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RESEARCH ARTICLE

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Gas-free initiation for free-radical frontal polymerization through charge transfer complexes

Daniel P. Gary | **Md Abdullah Al Mahmud** | **Madison G. Dawson** | **John A. Pojman**

Department of Chemistry and the Macromolecular Studies Group, Louisiana State University, Baton Rouge, Louisiana, USA

Correspondence
John A. Pojman, Department of Chemistry and the Macromolecular Studies Group, Louisiana State University, Baton Rouge, LA 70803, USA.
Email: john@pojman.com

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Abstract

Frontal polymerization is a process in which a localized reaction zone propagates through the coupling of thermal transport and the Arrhenius kinetics of exothermic polymerization. Most initiators that have been used produce volatile byproducts, which create bubbles and voids. Tetraalkyl ammonium persulfates have been used but these require synthesis and do not have long shelf lives. A charge transfer complex (CTC) composed of an iodonium salt, and a phosphine compound has been identified as a gas-free initiator for free-radical thermal frontal polymerization. This CTC has 4-(dimethylamino)phenyldiphenly phophine (DMAPDP) as the donor and p-(octyloxyphenyl)phenyliodonium hexafluoroantimonate as the acceptor (IOC-8). The CTC was tested with several acrylates, and all were found to support bubble-free fronts. We determined the CTC mole ratio for some monomers at which the front velocity reaches a plateau.

KEYWORDS

charge transfer complex, free-radical polymerization, frontal polymerization, thermal initiator, void-free polymer

1 | INTRODUCTION

Frontal polymerization (FP) was first discovered by Chechilo and Enikolopyan in the 1970s[1–4] and later independently discovered by Pojman in the 1990s.[5–11] The process allows the rapid curing of materials and has been applied in areas such as deep eutectic solvents,[12–15] hydrogels,[16] gradient materials,[17] cationic-initiated polymerization,[18–22] ring-opening metathesis polymerization,[23–25] and thin films.[26] The topic has been recently reviewed.[27]

One of the challenges of free-radical frontal polymerization is the generation of bubbles from small-molecule volatilization, especially from the gases formed as the initiator decomposes. (Such void formation is not an issue for frontal ring-opening metathesis polymerization because the catalyst does not decompose.[23,28]) These bubbles lead to pores, which can be detrimental to material performance.[26,29] Work to reduce porosity has been done using initiators that do not form gaseous byproducts. Pojman et al.[30] demonstrated the use of sodium persulfates as gas-free initiators for acrylamide, but this required the use of dimethyl sulfoxide as an organic solvent. In addition to requiring solvent, the shelf life was short. Masere et al.[31] synthesized quaternary ammonium persulfate initiators that are soluble in organic monomers. The initiator had a half-life of 40 days at 25 °C. Mariani et al.[31] demonstrated the use of phosphonium persulfate ionic liquids as organic soluble initiators for frontal polymerization but these also suffered from short shelf lives. More recently, Bomze[21,32] and coworkers studied benzopinacol(1,1,2,2-tetraphenylethanediol) as a non-peroxide gas-free initiator for use with frontal curing of epoxies but it has not been studied with acrylate polymerization. As of this work, all reported gas-free initiators for FP with acrylates require synthesis and have relatively short shelf-lives, that is, less than a week.

Charge transfer complexes (CTCs) are formed through an association between an electron donor and an electron acceptor. The formation of such complexes leads to a bathochromic shift, which extends their absorption into the visible range. Such complexes have been utilized for photoinitiated free-radical polymerization.[33] CTCs have been applied to the cationic photopolymerization of epoxy resins.[34–36] Garra et al.[36–38] studied various CTCs formed between an iodonium salt (the electron acceptor) and amines as the electron donor. Other studies utilized phosphines and indoles as electron-donating components for CTCs.[39,40] The application of CTCs as photoinitiators resulted in the manufacturing of thick and or filled polymeric materials. Despite the potential application of CTCs for shadow curing, the cure rate and conversion decreased as the depth increased.[37] Recently, Gary et al.[41] utilized CTCs based on amines and iodonium salts as novel initiators for frontal polymerization of acrylates. The utilization of CTCs through FP is a way to overcome the challenges of curing thicker samples, but the formation of voids remains an issue.

