Water sorption of poly(methyl methacrylate): 2. Effects of crosslinks*

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Glassy crosslinked networks were made by copolymerization of methyl methacrylate both with ethylene glycol dimethacrylate and with triethylene glycol dimethacrylate, using a redox initiator. Residual monomer was largely or wholly removed by extraction with water, by heating at 100°C, or by γ-irradiation. Water sorption conformed approximately to Fick's laws but with a retarded swelling component which increased with crosslink density. Approximate values were obtained for apparent diffusion coefficients both in sorption and desorption. The pattern of results was similar for both dimethacrylate systems. Values of diffusion coefficients were little influenced by crosslink density up to a dimethacrylate feed of 50 wt%. The saturation value for water uptake increased with increasing feed of dimethacrylate to more than twice the value for the linear polymer, i.e. poly(methyl methacrylate).

(Keywords: water; sorption; diffusion; crosslinks; glasses; polymethacrylates)

INTRODUCTION

The water sorption of crosslinked glassy polymers such as epoxy[1-6] and melamine–formaldehyde resins[7] has received special attention recently. However, it is very difficult to control crosslink density in these systems independently of other factors[3]. The purpose of the present work is to study the water sorption of better controlled networks made by copolymerization of methyl methacrylate (MMA) with increasing proportions of a dimethacrylate crosslinker. Estimates of the crosslink density of such networks can be made provided allowance is made for cyclization reactions and unreacted (pendant) double bonds[8,9]. However, for present exploratory purposes it will suffice merely to accept that crosslink density increases according to the proportion of dimethacrylate.

A considerable amount of work has been done on the water sorption of dimethacrylate networks because of their application as dental materials. For copolymers of MMA with both ethylene glycol dimethacrylate (EGDM) and triethylene glycol dimethacrylate (TGDM), water sorption was found to increase with an increase in crosslinking[10]. A similar conclusion was drawn independently, as an aside to other studies of proprietary crosslinked poly(methyl methacrylates)[11]. Studies of the water sorption of a wide variety of dimethacrylate networks prepared with redox initiators included infrared analyses of the degree of reaction of double bonds[12]. Results obtained for networks of poly(EGDM) and poly(TGDM) are cited because they are highly pertinent to the present work, having been prepared under similar reaction conditions.

See preceding paper (Polymer 1986, **28**, 293) for part 1.

Table 1 Properties of some polymethacrylates (Cowperthwaite *et al.*)[12]

Monomer	Reacted double bonds (%)	Solubility in water (%)	Water sorption (%)
MMA	98.6	1.3	2.00
MMA	95.8	3.5	–
EGDM	57.1	4.4	4.47
TGDM	67.9	6.1	5.53

Water sorption of the glassy linear polymer, PMMA, has been investigated extensively[13-20].

EXPERIMENTAL

Benzoyl peroxide, *N,N*-dimethyl *p*-toluidine, and liquid monomers (MMA, EGDM and TGDM) were used as supplied (Polysciences, Warrington, PA). Equimolar solutions of the peroxide (2.02 wt%) and the amine (1.14 wt%), in the whole range of MMA–dimethacrylate compositions, were vigorously mixed and pipetted into a mould in about 1 min. The mould consisted of two vertical glass microscope slides separated by glass strips, acting as spacers, which were held in place either with wax or with a crosslinked silicone rubber. The polymerization reaction proceeded rapidly, within minutes, and in some cases this resulted in fragmentation of specimens by cracking. Usually cracking could be prevented by dilution with unactivated monomer at the time of mixing. However, in the case of 100% feeds of EGDM, uncracked specimens could not be prepared.

Specimens were removed from the mould with care

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because ones made using high proportions of dimethacrylate, especially EGDM, were quite brittle. Because of this brittleness the edges of the specimens sometimes included microcracks but this region was removed by careful abrasion with alumina grit papers. Preliminary experiments showed that the presence of abraded surfaces did not influence the kinetics of sorption.

