

ROLE OF AMINIUM RADICAL IN THE INITIATION OF VINYL POLYMERIZATION

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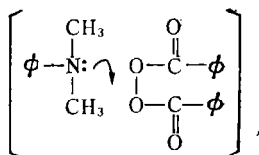
INTRODUCTION

Amine is usually considered as antioxidant, inhibitor or chain transfer agent^[1]. Aromatic secondary amine and hindered piperidine compounds are used as antioxidant and light stabilizers. Aromatic and aliphatic amines themselves will act as chain transfer agents in vinyl polymerization. On the other hand it is also well known that tertiary amines are used either with peroxide to form redox initiation system or with aromatic ketone to form photoinduced initiation system in vinyl polymerization.

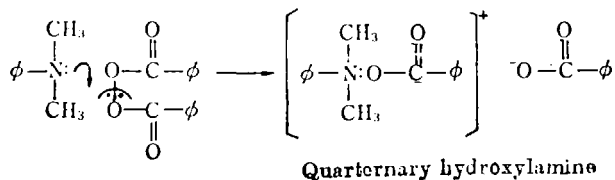
This review is concerned with some generalization regarding to the role of aminium radical in vinyl polymerization especially from the standpoint of reaction mechanism of the initiation system.

AMINIUM RADICAL IN DIACYL PEROXIDE-AMINE SYSTEM

The diacyl peroxide-amine system especially BPO (benzoylperoxide)-DMT (dimethyltoluidine) or BPO-DMA (dimethylaniline) has been used and studied for several decades, but there are still some controversies on its initiation mechanism in vinyl polymerization whether the first step is the formation of a charge transfer complex like



or a rate controlling step of nucleophilic displacement as Walling^[2] suggested:

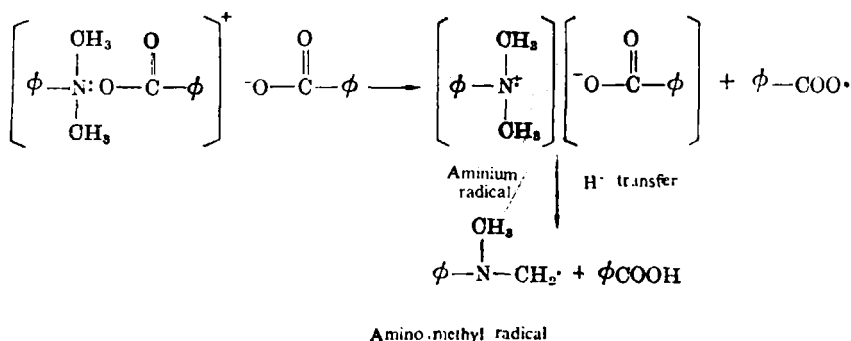


Qiu^[3] reported that the aromatic tertiary amine with electron-rich group on the nitrogen atom increases the rate of decomposition of diacyl peroxide with the result of increasing the rate of polymerization R_p and also determined the E_a of different peroxides and DMT in MMA (methyl methacrylate) polymerization with the following decreasing order, i.e.

Tertiary butyl perbenzoate (TBPB) > Lauryl peroxide (LPO) > BPO

As the acidity of carboxylate is concerned, benzoic acid is more acidic than lauric acid, the anion of the stronger acid will be the more reactive leaving group in nucleophilic displacement reaction, hence the rate of decomposition of BPO-DMT as well as its R_p is greater than that of LPO-DMT. All of the above results favour the Walling's suggestion.

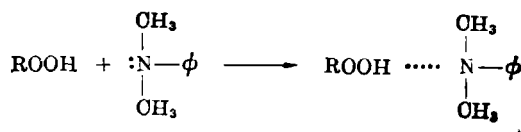
Then the second step will be the decomposition of the quarternary hydroxylamine derivative into aminium radical as intermediate with the following proposed mechanism:



Although Otsu^[4] et al. have studied BPO-DMA system by ESR technique and trapped the amino-methyl radical, yet there is still lack of direct proof of the existence of aminium radical and also no detail in the deprotonation step.

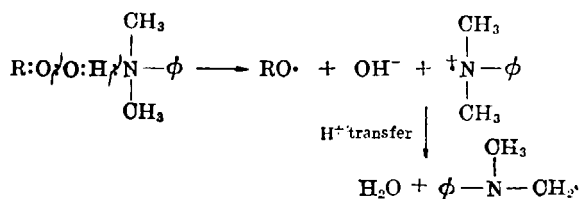
AMINIUM RADICAL IN ORGANIC HYDROPEROXIDE-AMINE SYSTEM

Much less attention has been paid to this system, but Qiu^[5] et al. have investigated the effect of amine structure on the R_p of MMA in bulk polymerization and found that in contrast to diacyl peroxide-amine system^[6], the values of R_p are in the same order whether the substituents are electron-donating group or electron-withdrawing group such as in the range of 0.9 to 1.1 times as much as that of DMA itself. Through the IR spectra of these types of the system, i.e. t-butylhydroperoxide (TBH)-triethylamine (TEA), TBH-DMT and cumene hydroperoxide (CHP)-DMT, and from the evidence of the shift of OH absorption bands to the lower frequency region, Sun^[7] et al. confirmed the formation of hydrogen-bond complex but not a quarternary ammonium salt. So we propose the first step as