In this work, a CTC based on a phosphine and iodonium salt was studied as a gas-free initiator for free-radical frontal polymerization of acrylates. 4-(dimethylamino)phenyldiphenyl phosphine (DMAPDP) was utilized as the electron donor while IOC-8 acts as the electron acceptor. The CTC was tested in different monomers, and the effect of the mole ratio of the phosphine to iodonium salt was explored. The effect of adjusting the donor mole ratio while keeping the acceptor quantity constant was also explored for TMPTA and HDDA. Bubble-free samples were produced without the use of synthesis, but relatively short shelf lives were found.

2 | EXPERIMENTAL SECTION

2.1 | Materials and methods

p-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-8) was purchased from Ambeed (Arlington Heights, IL) and Hampford Research Inc. (Stratford, CT). 4-(diphenylphosphino)-*N,N*-dimethylaniline (DMAPDP) was purchased from Ambeed (Arlington Heights, Il). Trimethylolpropane triacrylate (TMPTA) was Miwon Specialty Chemical Co. 1,6-hexanediol diacrylate (HDDA), neopentyl glycol propoxylate diacrylate [NPG $(PO)_2DA$], and EBECRYL® 130 were purchased from Allnex (Alpharetta, GA). 1,4-Butanediol diacrylate (BDDA) was purchased from TCI America (Portland, OR), and trimethylolpropane ethoxylate triacrylate (TMPEOTA) was purchased from Cytec. Milled carbon fiber was purchased from Zoltek, Inc. (St. Louis, MO).

A Seek Thermal Compact—All-purpose thermal imaging camera for iOS was used to collect front temperatures (Figure 1).

p-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-8) was used as the electron acceptor, and 4-(diphenylphosphino)-*N,N*-dimethylaniline (DMAPDP) was used as an electron donor. Figure 2 demonstrates the mechanism of the formation of reactive aryl radicals from the CTC. As the system is solvent-free, IOC-8 and DMAPDP are both solids that were dissolved in liquid acrylate monomers. The number of grams of material added per 100 g of resin is expressed as parts per hundred resins (phr). The mole ratio of DMAPDP was adjusted against 1 phr of IOC-8 salt. It was difficult to dissolve DMAPDP and IOC-8 in the same pot of acrylate due to polymerization before all of the particles were dissolved. The reagents were dissolved in separate jars to prevent polymerization. Three parts of the total liquid acrylate monomer were introduced to the DMAPDP container, while the remaining two parts were placed in the IOC-8 container because IOC-8 is easier to dissolve in acrylates than DMAPDP.

The solids were dissolved with the help of both a Fisher Scientific Digital Vortex Mixer and a M1800 Branson Ultrasonic Bath, 117 V. To dissolve DMAPDP, the sonication was set for 15–20 min, and the temperature was elevated to 45–50°C. To form a CTC, the acceptor was added to the monomer in terms of phr, and the donor was added to the monomer in terms of the mole ratio of donor to acceptor. After being combined, the resultant solutions were placed into borosilicate glass tubes with the dimensions of 16 × 150 mm. All the tubes holding polymerizable CTC monomer solution were heated with a soldering iron from the top. The front propagation was observed using a video camera, and the velocity was calculated by obtaining the slope of the position versus time plot. Every experiment was done in triplicate. Figure 3 shows a cured sample in a test tube.

2.2 | Shelf life

To evaluate the shelf lives of all the formulations, one sample of each recipe was covered in aluminum foil to block light while another sample was left open to ambient fluorescent lighting. The samples were kept in clear polyethylene terephthalate (PET) jars so that the gelation condition could be observed. All the samples for pot lives were 1:1 mole ratio of donor to the acceptor and contained 1.0 phr of the acceptor. The gelation state of the