Specimens ranged in thickness from 0.085–0.116 cm, and in area from 3 to 11 cm^2. They were subjected to various treatments, prior to testing, such as extraction with water at room temperature or at 37°C for several months. Another treatment involved heating specimens overnight at 100°C in air and then allowing them to cool slowly to room temperature. Preliminary experiments showed that similar sorption kinetics were obtained on specimens which had been heated at 100°C for several days in vacuum. Other specimens were exposed in air to γ-rays from a Cs-137 source at a dose rate of 0.8 Mrad/hour: ambient temperature = 35°C; maximum dose = 5 Mrad. Preliminary experiments showed that similar sorption kinetics were obtained when specimens were irradiated in nitrogen.

For sorption measurements, dry specimens (W_0) were immersed in distilled water at 24.2±0.7°C. They were periodically removed, mopped dry and weighed (W_t) using a Mettler Digital Balance of precision ±0.05 mg. After several weeks specimens approached a limiting weight (W_∞) which, within the precision of the balance, did not change significantly over a further period of 1 week. By convention, changes in weight were designated at $M_t = W_t - W_0$; $M_\infty = W_\infty - W_0$. Corresponding desorption data were obtained starting with specimens which had been subjected to the above sorption cycle or else had been extracted for several months in water. Specimens were dried in air over anhydrous calcium sulphate (Drierite, W. R. Hammond, Ohio).

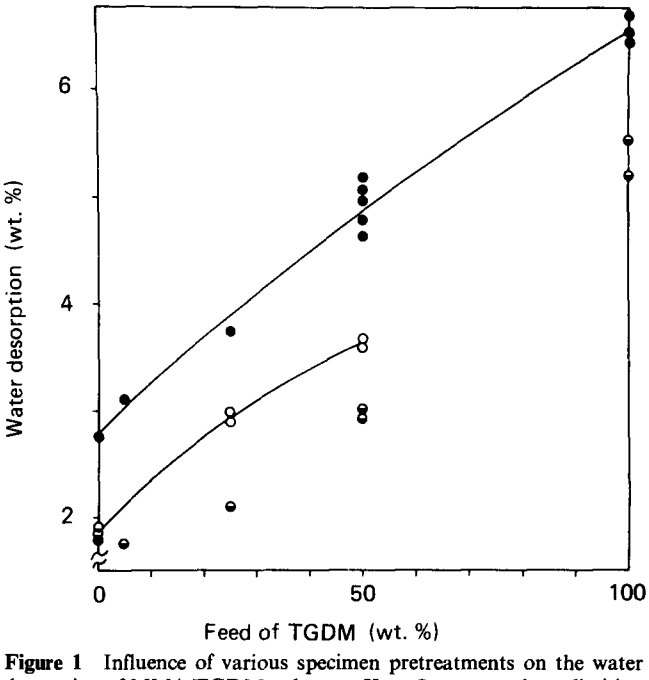

Figure 1 Influence of various specimen pretreatments on the water desorption of MMA/TGDM polymers. Key: ○, extracted to a limiting weight with water either at 24°C or 37°C; ◒, heated overnight at 100°C, followed by a first run in sorption; ●, exposed to γ-rays (2.5–4.0 Mrad), followed by a first run in sorption

RESULTS

Limiting values of sorption

Redox initiators provide free radicals which, at ambient temperature, yield a vitrified product containing several per cent residual monomer. Monomer has been observed to leach out in water for periods of up to one year. Under such circumstances reliable water sorption data were obtained only by the desorption technique[12]. An overview of the results of pretreatments which were selected mainly with the intention of eliminating, or at least reducing, residual monomer is given for products ranging in composition from 100% MMA to 100% TGDM (*Figure 1*). It will be seen that relative to specimens which had been pretreated by water extraction, preheating at 100°C generally decreases water sorption while pre-irradiation always results in an increase. A similar trend for results obtained for MMA/EGDM products is documented in more detail for MMA alone (*Table 2*) and for one-to-one copolymers of MMA with EGDM (*Table 3*).

The dependence of water sorption on polymer composition, obtained using pre-irradiated specimens, is shown for a range of MMA/TGDM (*Figure 2*) and MMA/EGDM (*Figure 3*) compositions. For comparison, previous results are included which were calculated using additional data[21] not given in ref. 10.

