Studies of Porous Polymer Gels. II. Structure and Porosity of Moderately Crosslinked Poly(Methacrylic Acid) Gels

HENRYK GALINA and BOŻENA N. KOLARZ, *Institute of Organic and Polymer Technology, Technical University of Wrocław, wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland*

Synopsis

The porosity of suspension copolymers of methacrylic acid (MA) and divinylbenzene (DVB) has been studied. The copolymers were prepared both directly from monomer blends and with toluene or n-octane as inert diluents. The pore volume and radii of pores were larger for copolymers containing 5.0% of DVB than those for copolymers containing 9.1% of DVB. The volume and radii of pores increased with increasing diluent content, but the effect of n-octane was more pronounced than that of toluene. Based on considerations of monomer reactivities and copolymer-diluent and copolymer-unreacted monomer interactions, the following model of structure of MA and DVB copolymers has been proposed: The copolymers are composed of microgels interconnected into a rigid skeletonlike structure, surrounded by lightly crosslinked and unentangled poly(methacrylic acid) chains.

INTRODUCTION

Moderately crosslinked poly(methacrylic acid) gels are widely used as carboxylic cation exchangers in water treatment and as specific sorbents, e.g., in separation processes for antibiotics.

Structure of carboxylic cation-exchangers has been considered to be more or less heterogeneous. Gustafson[1] assumed that the copolymer of methacrylic acid (MA) and 5% divinylbenzene (DVB) was a homogeneous gel, but other workers[2,3] assumed that crosslinked MA polymers are composed of chains having widely distributed lengths between the network junction points. The purpose of this work was to study the porosity-determining spatial distribution of the linear chains of poly(methacrylic acid) in MA and DVB copolymers as well as to consider factors affecting the structure of the gels in the polymerization systems.

THEORETICAL

The radical copolymerization of MA and DVB is a typical example of vinyl-divinyl copolymerization. The consideration of the vinyl-divinyl copolymerization and the prediction of a copolymer composition are much more complex than in the case of vinyl-vinyl copolymerization, due to both insolubility of the product and the fact that when one vinyl group in a divinyl monomer reacts two vinyl groups leave the monomer mixture.[4] Moreover, the DVB, the most commonly used divinyl monomer, is an example of a monomer in which the reactivities of vinyl groups are interdependent, e.g., the reactivity of the second vinyl group depends on whether the first has reacted or not.[5] Evaluation of the exact

vinyl-divinyl copolymer composition via the properties and behavior of the co-
polymer is also difficult due to network defects arising in the crosslinking poly-
merization. Such defects, e.g., unreacted vinyl groups, intramolecular loops
(cycles), and permanent entanglements have been described elsewhere.[4] One
possibility is to calculate the vinyl-divinyl copolymer composition at the very
beginning of the reaction. Assuming that a steady state of the reaction is reached
very quickly and neglecting a cyclization, e.g., assuming that pendant vinyl groups
in the copolymer have not yet reacted, the molar fraction F_2 of divinyl units
(component 2) in the copolymer is given by eq. (1) from ref. 6:

$$F_2 = (r_2 f_2^2 + f_1 f_2)/(r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2) \tag{1}$$

where f_1 and f_2 denote the molar fractions of the monovinyl and of the vinyls in
divinyl monomer in the initial monomer mixture, respectively, and r_1 and r_2
denote the respective reactivity parameters.

For the three-component system: first vinyl-divinyl–second vinyl monomer
(e.g., MA-mDVB-styrene) one may derive a similar equation for F_2 in the
form

$$F_2 = \frac{(f_2/r_{12}r_{31})B}{(f_1/r_{21}r_{31})A + (f_2/r_{12}r_{31})B + (f_3/r_{13}r_{21})C} \tag{2}$$

where

$$A = f_1 + f_2/r_{12} + f_3/r_{13} \tag{3a}$$

$$B = f_1/r_{21} + f_2 + f_3/r_{23} \tag{3b}$$

$$C = f_1/r_{31} + f_2/r_{32} + f_3 \tag{3c}$$

Each of the six parameters r_{ij} denotes the reactivity ratio of the ith monomer
in copolymerization with the jth one. Equations (1) and (2) may be readily
transformed to obtain the ratio of the molar fraction of divinyl units in copolymer
(F_2) to molar fraction of divinyl monomer vinyls in the initial mixture (f_2). The
ratio F_2/f_2 expresses a coefficient of enrichment of the copolymer for the divinyl
component at the beginning of the copolymerization. If one assumes that the
dilution of the monomers with a solvent, having a negligible chain transfer rate,
does not change the reactivity of monomers, the term F_2/f_2 is independent of
the solvent present.