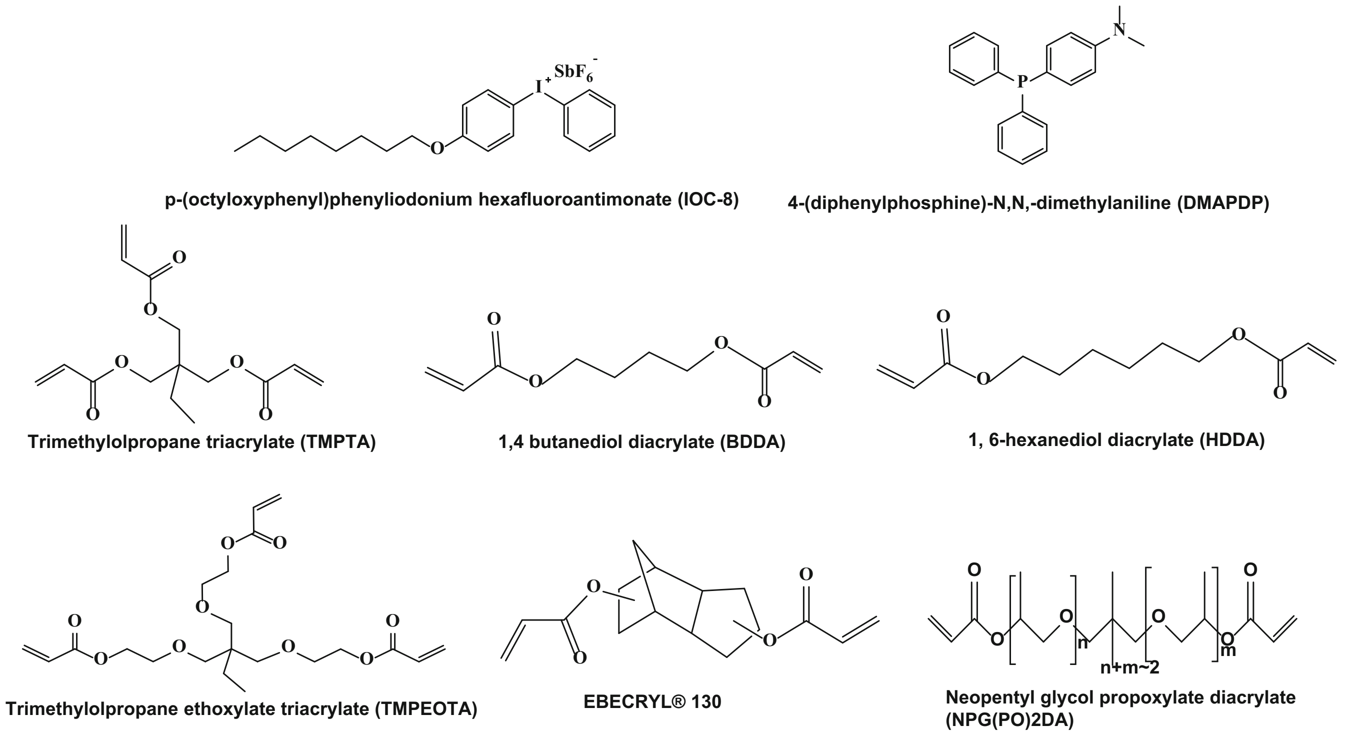

FIGURE 1 Reagents.

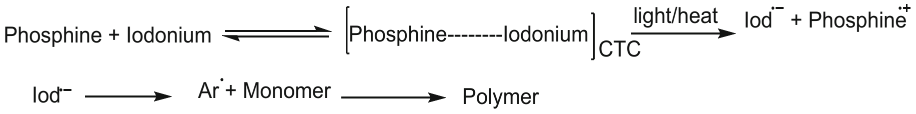

FIGURE 2 General mechanism scheme for the charge transfer complex as a thermal initiator.

FIGURE 3 Charge transfer complex formation indicated by the appearance of yellow color and polymer formation indicated by the disappearance of yellow color into a 16 × 150 mm glass tube. The cured material is in the upper section.

samples was checked at least once every day. The samples were tested to see if they still supported fronts while also seeing how the yellow color of the CTC changed over time. Some samples were refrigerated to determine the effect of temperature on CTC stability.

