Polymer Bulletin 43, 223–230 (1999)

Polymer Bulletin

10-I-3 Iodanes* as photoiniferters with spectral selectivity

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Received: 19 April 1999/Revised version: 3 August 1999/Accepted: 3 August 1999

Summary

A photoiniferter ability of the 10-I-3 iodanes* is established during the bulk polymerization of methyl methacrylate, styrene and N-vinylpyrrolidone. The observed spectral selectivity is its important peculiarity, opening new possibilities for the control of the macromolecule microstructure. Under visible light these iodanes initiate the "pseudoliving" radical polymerization, while a conventional radical or cationic polymerization are the consequences of the iodane decomposition under UV irradiation. It is suggested that the spectral selectivity of the 9-I-2 iodanyl radical decomposition and the relative instability of the ends of the iodane macromolecule are the reasons of this unusual iodane ability.

Introduction

We have already reported [1- 5] that 10-I-3 iodanes (($ArI(OAc)_2$, $ArI(CF_3COO)_2$) are effective photoinitiators of cationic and radical polymerization. The iodanes' ability to generate radicals was used in some other laboratories as well [6 - 8]. According to the mechanism proposed in these works, the homolytic decomposition of, e.g., $ArI(OAc)_2$ producing acyl and iodanyl radicals represents the primary process in photoinitiation:

$$(AcO)_2IAr \rightleftharpoons AcO\dot{I}Ar + AcO^{\bullet} \qquad (1)$$

Methyl radicals, forming after the $AcO^{\bullet}$ decarboxylation (proved by the radical scavenger method [9]), are actually the initiators of radical polymerization. It was supposed [4, 10] that the iodanyl radical can further undergo both homolytic and heterolytic decomposition:

$$AcO^{-} + ArI^{+\bullet} \xleftarrow{h\nu} AcO\dot{I}Ar \xrightarrow{h\nu} AcO^{\bullet} + ArI \qquad (2)$$

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[*] Polyvalent iodine species differ in the number of valence electrons (N) surrounding the central atom (I), the number of ligands (L) and their chemical structure. In terms of this designation, four structural types of polyvalent iodine species are the most important for chemistry. 8-I-2 and 10-I-3, called iodanes, are conventually considered as derivatives of trivalent iodane, and the next two, 10-I-4 and 12-I-5 periodanes, represent the most common structural types of pentavalent iodane.

The decomposition pathway to the right produces additional acyl (methyl) radicals, while the phenyliodide cation-radical, formed by the pathway to the left, is a precursor of the true cationic initiator [1, 4]. The existence of a third mode of the iodanyl radical utilization is discussed in the present work. In the light of the modern concepts of the hypervalent bonds, the role of the d-functions is to provide "orbital space" at the central atom to accept electron charge from the ligands (back-bonding). The resulting energy stabilization overcomes the strong ligand-ligand repulsion at the hypervalent atom. The d-orbital polarization functions also improve the overlup of the valence sp hybrids with the ligand orbitals [11]. Therefore, the mentioned above iodane radical intermediate (9-I-2 derivative of the trivalent iodine) would be relatively stable and less reactive because of the negative hyperconjugation and the partially ionic character of the I-O bond. For these reasons the reactivity of this primary radical to monomer molecules or its initiation efficiency decreases considerably. However, this does not exclude the possibility of the iodanyl radical to react with the propagation ones

$$\sim CH_2-C^{\bullet}(H)X + AcOI^{\bullet}Ar \rightleftharpoons \sim CH_2-C(H)X-I(Ar)-OAc \qquad (3)$$

The 10-I-3 iodane chain end is more unstable than the initial low-molecular iodane because of the two iodine-carbon bonds in its molecular structure [12, 13]. Therefore this terminal chain iodane could be considered as a "dormant" propagation end, capable to regenerate both the active propagation end and the iodanyl radical through the back reaction (3). The competition between the discussed three different manners of the iodanyl radical utilization (1, 2) depends on both the radical structure and the polymerization conditions, in particular on the light radiation energy. The results obtained in this work show that the iodanyl radical decomposition by reaction (2) predominates under UV-irradiation and therefore 10-I-3 iodanes initiate cationic and conventional radical polymerization. On the other hand, the above mentioned primary iodane decomposition proceeds under the action of visible light with a lower rate. However, the consumption of the iodanyl radicals mainly by the reversible reaction (3) in this case is the reason for the iniferter iodane ability.