When a solvent added to the monomer mixture poorly solvates the copolymer
chains, a phase separation takes place during the copolymerization due to syn-
eresis on contraction of the gel being crosslinked.[7,8] According to Dusek's theory
χ-induced syneresis of the gel occurs in that case.[8] The resulting copolymer is
macroheterogeneous, e.g., porous. Unreacted monomers should also be con-
sidered as diluents.[7] Millar et al.[9,10] have used the term SOL and NON-SOL
for the description of the type of diluent-copolymer interaction during a cross-
linking polymerization with solvating and poorly solvating diluent, respec-
tively.

EXPERIMENTAL

Preparation, conditioning, and characterization of the samples of suspension
poly(methacrylic acid) gels were described previously.[11] Macroporosity of the
gels in the dry state (H form) was determined using mercury porosimeter Carlo

Erba model AG-67. The reading on the capillary were mathematically smoothed. Microphotographs were obtained as follows. A bead of the dry copolymer was immersed in epoxide resin Epon 812 and after curing cut with a microtome (Tesla BS 478). The sections were then left in air of 70% relative humidity and for scanning microscopy stained with silver. A Jeol JSM-35 scanning microscope and an optical microscope (PZO Warsaw) were used.

RESULTS AND DISCUSSION

The composition and properties of the copolymer samples being studied are listed in Table I.

The product are classified in three groups differing in monomer composition. It can be seen from the table that pore volumes in the products increase in each group with increasing amount of diluent used. Copolymers obtained using n-octane as the diluent have higher pore volumes than those obtained using the same amount of toluene. Toluene and n-octane are both NON-SOL diluents for MA-DVB copolymers.

It was found by mercury porosimetry that also the pore radii in the copolymers studied depend on the nature and amount of the diluent used (Figs. 1 and 2).

As can be seen from Figure 1 and from Table I, MA-DVB copolymers containing 9.1% of DVB have smaller pore volumes and smaller radii of macropores than those containing 5.0% of the DVB. Although a similar dependence of the pore volume on crosslinking have been reported for porous α-chloroacrylonitrile-DVB copolymers,[12] this finding remains somewhat surprising. For other types of solvent-modified crosslinked copolymer, e.g., for styrene-DVB copoly-

TABLE I
Compositions and Porosity of Methacrylic Acid–Divinylbenzene Copolymers

Copolymer number	Monomer mixture composition[a]		Inert diluent parts/100 parts of monomers by volume		Apparent specific volume V_0 (cm³/g)	Pore volume[c,d] Q (cm³/g)	Macro-porosity[c,d] P (%)
	MA (%)	DVB[b] (%)	toluene	n-octane			
1	91.8	5.0	...	...	0.86	0.12	13
2	85.0	5.0	...	...	0.86	0.12	13
3	85.0	5.0	5	...	0.86	0.12	13
4	85.0	5.0	...	5	0.92	0.17	19
5	85.0	5.0	10	...	0.96	0.22	22
6	85.0	5.0	...	10	1.04	0.30	30
7	85.0	9.1	...	...	0.73	0	0
8	85.0	9.1	5	...	0.74	0.01	2
9	85.0	9.1	...	5	0.75	0.03	4
10	85.0	9.1	10	...	0.78	0.05	7
11	85.0	9.1	...	10	0.79	0.05	8
12	85.0	9.1	15	...	0.75	0.03	3
13	85.0	9.1	...	15	0.98	0.16	26