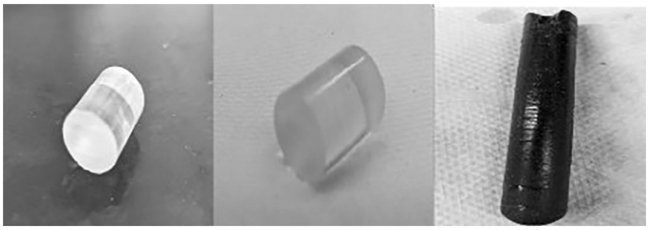

FIGURE 4 Example of some gas and void-free samples prepared in test tubes (15 mm diameter) of TMPTA (left), NPG(PO)$_2$DA (middle), and TMPTA with 10 phr of milled carbon fibers (right).

3 | RESULTS AND DISCUSSION

3.1 | CTC initiator for frontal polymerization

Figure 4 clearly demonstrates that the gas-free initiation of acrylates rendered void-free samples, on the scale of visible light observation. The front velocities of several acrylate monomers are shown in Figure 5. The front propagation with a 1:1 mole ratio of DMAPDP to 1.0 phr IOC-8 rendered bubble-free fronts. Among the monomers tested, BDDA produced the fastest front. TMPTA secured the second fastest fronts, ahead of HDDA. Bynum et al. determined that front velocity increased with the increase of acrylate functionality and decrease of molecular weight per functionality.[41] Therefore, TMPTA should have exhibited the fastest front because the TMPTA's functionality is greater than BDDA's, and its equivalent molecular weight per acrylate group is lower.

In 1991, Pojman reported that the presence of 4-methoxy phenol inhibitor did not affect the front velocity of methacrylic acid polymerization, citing the high concentration of benzoyl peroxide initiator.[5] We removed the inhibitor from TMPTA and BDDA. Strangely, the front velocity for each monomer decreased. BDDA went from 2.9 to 2.4 cm/min, and TMPTA's velocity decreased from 2.25 to 1.5 cm/min. We do not have an explanation for the decrease in velocity nor do we have explanation on why TMPTA supports fronts that are slower than BDDA, a diacrylate.

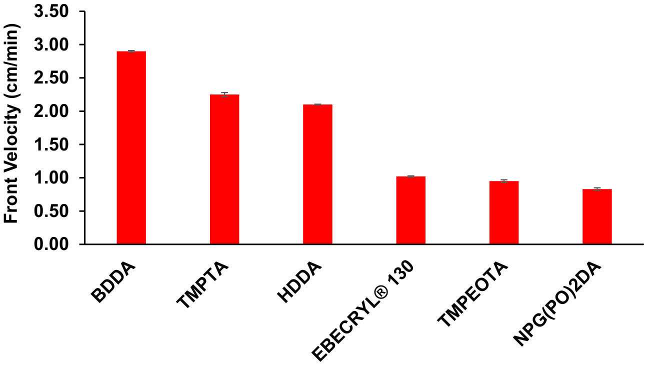

FIGURE 5 Front velocities of different acrylate monomers thermally initiated by 1:1 mole ratio of DMAPDP and 1 phr IOC-8.

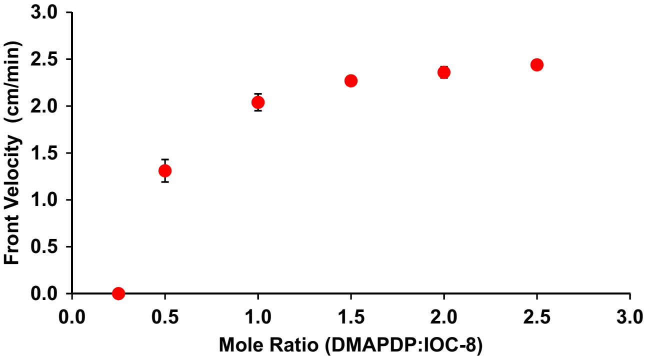

FIGURE 6 Effect of mole ratio of 4-(diphenylphosphino)-*N,N*-dimethylaniline (DMAPDP) on the front velocity of HDDA with 1 phr of the electron acceptor, IOC-8.

The final polymer samples of BDDA, TMPTA, HDDA, EBECRYL® 130, TMPEOTA, and NPG(PO)2DA were obtained using gas-free initiation and were all void-free and rigid. We prepared a sample containing milled carbon fiber to demonstrate the capability of producing void-free composites.

CTCs have been applied to the cationic photopolymerization of epoxy resins.[34–36] We tested our CTC with trimethylolpropane triglycidyl ether and bisphenol A diglycidyl ether but frontal polymerization could not be achieved.

