

Ion-Exchange Copolymers Based on Tetrafluoroethylene, Hexafluoropropylene, and Acrylic Acid

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SYNOPSIS

Peroxide-induced copolymerization of tetrafluoroethylene (TFE) with hexafluoropropylene (HFP) and acrylic acid (AA) at different molar ratios of monomers, reaction time, pressure, and initiator concentration was studied. By means of IR spectroscopy and temperature and phase characteristics of the copolymers obtained it was proved that a ternary copolymer of TFE, HFP, and AA was synthesized. Fluoro-containing polymers with ion-exchange capacities up to 0.8 meq/g were obtained. The composition of binary TFE-HFP and ternary TFE-HFP-AA copolymers and some of their characteristics were determined. Copolymerization takes place mainly in the stationary state with an induction period. Polymerization rate $R \sim [\text{In}]^{0.7}$, which is presumably connected with chain transfer reaction to AA.

INTRODUCTION

The synthesis of copolymers of TFE and AA, and other similar monomers, as well as their chemical modification is a point of interest for obtaining ion-exchange copolymers and the corresponding membranes.¹⁻²

Introduction of HFP into the polymer chain is known to decrease both melting (T_m) and crystallization (T_c) temperatures. Enthalpies of the copolymers obtained also decrease and their processability is improved.³⁻⁷ Copolymers of TFE with AA^{1,2,8-10} possess relatively good ion-exchange properties, however, their decomposition temperature (T_d) is lower than T_m and they cannot be processed into films. Terpolymers of TFE, HFP, and AA make it possible to obtain products with lower T_m and good ion-exchange properties.¹¹

In this paper copolymerization of TFE, HFP, and AA is studied and some basic temperature and phase characteristics of synthesized copolymers are determined.

EXPERIMENTAL

Materials

TFE and HFP in molar ratio from 73/27 to 100/0 were obtained by the method described in a previous paper¹² as follows:

TFE and TFE-HFP mixtures were prepared by thermal depolymerization (pyrolysis) of poly(tetrafluoroethylene) (PTFE) waste in a vacuum pyrolysis line consisting of an electric furnace and a vacuum manifold system. The latter was connected to cold traps for TFE or TFE-HFP mixture (83 K) and higher boiling gases (193 K) which were the pyrolysis products. The heating rate of the electric furnace was adjustable.

The composition of TFE and TFE-HFP mixture was measured by gas chromatographic analysis.

The composition of the TFE-HFP mixture depended on the conditions employed, eg, a pressure within 2 and 250 mm Hg and temperature within 777 and 973 K.

The pyrolysis of PTFE waste gave TFE with a purity up to 99.5% or TFE-HFP mixture containing fluoro-olefins in molar ratio from 73/27 to 99.5/0.5%.

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AA (purity above 99%) was a commercial product of Fluka, Germany. The initiator used was ammonium peroxodisulphate obtained from Reachim (USSR).

Copolymerization was carried out in a 0.5 dm³ Buchi stainless steel reactor (Germany) equipped with a safety valve and a heating jacket. The copolymerization procedure was described¹¹ and is outlined as follows. Copolymerization of TFE, HFP, and AA was conducted in an aqueous medium in the presence of water-soluble initiators (ammonium or potassium peroxydisulfates, 0.2–4.0 mass % with respect to the starting monomers). The initial molar ratio of TFE/HFP was from 60/40 to 98/2, whereas the fluoro-olefins/AA ratio was within 40/60 and 95/5. The water/monomer mixture ratio employed varied between 2/1 and 12/1. Copolymerization experiments were carried out under a pressure between 0.5 and 5.0 MPa and temperature between 323 and 358 K for time from 2.0 to 5.5 h.

The ion-exchange copolymers prepared have an ion-exchange capacity within 0.20 and 0.85 meq/g. The corresponding melting and crystallization temperatures were between 560 and 596 K and 555 and 585 K respectively. The HFP content in the copolymers prepared was found to be up to 3.5–4.0 mol %.

The copolymerization procedure was carried out as follows. A stainless-steel reactor of 500 cm³ volume provided with a heating jacket and electromagnetic stirrer was evacuated. Two hundred-fifty grams deionized water, 1.1 g ammonium peroxydisulfate, and 17.5 g AA were charged preceded by flushing with nitrogen. The mixture was agitated vigorously followed by introducing the TFE–HFP mixture in a molar ratio 90/10. Copolymerization was carried out at 348 K for 4.45 h.