Experimental

All monomers (methyl methacrylate (MMA), styrene (St) and N-vinylpyrrolidone (VP) (Fluka)) and solvents are purified by conventional drying and distillation procedures. (Diacetoxyiodo)benzene (DAI) and [bis(trifluoroacetoxy)iodo]benzene (TFI) are tested as iniferters. They are synthesized by standard methods [14]. The basic polymerization experiment includes the suspension of the initiator in a given amount of the monomer using a glass vessel coated with black paper. After stirring for 1h, the obtained suspension is centrifuged for 20 min (2000 rpm). The DAI concentration in the centrifugate is 9.085×10^{-4} M at room temperature. Glass or quartz tubes are filled with a definite volume of this centrifugate and after a 30 min saturation with nitrogen they are sealed and placed in a thermostat at 25°C. The polymerization initiation is accomplished by the hypervalent iodine compound decomposition at this temperature by UV (Hg discharge 125 W lamp emitting at 254 and 265 nm), visible (irradiatiation with a xenon arc ($\lambda > 420$ nm) through water filter) and day light. The distance between the light source and the polymerization tubes is 10 and 50 cm in the first and second case, respectively. After a predetermined time period the tubes are opened and the poly(methyl methacrylate) (PMMA) and poly(styrene) (PSt) formed are precipitated in methanol, while the poly(N-vinylpyrrolidone) (PVP) is precipitated in diethyl ether. These polymers are purified by double precipitation from acetone solutions.

Yields are determined gravimetrically. The reduced viscosities are determined at 25°C using an Ubbelohde viscometer. Molecular weight and molecular-weight distribution (MWD) are determined by size exclusion chromatography (SEC) using Waters 510 HPLC with a 410 differential refractometer and UV detector with THF as eluent at a flow rate of 1.0 mL.min^{-1} and three Ultrastyragel columns (10^2, 5.10^2, 10^3, 10^4, 10^5 Å, and linear) in series. The molecular weight calibration curve was obtained using poly(methyl methacrylate) standards.

Results and discussion

Initiation under visible light

The kinetic dependences in Fig. 1 show that under visible light 85% MMA conversion is reached for about 65 hours. A characteristic feature of these dependences is their nonlinearity. The M_n and M_w/M_n dependences on the conversion of the MMA are represented in Fig. 2. Some of the SEC-traces, the parameters of which are used for tracing these curves, are shown in Fig. 3.

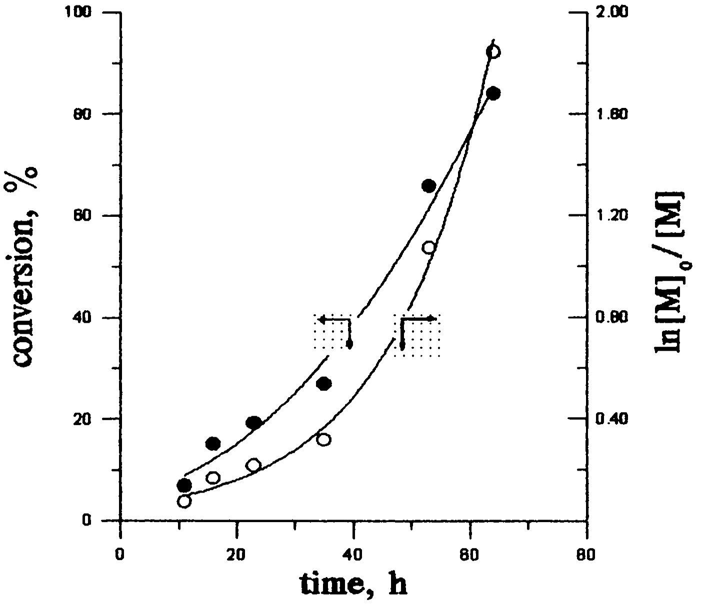


Figure 1. Dependence of conversion (•) and ln([M]$_0$/[M]) (o) versus time for bulk polymerization of MMA at 25°C under visible light.
[DAI] = 9.085x10^{-4} M.