3.2 | Mole ratio study

Figure 6 demonstrates that the front velocity of HDDA increased monotonically as a function of the mole ratio of 4-(diphenylphosphino)-*N,N*-dimethylaniline (DMAPDP) to IOC-8. Because HDDA is highly reactive (because of its low amount of inhibitor), determining the front velocity after a ratio of 2.5:1 was impossible because HDDA polymerized inside the container within a minute with a mole ratio of 3:1 donor to acceptor.

The front velocity of TMPTA fronts was a maximum at a mole ratio of 2:1 donor to acceptor. Optimal ratios of phosphine and iodonium salt were found: 2:1 DMAPDP to IOC-8 for TMPTA and 2.5:1 for HDDA (Figure 7). Upon reaching these ratios, the front velocity for TMPTA reached a maximum velocity despite the addition of more phosphine. Gary et al. demonstrated that front velocity reaches a plateau upon maximum complexation of the donor and acceptor.[40]

We measured the surface temperature of the test tubes using an infrared camera (Figure 8). This is not the same as measuring the front temperatures with a thermocouple but the values are proportional to the maximum

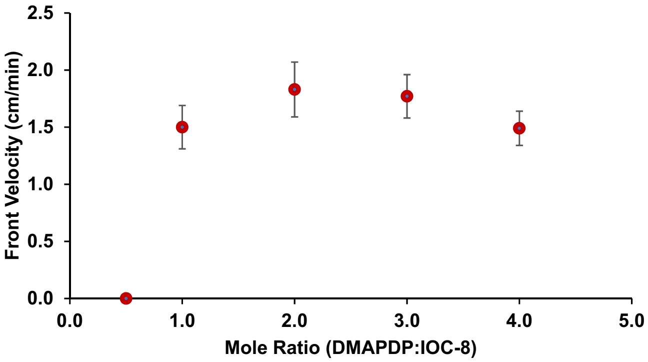

FIGURE 7 Mole ratio effect of DMAPDP to IOC-8 on the front velocity of TMPTA. IOC-8 was kept constant.

front temperatures. These values are significantly lower than values reported by Bynum et al.[42] The front velocities in that study were an order of magnitude larger, which would have reduced the time for heat loss and resulted in higher front temperatures.

3.3 | Shelf-life study

Shelf-life experiments were conducted for all the monomers with a 1:1 donor to acceptor molecule. Except TMPTA and TMPEOTA, all the monomers with the CTC initiator exhibited short pot lives. Table 1 shows that the pot lives of BDDA and HDDA were the shortest, while TMPEOTA, EBECRYL® 130, and NPG(PO)2DA had slightly longer shelf lives than HDDA and BDDA. TMPTA, on the other hand, does not have a measurable shelf life as because the CTC eventually decomposes, and Figure 9 depicts that the decrease in the amount of a CTC was confirmed by a gradual shifting of intense yellow color to light yellow. The front velocities of pot life samples for TMPTA initiated by a 1:1 mole ratio of IOC-8 to DMAPDP were found to decrease over time (Figure 10); after 90 min no fronts would occur. The decrease in front velocity can be attributed to the decomposition of the CTC into unreactive species.

Samples were kept at -5 °C to investigate the effects of the temperature on pot life and front velocity. This increased the shelf life of the TMPTA-CTC to 6 h and the pot-life of the TMPEOTA to 4 days. The front velocity of TMEPOTA was 0.43 cm/min after 4 days. However, TMPTA did not support fronts after 6 h. For the other CTC-resins, such as BDDA, HDDA, EBECRYL® 130, and NPG(PO)$_2$DA, reduced temperature did not increase the pot lives.