After finishing the reaction, unreacted fluoromonomers were removed. The copolymer was filtered, washed with hot distilled water and/or methanol, and dried under vacuum to a constant mass. The ion-exchange capacity of copolymer was found to be 0.51 meq/g.

Properties of Copolymers

IR spectra were measured by a Specord M-80 spectrophotometer (GDR) in 100–200 μm thin films (for TFE–HFP copolymers) or in tablets with potassium bromide (for AA-containing copolymers). T_m and T_c and the corresponding enthalpies, ΔH_m and ΔH_c , were calculated from the curves obtained by a DSC-111 calorimeter (Setaram, France). Ion-exchange capacity was determined in the sodium form of co-

polymers by back titration with 0.1 N HCl.¹³ Melt index of binary TFE–HFP copolymers was measured by using an IIRT-M apparatus (USSR) at 643 K, loading 49.05N, and nozzle diameter 2.095 mm.¹⁴ Polymer composition was determined from elemental analysis of carbon (1104–Carlo Erba automatic analyzer), fluorine (determined from content of fluorine anions using an ion selective electrode produced by Kritur, Czechoslovakia) and ion-exchange capacity.

RESULTS AND DISCUSSION

The influence of stirring speed (from 11.7 to 21.7 s⁻¹), initiator concentration (from 0.5 to 3.7 mass % related to the monomers), molar ratio TFE–HFP/AA (from 50/50 to 100/0), and reaction time (from 2.15 to 4.45 h) on copolymerization of TFE with HFP and AA, and the properties of copolymers formed were studied. Polymerization temperature was 348 K.

Copolymers synthesized are white powdery products, insoluble in organic solvents, with different degree of swelling in water depending on AA content in polymer.

The characteristic bands in IR spectra at 515, 560, and 650 cm⁻¹ could be assigned to deformation vibrations of >CF_2 groups. The bands at 1150 and 1250 cm⁻¹ are assigned to stretching vibrations of these groups. The characteristic bands at 2930, 2970, and 1780 cm⁻¹ are due to stretching vibrations of >CH_2 and —COOH groups in AA, respectively.

To establish the presence of HFP in binary TFE–HFP copolymers and ternary TFE–HFP–AA copolymers, IR spectra of the following polymers were measured: poly(tetrafluoroethylene) (PTFE), TFE–HFP, and TFE–HFP–AA copolymers with different HFP content, and commercial TFE–HFP copolymer (Teflon FEP-100, Du Pont, USA). Spectral analysis indicated the presence of a band at 980 cm⁻¹ which is a characteristic of —CF_3 ^{15,16} or >CF ^{17,18} groups in HFP (Fig. 1).

HFP content in binary and ternary copolymers increases up to 2.6 and 3.7 mol %, respectively. TFE content in ternary copolymers was found to decrease down to 88.3 mol % (Table I). HFP content in ternary copolymers was higher than in binary copolymers although HFP content in the initial monomer mixture in the latter case was higher.

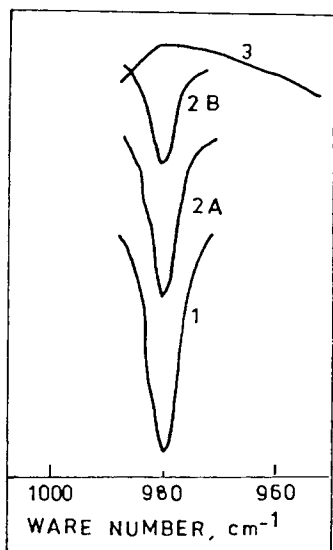


Figure 1 Characteristic absorption bands assigned to C—F bond at a secondary carbon atom (980 cm^{-1}) in IR spectra of: 1—TFE—HFP copolymer; 2(a,b)—ternary copolymers of TFE, HFP, and AA with different HFP content; and 3—PTFE.