[a] The rest up to 100% being styrene and ethylstyrenes.
[b] Calculated for pure DVB isomers in a technical product containing 43.3% m-DVB, 17.4% p-DVB, and ethylstyrenes.
[c] For gels in the dry state (H form).
[d] $Q = V_0 - V$, $P = (1 - V/V_0) \times 100$, V–true specific volume (0.73–0.75 cm³/g).
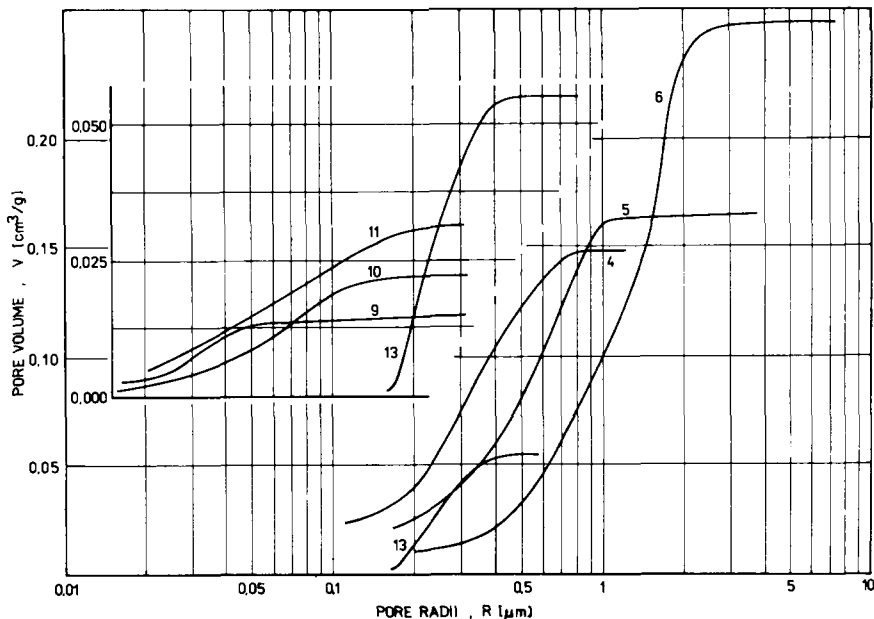
Fig. 1. Volume of pores vs. radii of pores from the mercury porosimeter measurements. Number at curves corresponds to the copolymer number in Table I.
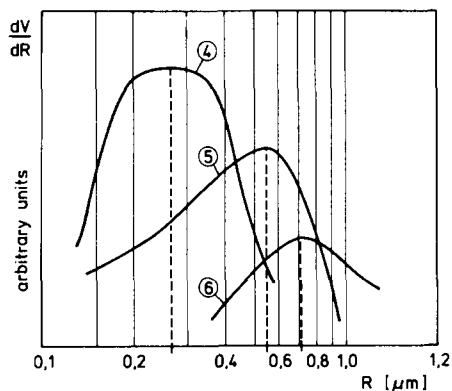

Fig. 2. Differential curves calculated from the mercury porosimeter measurements. Each maximum corresponds to the pore radius whose fraction is the largest among determining the whole pore volume.

mers containing up to about 30% of DVB, an increase of crosslinking degree causes an increase of pore volume.[13]

The effect of monomer mixture composition and nature and amount of diluent present on the porosity of the MA-DVB copolymers can be explained on the ground of the monomer reactivities and the interaction during the copolymerization between the copolymer formed and the other component of the system.

We have not found reactivity parameters for copolymerization of MA and the isomers of DVB. To approach their values we used the Alfrey-Price scheme with $r_1 = 0.15$ for MA and $r_2 = 0.02$ for m-DVB. Then we have calculated enrichment coefficients for DVB in the system MA-DVB-styrene, to simplify the calculations

assuming that the reactivity of p-DVB is the same as that of m-DVB and the reactivities of ethylstyrenes are the same as that of styrene. These assumptions, especially those for DVB isomers, deviate from reality.[14] The content of p-DVB in a technical DVB, however, is always three to four times lower than that of m-DVB (Table II, refs. 15 and 16).

