotactic poly(methallyl acid phthalate)(trace I),poly(methallyl-N-phthalyl-glycinate)(trace II), poly(methallyl-N-phthalyl-L-phenylalanate)(trace III), and poly(methallyl-N-carbobenzoxy-L-tryptophanate)(trace IV)

by way of expanded partial spectra, this method of assignment is not certain for polymers, in as much as the assignment may have to be exchanged in pairs of peaks. The conclusions drawn here are, however, not affected by this consideration. All ^{13}C spectra show the expected resonances and approximate chemical shifts for the polymers.

These and other polymer analogous esterifications on tactic poly(methallyl alcohols) may be useful for the preparation of tactic homo- and copolymers possessing optical activity and a large variety in structures, including those which possess reactive functional groups.

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