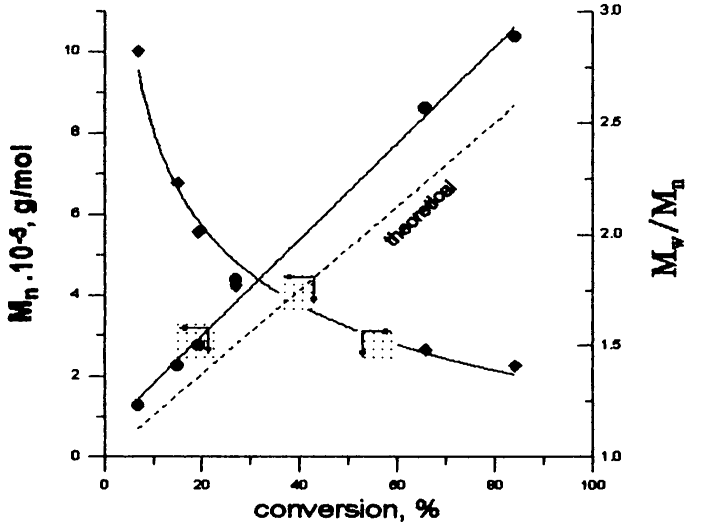


Figure 2. Dependence of M_n (experimental (•), theoretically calculated (---)) and M_w/M_n (■) versus conversion for bulk poly-merization of MMA at 25°C under visible light [DAI] = 9.085x10^{-4} M.

The observed almost linear M_n increase with conversion is the most frequently used indication [15 - 21] of a "pseudoliving" radicalpolymerization. At the same time, this is the first experimental evidence of the assumptions for the DAI iniferter capability and for the third mode of the iodanyl radical utilization (3).

Another confirmation of these assumptions is the monotonously decreasing polydispersity of the produced PMMA as a function of conversion (Fig. 2). The large M_w/M_n values at low conversions and their further nonlinear decrease are in conformity with the theoretical analysis of this dependence by the condition that the iniferter decomposition is not instantaneous [22]. Similar dependences are established experimentally for other "pseudoliving" radical polymerizations [23, 24] too. The slow decomposition could also be one of the possible reasons for the non-linearity of the kinetic dependences (Fig. 1), as well as for the deviation from linearity of the "ln($[M]_0/[M]$) - t" dependences, taking place at instantaneous iniferter decomposition only [15, 16, 25]. The deviation of the experimental M_n values from those calculated by the equation $M_n = q[M]_0M_{MMA}/[DAI]_0$ [16] (theoretical curve in Fig. 2) and the relatively large polydispersity values even at high conversions could also be a consequence of this slow DAI decomposition. The discussed results suggest that under visible light DAI is a slowly decomposing photoiniferter of the MMA bulk polymerization at room temperature in nitrogen atmosphere. Analogous, but not so strict quantitative results are obtained for the bulk St and VP polymerizations with both DAI and TFI as iniferters. It is interesting to check also the capability of the 10-I-3 iodanes as iniferters in day light. In our previous work [4], it was established that the rate of the radical polymerization photoinitiated by DAI under day light is negligible, compared to that under UV irradiation. It turns out that (compare the kinetic dependences in Fig. 1 and Fig. 4) it is considerably lower (by more than one order of magnitude) than that under visible light.

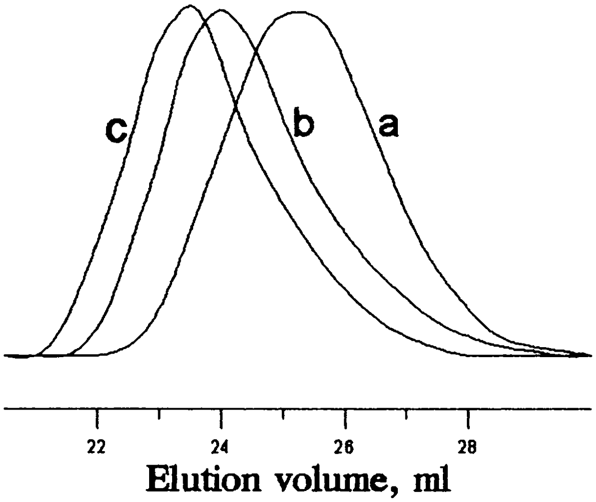


Figure 3. Evolution of SEC traces of PMMA as a function of conversion for bulk polymerization of MMA at 25°C under visible light. $[DAI] = 9.085 \times 10^{-4}$M. Conversion (q) = 0.069 (a); 0.270 (b); 0.842 (c).