It can be seen from the calculated F_2/f_2 values that the polymer formed at the beginning of copolymerization contains much more DVB units than the initial monomer mixture. These values, calculated with quite rough approximation, cannot be used for quantitative prediction of the composition of MA-DVB copolymers. They show, however, the tendency of the system to more rapid relative consumption of DVB over MA. This means that chains formed at the beginning of reaction will be more densely crosslinked than those formed at a high conversion degree. Intramolecular crosslinks will additionally reduce the crosslinking degree of the chains formed at high conversion. There was found[17] that only about $\frac{1}{7}$ of DVB units in the styrene-DVB copolymer formed up to the gel point may serve as potential crosslinking units, the rest being engaged in intramolecular cycles. Thus, our conclusion is that the crosslinking degree of MA-DVB copolymers decreases gradually with conversion of monomers. The copolymer portions formed at the beginning of the copolymerization are similar to those postulated by Millar et al.[9] and other workers[18] to exist in styrene-DVB copolymers. These portions have been called "nuclei" or "microgels." They were found microscopically in styrene-DVB copolymers by Mikes,[19] by NMR in sulfonated crosslinked polystyrenes by Tao et al.,[20] and electron microscopically by Jacobelli and Flodin[21] in methylisopropenylketone-DVB copolymers.

Now, we are going to show that portions of copolymers which differ in crosslinking degree may occupy different parts of the copolymer bead. A consideration of polymer-solvent interaction is necessary for this purpose.

Early formed copolymer portions, rich in aromatic units, being internally crosslinked by intramolecular links are poorly solvated by unreacted monomers. MA, the main component of the system, is a poor solvent. Thus, the monomer mixture being at least partly excluded from the copolymer just formed polymerizes outside of early formed copolymer portions. At a certain conversion, a phase separation takes place. At this moment, however, the conversion degree is high enough to prevent the separation of the copolymer into powder. After the phase separation, the exclusion of reacted monomers from the copolymer gel is the fact[7] and the conditions of the reaction change on. Lightly crosslinked

TABLE II
Enrichment Coefficients for Divinylbenzene in the MA-DVB-Styrene Systems at the Beginning of Copolymerization

Copolymer numbers	Methacrylic acid $r_{12} = 0.15$ $r_{13} = 0.15$, ref. 15 % by weight	f_1	Divinylbenzene $r_{21} = 0.02$ $r_{23} = 0.60$, ref. 16 % by weight	f_2	Styrene and ethylstyrenes $r_{31} = 0.70$, ref. 15 $r_{32} = 0.65$, ref. 16 % weight	f_3	Enrichment coefficient F_2/f_2
1	91.8	0.917	5.0	0.063	3.2	0.020	3.3
2–6	85.0	0.865	5.0	0.064	10.0	0.071	2.5
7–13	85.0	0.848	9.1	0.115	5.9	0.037	2.3

portions of MA-DVB copolymer are formed mainly outside the relatively highly crosslinked copolymer portions which form rigid skeletonlike structure. Thus, we assume that MA-DVB copolymers comprise microgels containing high amounts of aromatic units interconnected into a rigid structure and surrounded by copolymer portions composed of comparatively long linear poly(methacrylic acid) chains formed at a high conversion degree. The linear chains are probably lightly entangled due to "precipitating" action of MA and diluents at the post-phase separation conversion.

When the copolymer is subject to contact with a good solvent, e.g., with water, the gel portions composed mainly of linear chains can swell easily while microgels cannot. In reverse, when the copolymer swollen with a good solvent is dried, microgel domains do not collapse as much as lightly crosslinked regions do. Drying leads to the conversion of the gel from a rubberlike swollen state into a rigid glassy state.[4] If the drying takes place slowly enough, the transition is probably reached sooner in the microgel regions than in other portions of the gel. Thus, the transition is gradually reached from region to region with decreasing degree of crosslinking. Rigid portions of partly dried copolymer beads prevent the homogeneous collapse of lightly crosslinked portions of the gel. As a consequence these portions collapse around microgel regions. In the dry copolymer beads the pores are formed between the microgel regions which are surrounded by essentially linear poly(methacrylic acid).

The pores are expected to be larger in dimensions and volume when the rigid portions have smaller dimensions. Also a decrease in the entanglement of the linear chains should favour their collapse and an increase of pore dimensions and volume should be observed.