Kinetics of sorption

Results are analysed by reference to a theoretical equation for diffusion in a plane sheet according to Fick's laws (equation (1)), in which M_t and M_∞ are the masses of penetrant either taken up or lost at times t and infinity, respectively; $2l$ is the thickness of the sheet; D is the diffusion coefficient. A value of D was obtained from the initial slope, determined by the method of least squares, using Stefan's approximation (equation (2))[13,14].

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{n=\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4l^2}\right] \quad (1)$$

Table 2 Influence of pretreatment on water sorption and desorption of PMMA

Specimen number	Treatment prior to testing	Run number s = sorption d = desorption	D ($cm^2\ s^{-1} \times 10^8$)	Change in weight[a] (%)
1	Irradiated (4 Mrad)	1s	0.40	2.51
		2d	0.79	2.75
2	Heated at 100°C overnight	1s	1.17	1.74
		2d	1.80	1.80
3	Extracted with water at 24°C	1d	3.59	1.84
4	Extracted with water at 37°C	1d	3.44	1.89

[a] 100 (weight, wet − weight, dry)/weight, dry

Table 3 Influence of pretreatment on water absorption and desorption of copolymers (MMA:EGDM 1:1)

Specimen number	Treatment prior to testing	Run number s=sorption d=desorption	D ($cm^2\ s^{-1} \times 10^8$)	Change in weight (%)
1	Irradiated (2.5 Mrad)	1s	0.32	4.27
		2d	1.22	4.67
2	Irradiated (5 Mrad)	1s	0.35	3.64
		2d	0.94	4.32
3	Heated at 100°C overnight	1s	0.51	3.45
		2d	3.08	4.18
4	Extracted with water at 24°C	1d	2.05	4.82
		2s	0.88	3.63
		3d	2.16	3.87

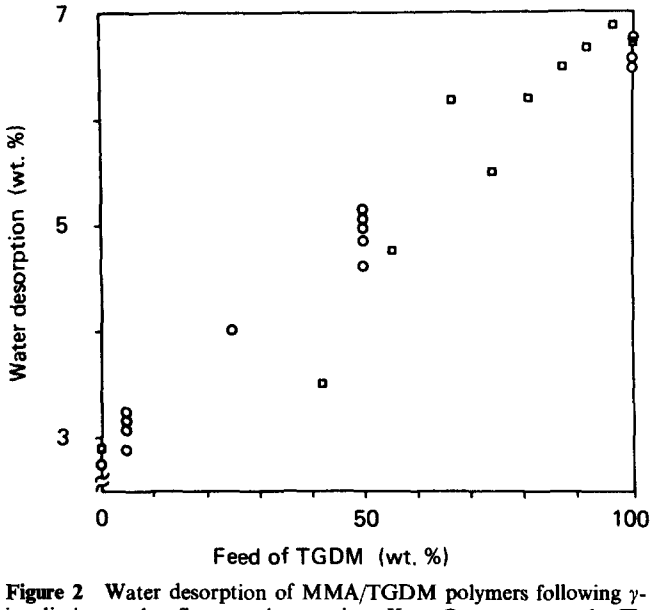

Figure 2 Water desorption of MMA/TGDM polymers following γ-irradiation and a first run in sorption. Key: ○, present work; □, sorption data calculated from ref. 10

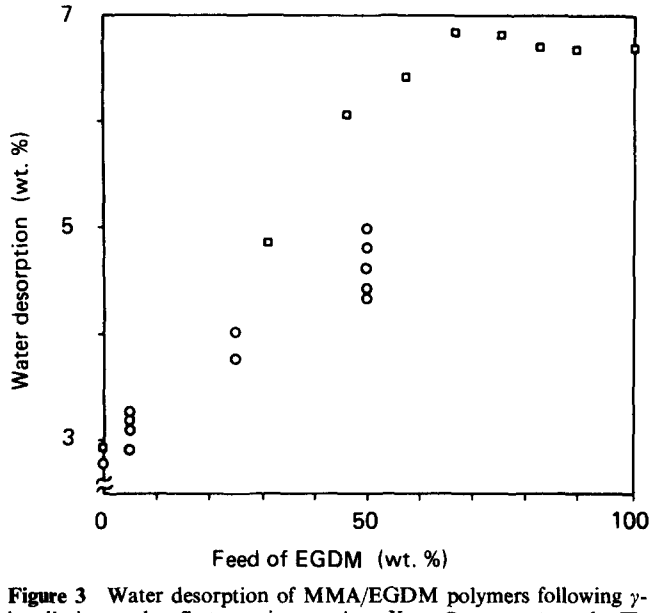

Figure 3 Water desorption of MMA/EGDM polymers following γ-irradiation and a first run in sorption. Key: ○, present work; □, sorption data calculated from ref. 10