As is well known [26 - 28], the low stationary radical concentration is a necessary condition for "pseudo-living" radical polymerization. This circumstance, together with the 10-I-3 iodane iniferter capability under visible light discussed in the previous section, make reasonable the expectation that these iodanes preserve their capability under day light, too. This is confirmed by the monotonously increasing reduced viscosity (η_{sp}/c = 0.93; 1.11; 1.25; 1.60 and 2.08 dl/g) with conversion (q = 1.52; 3.08; 7.82; 13.64 and 17.65 %, respectively) of the PMMA solutions in acetone.

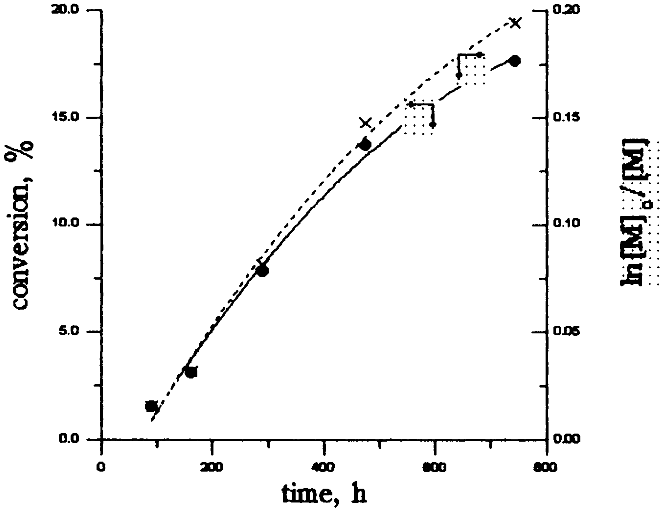


Figure 4. Relationship between conversion (•), ln $[M]_0/[M]$ (x) and time for bulk polymerization of MMA at 25°C under day light.
$[DAI] = 9.085 \times 10^{-4}$ M.

Initiation under UV irradiation

The reaction mixture of MMA and DAI ($\lambda_{\max,1}$ = 226 nm, strong; $\lambda_{\max,2}$ = 255 nm weak) behaves quite differently under UV light. The polymerization kinetics in this case is represented in Fig. 5. It is evident that the initial polymerization rate is many times higher than that under visible (Fig. 1) and day (Fig. 4) light. Moreover the kinetic dependences in this case are protuberant with a well expressed levelling tendency. A similar tendency was observed in our previous works [2, 3] and could be related to the inhibitor effect of the iodine produced upon UV-irradiation. These peculiarities of the kinetic dependences are in disagreement with the assumption of a "pseudoliving" radical polymerization under UV light. This uncertainty is confirmed by the M_n and M_w/M_n dependences on conversion (Fig. 6).

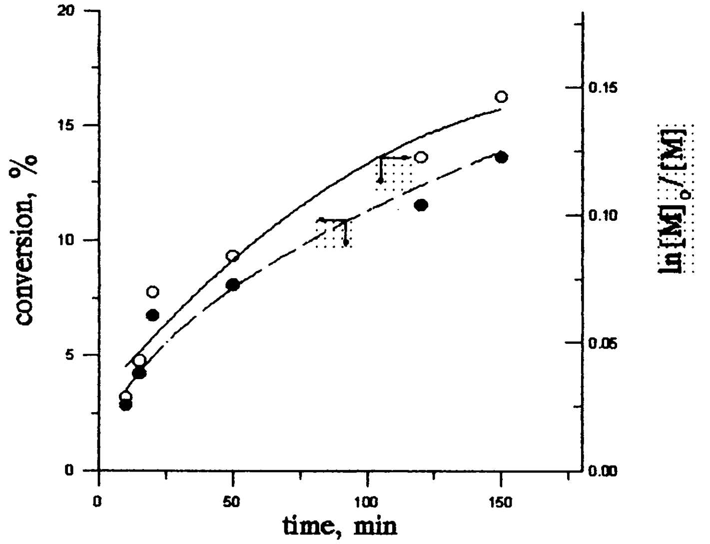


Figure 5. Dependence of conversion (●) and ln $[M]_o/[M]$ (o) versus time for bulk polymerization of MMA at 25°C under UV light.
[DAI] = 9.085x10^{-4} M.