Fig. 3. Scanning microphotograph of the bead section of the copolymer number 6.
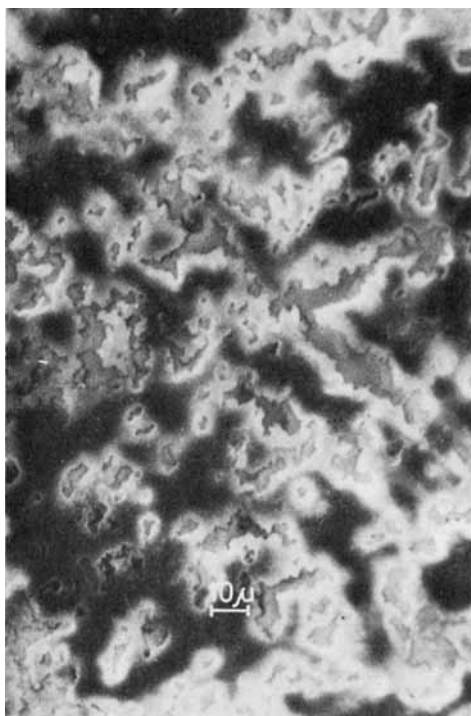
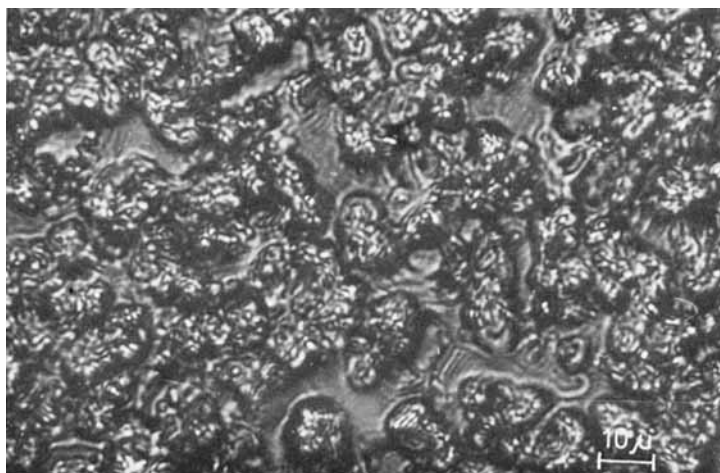Fig. 4. Scanning microphotograph of the bead section of the copolymer number 5.

Fig. 5. Optical microphotograph of the bead section of the copolymer number 6.

It is reliable that in the copolymers obtained with 9.1% of DVB the dimensions of the densely crosslinked regions are larger than those in the copolymers obtained with 5.0% DVB. Therefore, the copolymers of MA and DVB containing 5.0% DVB should have higher porosity than those containing 9.1% DVB which is verified experimentally.

The NON-SOL diluents—toluene and n-octane—make the distances between microgel domains larger. In this way the diluents increase the porosity of the
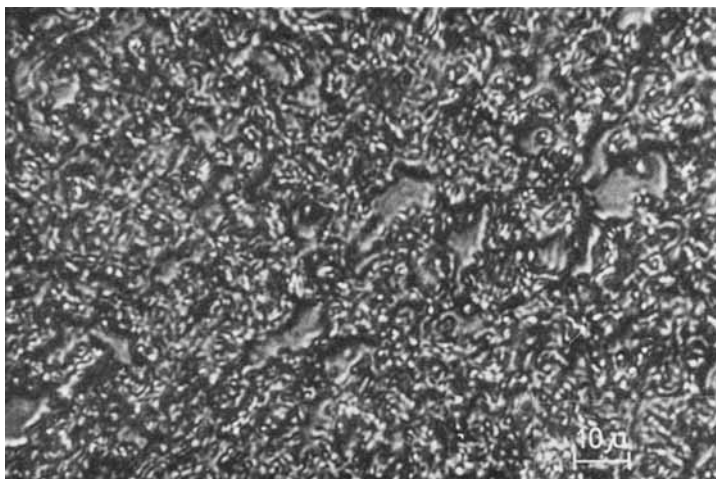
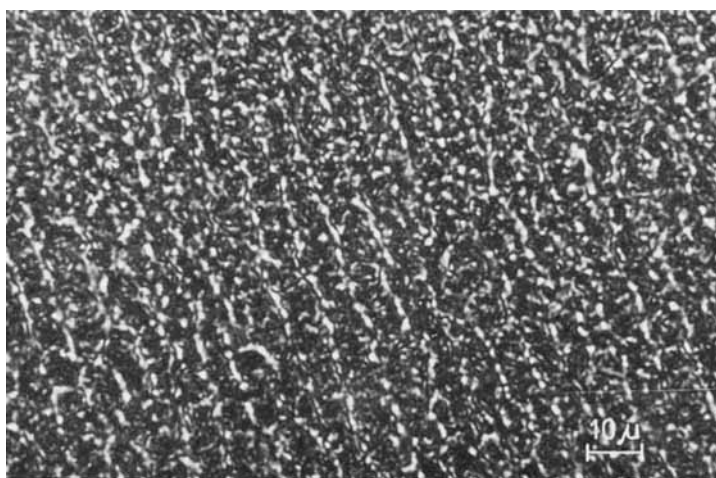Fig. 6. Optical microphotograph of the bead section of the copolymer number 5.