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \quad (2)$$

Plots of data according to equation (2) are shown for PMMA and a MMA/EGDM (1:1) copolymer (*Figure 4*). Slopes are approximately linear up to M_t/M_∞ values of about 0.5, in the range of validity of Stefan's approximation, and then decline in conformity with equation (1). Generally departures from Fick's laws increase with increase in the limiting water sorption. A first indication of a departure is that the linear portion of plots such as *Figure 4* holds to higher values of $M_t/M_\infty = 0.5$. This latter effect is most pronounced for networks which take up most water, made from 100% TGDM. An example of a plot from this system is reported elsewhere[22]. More extreme cases of this kind of departure from Fickian kinetics, involving an upward curvature, have been reported previously for water sorption by melamine–formaldehyde resins and analysed by incorporation of a stress relaxation factor[23,24]. It was shown that the value of D obtained by this procedure was close to that obtained by use of equation (2). Therefore in the present work, where departures from Fickian kinetics are much smaller, it seems justifiable to use equation (2) to

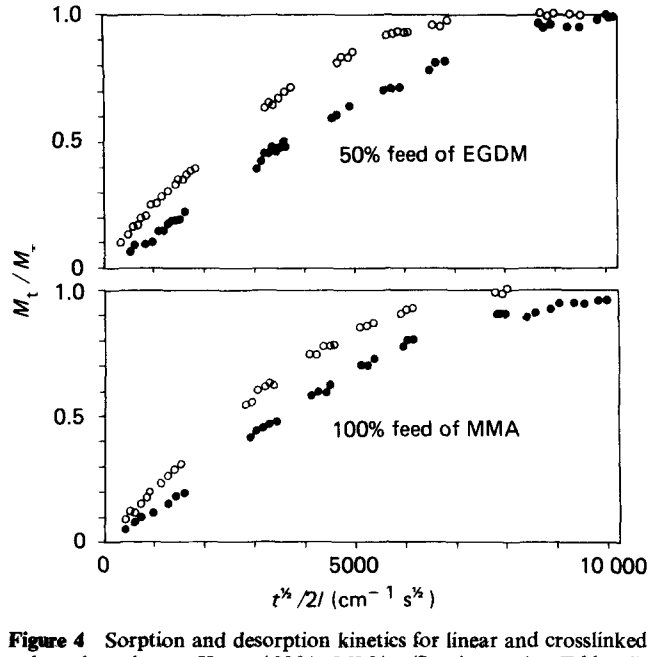

Figure 4 Sorption and desorption kinetics for linear and crosslinked polymethacrylates. Key: 100% MMA (Specimen 1: *Table 1*). MMA/EGDM (Specimen 2: *Table 2*). ●, sorption; ○, desorption

provide apparent values of D. The dependence of D on polymer composition is shown in *Figures 5* and *6*.

All the data reported in *Figures 2–6* were obtained using irradiated specimens, the first run being in sorption and the second in desorption. It was found that this pre-treatment favours closer conformity to Fick's laws in sorption. It also gives lower values for D, both in sorption and desorption (*Tables 2* and *3*), which are in good agreement with previously reported values for PMMA in which plasticization by residual monomer was not a problem[20]. Irradiation is believed to polymerize residual monomer.