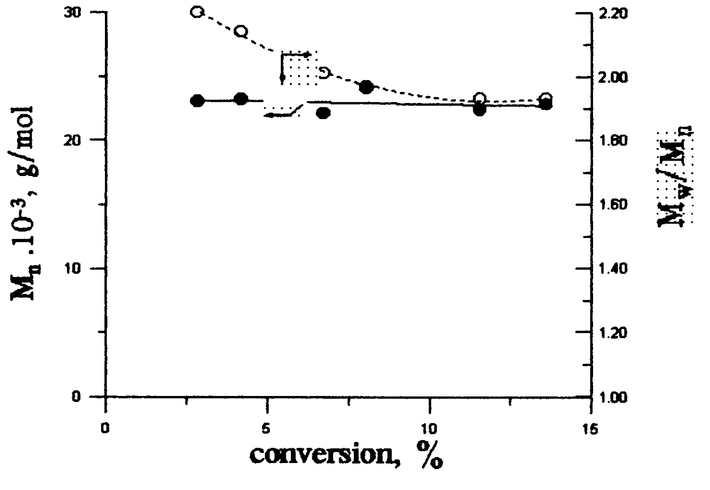


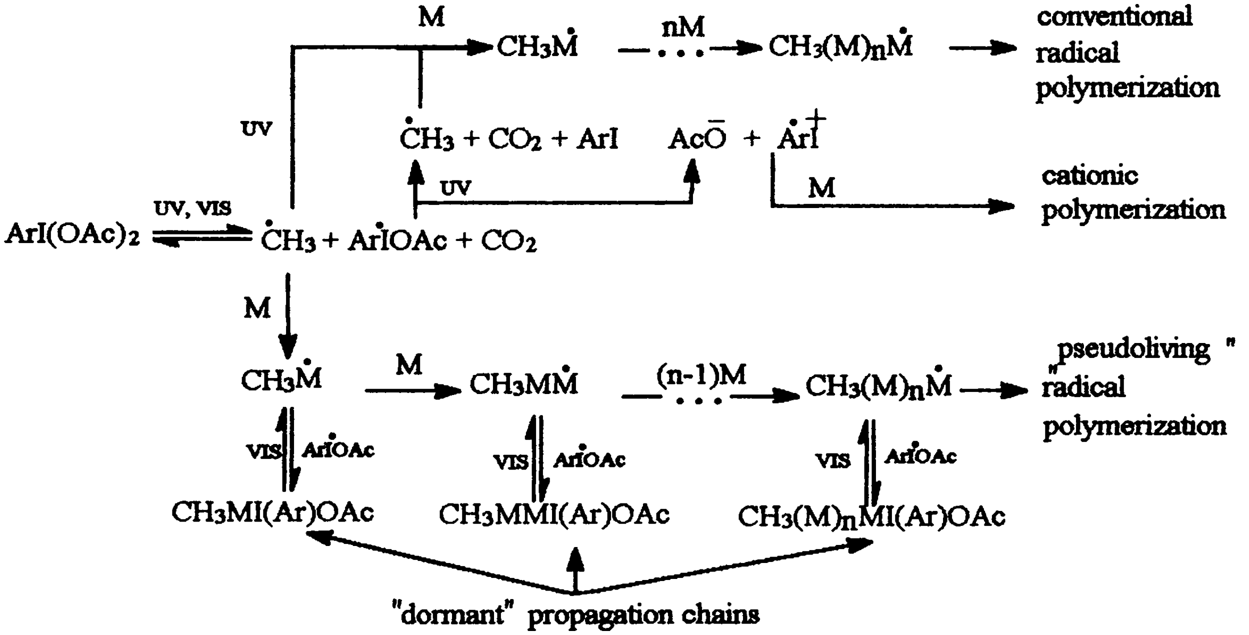
Figure 6. Relationship between Mn (●), Mw / Mn (o) and conversion for bulk polymerization of MMA at 25°C under UV light.
[DAI] = 9.085x10^{-4} M.