Temperature and phase transitions of some polymers formed were studied. Table I shows that introduction of HFP decreases T_m and T_c and ΔH_m and ΔH_c , respectively. T_m decreases almost linearly with increase in HFP content. A similar tendency by other authors also.³ Melt index of binary copolymers increases considerably with increase in HFP content in copolymers. The data in Table I and IR spec-

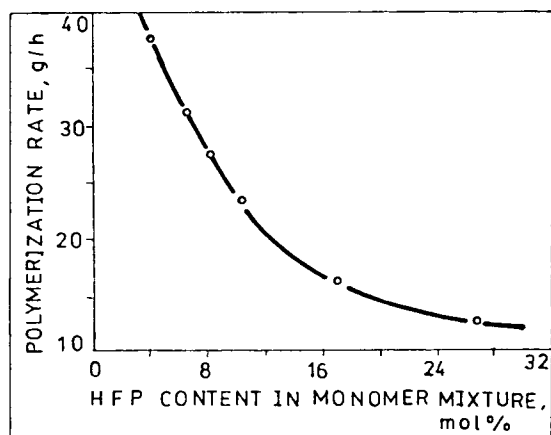


Figure 2 Dependence of polymerization rate of TFE with HFP on HFP mole content in initial monomer mixture. Copolymerization conditions: amount of initiator, 1.2 mass %; temperature, 348 K; stirring speed, 15 s^{-1} ; polymerization time, 2 h.

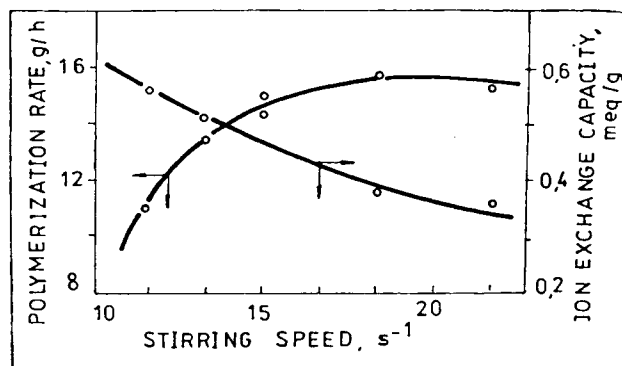


Figure 3 Dependence of copolymerization rate of TFE, HFP, and AA, and ion-exchange capacity of copolymer on stirring speed. Copolymerization conditions: mole ratio TFE/HFP/AA = 72.2/3.0/24.8; amount of initiator, 2.0 mass %; temperature, 348 K; polymerization time, 2.15 h.

troscopy prove the synthesis of both binary TFE—HFP and ternary TFE—HFP—AA copolymers.

Copolymerization rate of TFE with HFP (Fig. 2) largely depends on HFP mole content in the initial monomer mixture. This can be explained by the fact that HFP reactivity is considerably lower than TFE.⁵

Copolymerization rate of TFE with HFP and AA, under the polymerization conditions employed was not affected practically by stirring speed above 15 s^{-1} . This shows that copolymerization takes place

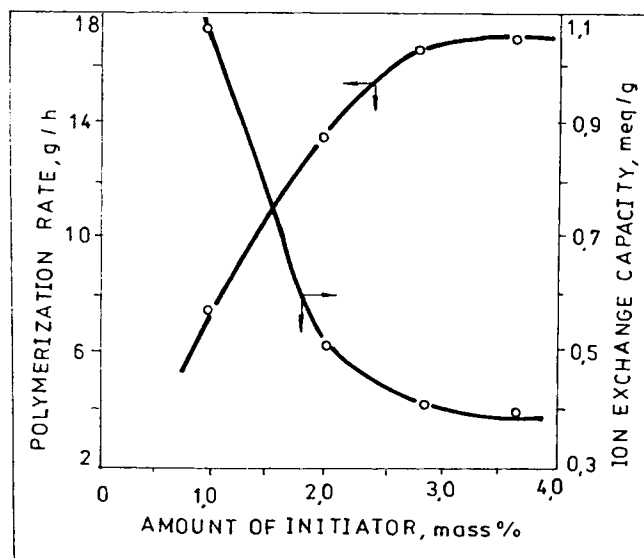


Figure 4 Dependence of copolymerization rate of TFE, HFP, and AA, and ion-exchange capacity of copolymer on amount of initiator. Copolymerization conditions: mole ratio TFE/HFP/AA = 72.2/3.0/24.8; stirring speed, 15 s^{-1} ; temperature, 348 K; polymerization time, 2.15 h.