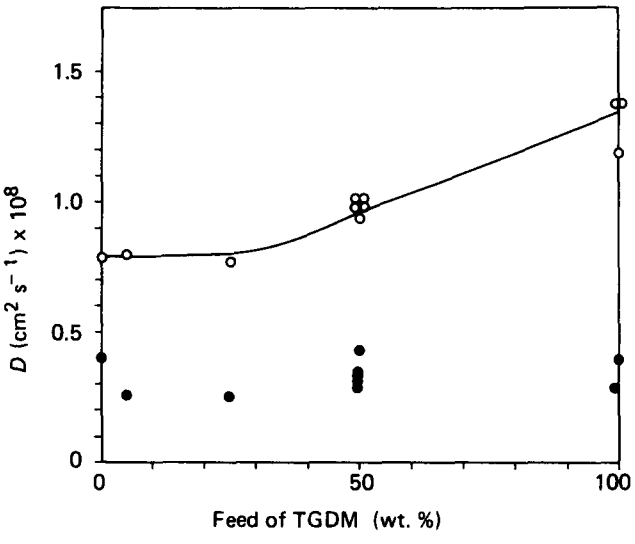

Figure 5 Dependence of D on feed of TGDM. Key: ●, sorption; ○, desorption (pre-irradiated specimens)

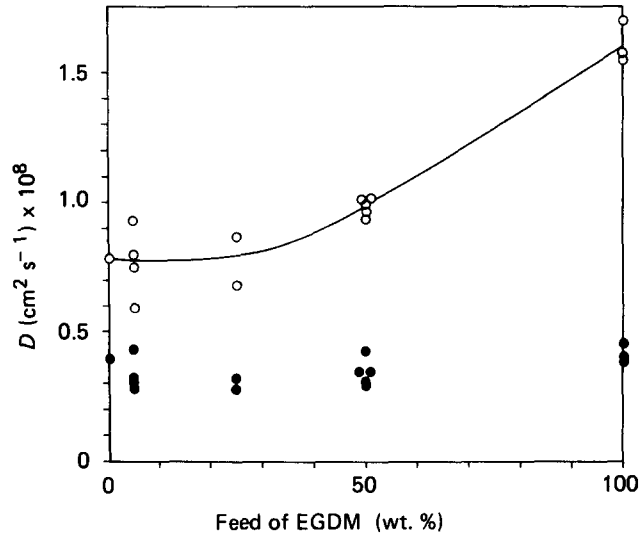

Figure 6 Dependence of D on feed of EGDM. Key: ●, sorption; ○, desorption (pre-irradiated specimens)

DISCUSSION

Limiting water sorption

The amount of water taken up by a glassy polymer depends on the concentration of hydrophilic groups and their accessibility. In addition, water may be accommodated by processes which are accompanied by little or no increase in volume of the polymer specimen. The nature of such processes has long been a matter of discussion but more specific suggestions invoke Langmuir adsorption in 'holes', or 'microvoids'[25], or saturation of a definite free volume fraction of 0.025[1]. In the case of PMMA immersed in water at room temperature it is known that swelling of the polymer only accounts for about one-half of the uptake of water, but the mechanism of accommodation is not known[20].

The increase in water uptake which results from copolymerization of TGDM with MMA (*Figure 2*) might be attributed to an increase in concentration of hydrophilic ethoxy groups but this explanation would not account for the similar results obtained using EDGM (*Figure 3*). Information about whether such networks accommodate additional water without swelling can be obtained by an analysis of data reported by Atsuta, Hirasawa and Masahara[10], as in *Table 4*. Contrary to the above hypothesis, the results indicate that the fraction of water taken up without swelling does not increase in proportion to the feed by EGDM. On the contrary, there is a small decline (column 7). *Table 4* also includes other data which are consistent with the expectation that crosslink density does increase with increasing feed of EDGM. The density of the product increases (column 2) while equilibrium swelling in acetone decreases (column 3). Changes in density indicate a conversion of 67% of the double bonds in forming poly(EGDM), which is in agreement with the value of 64% reported by Loshaek and Fox[8].

Another possible explanation for increased water sorption might be sought in the increasing concentration of pendant (unsaturated) groups left in the networks with increasing feed of EGDM. However, this idea seems unlikely because the fully unsaturated EGDM monomer itself takes up less water (about 2%) than does poly(EGDM)[26]. Yet another factor which might

Table 4 Analysis of data of Atsuta *et al.*[10] on MMA/EGDM copolymers

Feed by EGDM (wt.%)	Density of polymer (g cm^{-3})	Swelling in acetone (wt.%)	Water sorption (wt.%)	Calculated volumetric expansion[a] (vol.%)	Estimated volumetric expansion[b] (vol.%)	Fraction water taken up without swelling[c]
0	1.187	soluble	2.91	3.45	1.24	0.64
33.1	1.210	18.2	4.86	5.88	2.02	0.66
56.9	1.234	2.8	6.43	7.93	3.15	0.60
74.8	1.243	0.3	6.80	8.45	3.55	0.58
88.8	1.241	−0.1	6.66	8.27	4.10	0.50
100	1.254	−1.0	6.71	8.41	4.48	0.47