The practical independence of M_n and M_w/M_n on conversion is a convincing proof of the "nonliving" character of the MMA polymerization with DAI as an initiator under UV light. The M_n values in this case (Fig. 6) are lower by more than one order of magnitude than that of PMMA, produced under visible light (Fig. 2). This difference could be explained by the difference in the polymerization rates under different irradiations. The higher initiation rate under UV light provides for a higher stationary concentration of the propagation radicals and the probability of a bimolecular termination, typical of the conventional radical polymerization, is higher than that under visible light. This is the first possible reason for the "nonliving" character of the polymerization under UV light. Another reason is the primary utilization of the iodanyl radicals according to reactions (2) while the "dormant" propagation end formation by reaction (3) is less probable under this irradiation. Maybe this is the crucial reason for the observed difference between the polymerization character under visible and UV light. However, there is one more - the third reason for the "nonliving" polymerization under UV irradiation. It was mentioned in the introduction that the propagating iodane produced by reaction (3) is more unstable than the initial one. This is a precondition for its reversible homolytic decomposition to the active propagation and iodanyl radicals, i.e., for the attribution of the propagating iodane with two iodane-carbon bonds to the "dormant" propagation ends. In addition to the reversible reaction (3), there is another - heterolytic pathway for the decomposition of this iodane:

$$\sim CH_2{-}C(CH_3)COOCH_3{-}I(Ar){-}OAc \rightleftharpoons \sim CH_2{-}C(CH_3)COOCH_3{-}\overset{+}{I}{-}Ar + AcO^- \quad (4)$$

The produced terminal alkylaryliodonium salt is inactive in the "pseudoliving" radical polymerization. It is reasonable to assume that the more energy rich irradiation (λ^{-1} value) causes the stronger shift to the right of equilibrium (4) as a result of both the more effective excitation of the terminal iodane with two I-C bonds and the more rapid decomposition of the produced terminal alkylaryliodonium salt by the mechanism discussed in [4, 10]. The result of the two-stage polymerization experiment is an indirect proof of this assumption. Initially the probes are irradiated with UV (120 min) and immediately after that with visible light (33 hrs). The conversions and molecular-weight characteristics of the obtained PMMA samples before (q = 0.115, Mn = 2.24×10^4 g/mol, Mw/Mn = 1.93) and after irradiation with visible light (q = 0.116, Mn = 2.23×10^4 g/mol, Mw/Mn = 1.95) remain practically the same. This result shows that nonreversible decomposition of both DAI and iodanyl radicals during the UV irradiation excludes the next radical and, in particular, the next "pseudoliving" radical polymerization.

The above results and assumptions suggest the following scheme for the radical and cationic polymerizations with DAI under UV and visible light, reflecting the fundamental



difference in the iodanyl radical utilization. Homo- and heterolytic decomposition under UV light enable the initiation of cationic and conventional radical polymerization, while the predominating interaction of this radical with the propagation radical under visible light produces the "dormant" propagation chains and reveals the iniferter capability of 10-I-3 iodanes.

Conclusion

The discussed results, together with those of our previous works [1 - 5] show convincingly that the possibilities of the hypervalent iodine compounds to initiate and control the polymerization processes are not limited to those of the 8-I-2 diaryliodonium salts, investigated by Crivello et al. [29 - 34]. The fact that 10-I-3 iodanes initiate both cationic [1, 4] (like diaryliodinium salts) and radical [2, 3, 5] polymerization is the first confirmation of this statement. The present work opens essentially new possibilities for the application of the hypervalent iodine compounds as photoiniferters. Probably, during the systematic investigation of the detailed mechanism of this iniferter effect and its spectral selectivity, new possibilities for an application of both the 8-I-2 or 10-I-3 hypervalent iodine compounds and the nonstudied in this respect 12-I-5 periodinanes will be outlined. The identification of other hypervalent iodane intermediates, in addition to the discussed 9-I-2 iodanyl radicals, is also possible.

Acknowledgement. This work was supported by the Bulgarian Science Fund (Grant N° X-814). The author thanks Prof. P. Markov, Dr. E. Kamenska, Dr. Z. Mincheva, Mag. Chem. N. Tzarevsky, L. Christov, V. Petkova and M. Berberska for stimulating discussion and help with SEC.

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