Table I Composition and Properties of TFE-HFP-AA and TFE-HFP Copolymers*

Run No.	Monomer Composition (mol %)			Polymer Composition (mol %)			Physicochemical Characteristics					
	TFE	HFP	AA	TFE	HFP	AA	T_m (K)	T_c (K)	ΔH_m (J/g)	ΔH_c (J/g)	Ion-Exchange Capacity (meq/g)	Melt Index (g/10 min)
1	71.4	3.0	25.0	95.2	0.4	4.4	596	584	47	51	0.44	—
2	72.2	3.0	24.8	92.1	0.7	7.2	594	586	51	55	0.74	—
3	69.0	7.7	23.3	93.8	1.1	5.1	590	577	36	44	0.51	—
4	64.1	7.1	28.8	90.2	1.8	8.0	584	572	15	22	0.81	—
5	61.2	15.3	23.5	88.3	3.7	8.0	567	564	16	18	0.80	—
6	100	0		100	0		600	588	67	67	—	—
7	96	4		99.7	0.3		597	586	55	54	—	0.1
8	92	8		98.9	1.1		590	581	46	49	—	1.3
9	90	10		98.7	1.3		588	578	46	45	—	3.3
10	83	17		98.3	1.7		585	572	30	39	—	5.0
11	73	27		97.4	2.6		577	565	22	32	—	Over 50

* Amount of initiator (mass %) for: TFE-HFP-AA copolymers 1.0 (run nos. 2-5); 1.2 (run no. 1); TFE-HFP copolymers 1.2 (run nos. 6-11).

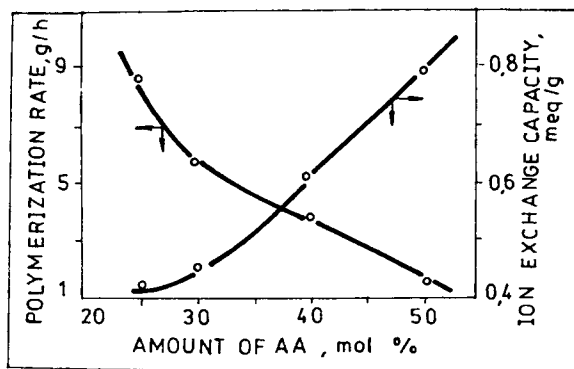


Figure 5 Dependence of polymerization rate of TFE-HFP with AA, and ion-exchange capacity of copolymer on initial mole content of AA. Copolymerization conditions: TFE/HFP = 96/4 mol %; amount of initiator, 2.0 mass %; stirring speed, 15 s^{-1} ; temperature, 348 K; polymerization time, 4.15 h.

in the kinetic region and the corresponding stirring speed was employed. The amount of initiator influences the copolymerization rate (Fig. 4). Using the dependence of copolymerization rate R on initiator concentration In in logarithmic coordinates, it was found that $R \sim [In]^{0.7}$. Exponent value is greater than 0.5, which might be due to chain transfer reactions to a monomer. The presence of α -hydrogen atom in AA makes such chain transfer reactions possible.

Copolymerization rate decreases sharply at lower concentrations of AA. It decreases almost linearly within the range from 30 to 50 AA mol %.

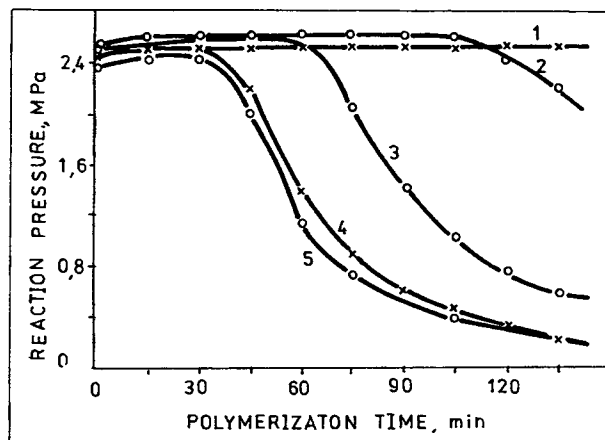


Figure 6 Dependence of reaction pressure on copolymerization time of TFE with HFP and AA at different amount of initiator (mass %): 1—0.5; 2—1.0; 3—2.0; 4—2.8; 5—3.7. Copolymerization conditions: mole ratio TFE/HFP/AA = 72.2/3.0/24.8; stirring speed, 15 s^{-1} ; temperature, 348 K; polymerization time, 2.15 h.