[a] Calculated from wt.% assuming additivity of volumes of polymer plus sorbed water (V_w)
[b] Calculated from reported values of linear expansion in water, assuming isotropic expansion (V_L)
[c] Calculated as $1 - V_L/V_w$

influence water sorption is how far the temperature of measurement is below the glass transition temperature, T_g. For example, it has been shown that the Langmuir 'hole' component of dual mode absorption of gases increases with decrease in temperature below T_g[27]. The glass transition temperatures of MMA/EGDM products increase from about 105°C (for PMMA) to 130°C for poly(EGDM)[28]. Nevertheless this explanation seems unlikely inasmuch as water uptake by PMMA is insensitive to temperature in the range 4°C–60°C[18].

In conclusion, a similar pattern of results is obtained for the dependence of water sorption of both TGDM and EGDM copolymers. The data for TEGDM copolymers of Atsuta *et al.* are similar to those given in *Table 4* but have not been detailed here. However, the reason for this trend is not known.

Kinetics of water sorption

Generally diffusion in a glassy polymer is influenced by plasticization and by clustering of water molecules. There is ample evidence that water does plasticize PMMA. For example, water depresses the glass transition temperature[29] in accordance with the Kelley–Bueche equation[30]. More to the point, at room temperature considerable changes in mechanical properties are consistent with a plasticizing action[30,31]. Notwithstanding expectations that D should be increased considerably by plasticization it has been found experimentally, by stepwise additions of water vapour to PMMA specimens containing various stationary concentrations of water, that D actually decreases. The decrease is by a factor of about one-half as the concentration of water is increased from zero towards a saturation value of about 2%. It was pointed out that this trend is consistent with Crank's explanation for a rate of desorption higher than sorption (see also ref. 32). It was suggested that diffusion in PMMA is controlled predominantly by immobilization of water molecules in clusters[19,33].

The views expressed above about water sorption of PMMA are based on a considerable volume of work which needs to be repeated on crosslinked networks. In the meantime it is assumed, provisionally, that similar factors are at play. In the sorption process effects due to plasticization and clustering offset each other throughout the range of measurements (*Figures 5* and *6*), i.e. as water sorption increases from about 3 to 7%. A similar balance holds in desorption measurements up to 50% feed of dimethacrylate, i.e. as water sorption increases from about 3 to 5%. Only with 100% feed of dimethacrylate, i.e. with 7% water, does the plasticizing effect predominate.

In contrast to the above findings crosslinking markedly decreases the transport of gases in polymers[34]. Such transport has been shown to correlate with the influence of plasticizer on main chain motions, as studied by nuclear magnetic resonance[35]. Possibly main chain motions do not control events in water transport in polymer systems in which water is a poor solvent. In this respect it has been pointed out that the diffusion coefficient of water in certain linear polymers, both below and above T_g, is independent of water content[36]. In work on poly(methyl acrylate) and poly(vinyl acetate) it was shown that data do not conform to a free volume theory which had been found satisfactory for penetrants other than water. Transport of water was ascribed to 'solid-like vibrations of monomer units'[37].

CONCLUSIONS

(1) Water sorption of copolymers of methyl methacrylate with either ethylene glycol dimethacrylate (EGDM) or triethylene glycol dimethacrylate (TGDM) conforms approximately to Fick's law, although there is a retarded swelling component which increases with the proportion of dimethacrylate.

(2) The results obtained using either EGDM or TGDM follow a similar pattern:

(i) Limiting water sorption approximately doubles as the proportion of dimethacrylate increases from 0 to 100%.

(ii) In sorption, the value of the apparent diffusion coefficient is little changed as the proportion of dimethacrylate increases from 0 to 100%. In desorption, the value of the apparent diffusion coefficient increases noticeably only when the proportion of dimethacrylate exceeds 50 wt%.

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