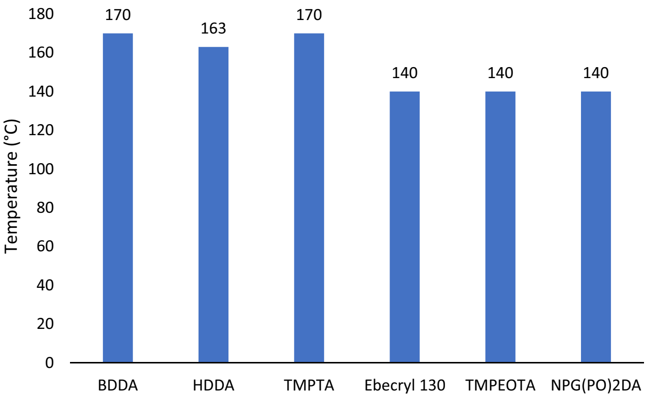

FIGURE 8 The maximum surface temperature of the glass test tubes was measured with an infrared camera, as an indication of the relative front temperatures.

TABLE 1 Shelf lives of acrylate-CTC formulations at ambient condition.

Initiator	Monomers	Shelf lives
1:1 mole ratio of IOC-8 to DMAPDP	TMPTA	<90 min
	TMPEOTA	<60 min
	EBECRYL® 130	<40 min
	NPG(PO)$_2$DA	<40 min
	HDDA	<20 min
	BDDA	<20 min

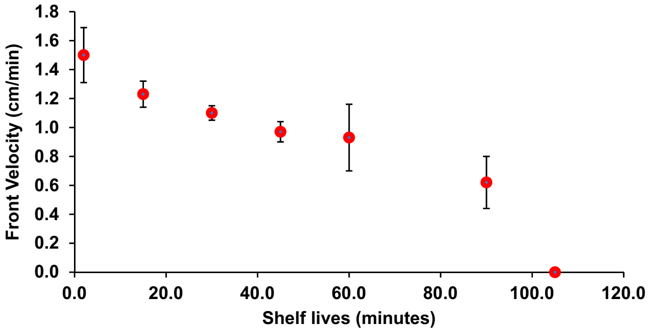

FIGURE 10 Effect of storage time (at ambient condition) on the front velocity of TMPTA with a 1:1 mole ratio of DMAPDP to IOC-8.

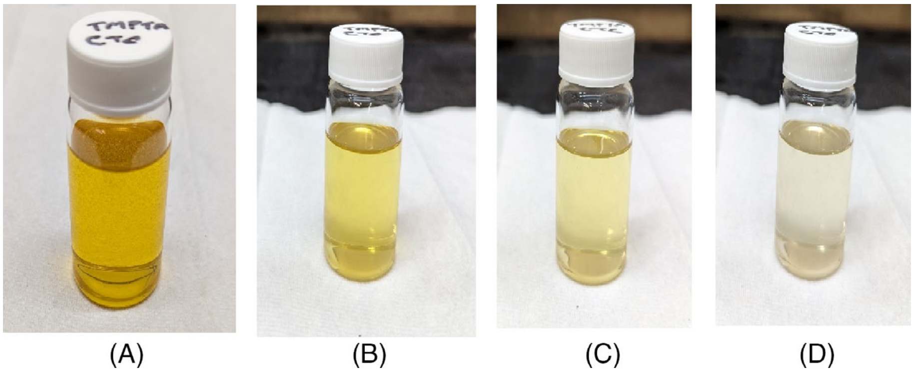

FIGURE 9 Example of TMPTA-CTC color fading overtime, (A) initial color of CTC (left), (B) after 15 min (C) after 60 min, and (D) overnight (right).

4 | CONCLUSION

This CTC initiator involves the formation of a complex between an electron donor and an electron acceptor molecule, which when triggered by heat, initiates frontal polymerization without the generation of gas. This system is a one-pot solvent-free formulation, which means that the solid donor and acceptor molecules were dissolved in the bulk resin. We demonstrated that void-free samples could be prepared by frontal polymerization without synthesis of the initiator. The front velocities were slower than can be achieved with peroxides.

The shelf-life experiments show that the CTC in TMPTA decomposed over time. As the shelf lives of all formulations were discovered to be short, some samples were maintained at low temperatures to investigate if this could increase the shelf lives with active fronts. The reduction in temperature increased the shelf life of the TMPTA and TMPEOTA samples.

TMPTA produced fronts with lower velocities than the diacrylate, BDDA. We do not have an explanation for this unexpected result. Removing the inhibitor reduced the front velocities for both monomers, which is also surprising.

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ORCID

John A. Pojman https://orcid.org/0000-0003-4788-8767

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