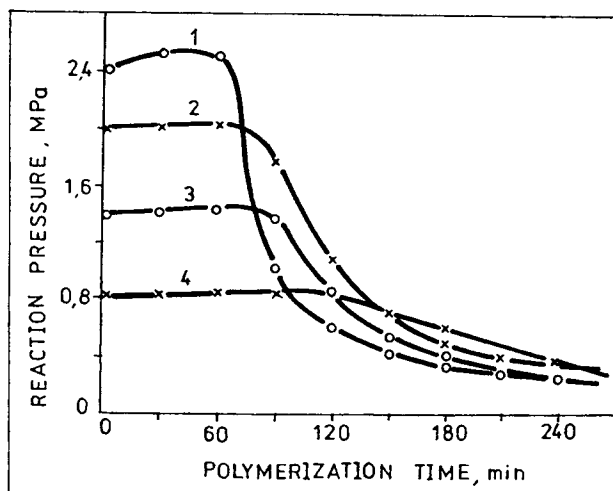


Figure 7 Dependence of reaction pressure on polymerization time of TFE with HFP and AA at different mole ratios TFE/HFP/AA: 1—73.7/1.4/24.9; 2—69.1/1.2/29.7; 3—59.7/1.1/39.2; 4—47.2/0.9/51.9. Copolymerization conditions: amount of initiator, 2.0 mass %; stirring speed, 15 s^{-1} ; temperature, 348 K; polymerization time, 4.15 h.

Analysis of the results obtained shows that ion-exchange capacity of copolymers (Figs. 3, 4, and 5) largely depends on the amount of initiator and the mole ratio TFE/HFP/AA. Copolymers with comparatively good ion-exchange properties (above 0.6 meq/g) were obtained at AA content in the initial monomer mixture above 40 mol %.

Kinetic curves of reaction pressure vs. time with different amounts of initiator and different molar ratios TFE/HFP/AA are given in Figures 6 and 7.

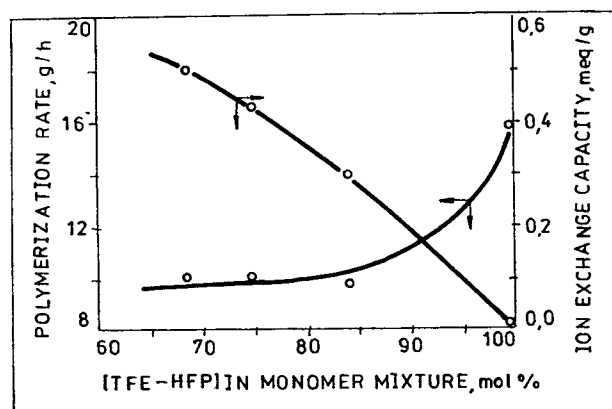


Figure 8 Dependence of copolymerization rate of TFE and HFP with AA and ion-exchange capacity of copolymers on mole ratio of TFE-HFP in initial monomer mixture. Copolymerization conditions: TFE/HFP = 96/4 mol %; amount of initiator, 1.2 mass %; stirring speed, 15 s^{-1} ; temperature, 348 K; copolymerization time, 4.15 h.