Fig. 7. Optical microphotograph of the bead section of the copolymer number 13.

modified copolymers compared with the unmodified ones. The effect on the copolymer porosity of toluene present during the copolymerization is less pronounced than that of n-octane. The reason is that toluene, but not n-octane, can swell the microgels to some extent and cause copolymer chains to be entangled within the microgels. Therefore, the microgel portions of the copolymer grow in dimension and the porosity decreases.

A splitting of the copolymer structure on a quite different rigid portion and lightly crosslinked unentangled portion is an oversimplification of the system, as is the consideration of dimensions of microgels. Rather, the copolymer gel should be considered as more or less heterogeneous in crosslinking, entanglement, and distribution of the crosslinking units. The proposed schematic picture of the copolymer, however, helps to interpret its porosity and behavior in the swollen state[22] (Figs. 3–8).

On the microphotographs the sections of the MA-DVB copolymers are shown. The first two microphotographs were obtained using a scanning microscope.
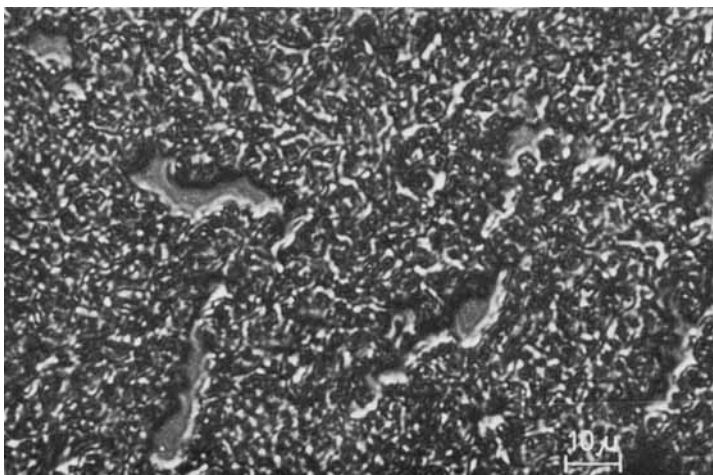
Fig. 8. Optical microphotograph of the bead section of the copolymer number 5. Very large voids are observable, but this picture is not a representative one.

Dark places with sharply drafted edges correspond to the macropores, light regions to the dry resin and dark ones without edges are shadows on the relaxed sample surface. The next microphotographs were obtained using the optical microscope. Essentially monocolored grey regions correspond to the macropores and the grainlike or continuous regions are copolymer fractions. The copolymer regions are transparent and interfere giving black and white reflections recordered on the photographs. Copolymer grains are agglomerates formed by collapse of the lightly crosslinked portions of the copolymer over its rigid portions.

Both macropores and copolymer grains are larger in copolymers containing 5.0% DVB than those in the copolymer containing 9.1% DVB. The pore dimensions found microscopically are comparable with those determined by the mercury porosimetry, although very large pores with radii higher than detectable with mercury methods (7.5 μm) have been also found.

CONCLUSIONS

The suspension copolymers of MA and DVB modified with toluene and n-octane are NON-SOL gels of a structure close to ideal NON-SOL ones. Due to the monomer reactivities they are composed of highly crosslinked regions distributed throughout the copolymer bulk and thus forming the skeletonlike structure. The regions are surrounded by the essentially linear or more exactly by lightly crosslinked poly(methacrylic acid) chains.

The change in the amount of a NON-SOL diluent affects the distribution of the structural regions in the copolymer beads.

The change of the diluent amount affects the number of chain entanglements, if its solvating action with the copolymer chains is taken into account and other interactions are of negligible importance.

Heterogeneity of the copolymer composition and the diluent action determine the porosity of MA-DVB copolymers.

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