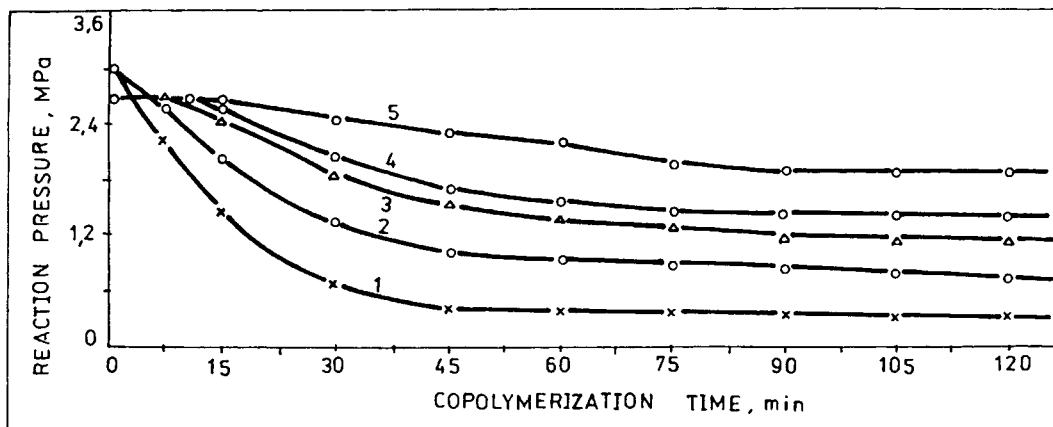


Figure 9 Dependence of reaction pressure on time in copolymerization of TFE with HFP at different mole ratios TFE/HFP: 1—96/4; 2—94/6; 3—90/10; 4—83/17; 5—73/27. Copolymerization conditions: amount of initiator, 1.2 mass %; stirring speed, 15 s^{-1} ; temperature, 348 K; copolymerization time, 2 h.

Reaction induction period was determined from these curves. It increases almost linearly with the AA mole content, which is probably due to chain transfer reaction to AA and subsequent formation of conjugated structure with lower activity.

To increase HFP content in copolymers, copolymerization of TFE with HFP and AA was carried out at initial pressure higher than 2.5 MPa and increased HFP content in the monomers mixture. Copolymerization rate at this pressure (Fig. 8) does not depend significantly on TFE and HFP mole content up to 85 mol %. Higher fluoro-olefin content leads to an abrupt copolymerization rate increase.

Ion-exchange capacity of the copolymers obtained depends largely on the composition of the initial

monomer mixture (Table I, run nos. 3–5) particularly on AA content (Fig. 8).

These tendencies are also confirmed by the dependencies between the reaction pressure and copolymerization time in the binary copolymerization of TFE with HFP (Fig. 9) and in ternary copolymerization of TFE with HFP and AA (Fig. 10). Reaction induction period in copolymerization of TFE with HFP is relatively short (from 1–2 min to 8–10 min), and it increases with the increase in HFP mole content in the initial monomer mixture. In the copolymerization of TFE with HFP and AA, the induction period increases sharply (from 45 min to 1.30 h) depending on the composition of the initial monomer mixture.

Analysis of the above results shows that HFP content up to 20 mol % in the initial fluoromonomer mixture, initial pressure from 1.6 to 3.5 MPa, reaction time from 2 to 5 h, and initiator concentration from 0.5 to 3.5 mass % are suitable for the synthesis of these copolymers, thus providing an appropriate polymerization rate and good ion-exchange properties.

Such copolymers with comparatively low T_m and mobile α -hydrogen atoms in the macromolecular chain are considered to be modified by sulphonation in order to obtain sulphonic and carboxylic groups containing polymers with a higher ion-exchange capacity and good processability. This study will be an object of our further work.

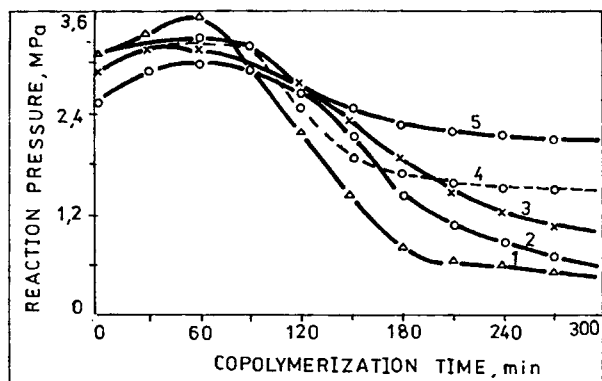


Figure 10 Dependence of reaction pressure on time in copolymerization of TFE with HFP and AA at different initial mole contents of TFE/HFP/AA: 1—82.3/1.5/16.2; 2—71.4/3.0/25.6; 3—65.9/1.2/32.9; 4—69.0/7.7/23.3; 5—61.2/15.3/23.5. Copolymerization conditions: amount of initiator, 1.2 mass %; stirring speed, 15 s^{-1} ; temperature, 348 K; polymerization time, 4.45 h.

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