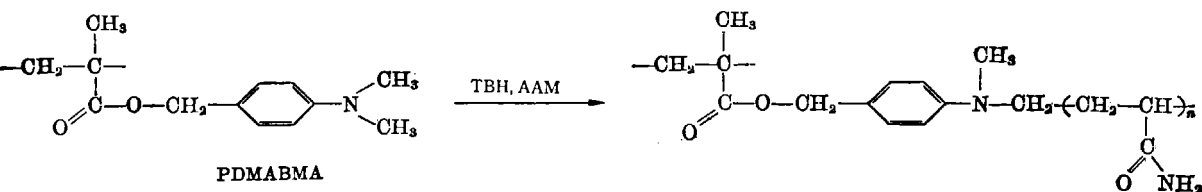


Through ESR technique the same radical as that of BPO-DMT system but with weaker signal

has been obtained. Therefore the above results favour the formerly proposed mechanism by Feng and Qiu^[8] as follows:



The presence of the above aminomethyl radical has also been verified^[9] through UV analysis of the polymer formed such as PAN (polyacrylonitrile) or PMMA with the characteristic band as the end groups. Moreover when the polymer containing DMT moieties such as in the following polymer PDMABMA and TBH were used as initiation system to polymerize acrylamide (AAM), some graft polymer was obtained according to the following scheme:

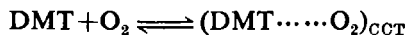


Through chromatographic analysis of the TBH–DMT reaction products we have also detected the presence of H_2O as the above proposed mechanism required in the deprotonation step.

AMINIUM RADICAL IN AMINE– O_2 SYSTEM^[10]

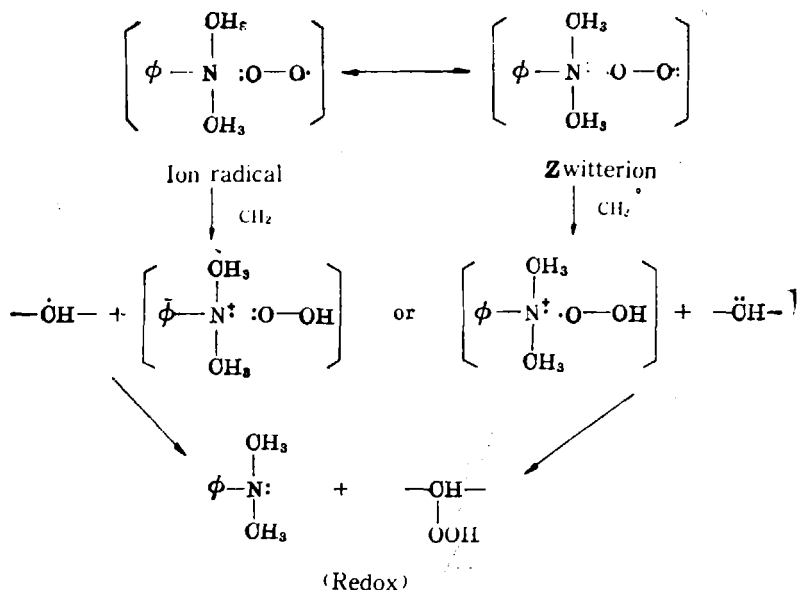
Cao and Feng^[11,12] have discovered that amine compounds such as DMT, DMA or PHZ (phenylhydrazine) in the presence of micro amount of O_2 will act as initiation system of vinyl polymerization for those monomers with $\alpha\text{-CH}_3$ linkage as in MMA or with active $-\text{CH}_2-$ linkage as in methoxyethyl methacrylate (MEMA). We have also verified that in a closed-air system in the presence of catalytic amount of amine and monomer, the oxygen content will drop down and polymerization proceeds. The amine molecule will enhance the oxygen absorption and the aromatic tertiary amine with electron-donating group on the benzene ring will still increase the oxygen absorption as well as the rate of polymerization.

Through careful IR analysis the characteristic band of $-\text{OOH}$ at 3400 cm^{-1} has been verified. From kinetic studies of vinyl polymerization with DMT– O_2 system, the E_a was determined with low values corresponding to redox initiation system and the values R_p appear to be proportioned to $[\text{DMT}]^{1/2} [\text{MMA}]^{3/2}$. So it is quite reasonable to consider the amine– O_2 system as the precursor of DMT– ROOH system with the following first step as



The formation of contact charge transfer (CCT) of amine– O_2 has been verified from absorption spectra^[13]. The structure may be assigned either as ion-radical or zwitterion as the

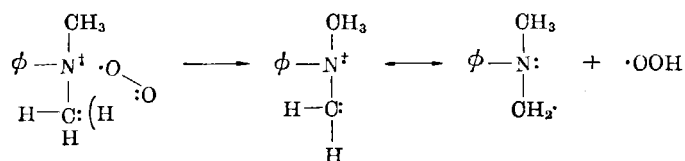
following:



In the absence of monomer we found that DMT-O₂ CCT in acetonitrile solvent will react itself to form oxidized products such as



So we propose that deprotonation from the α -carbon atom as the intermediate step:

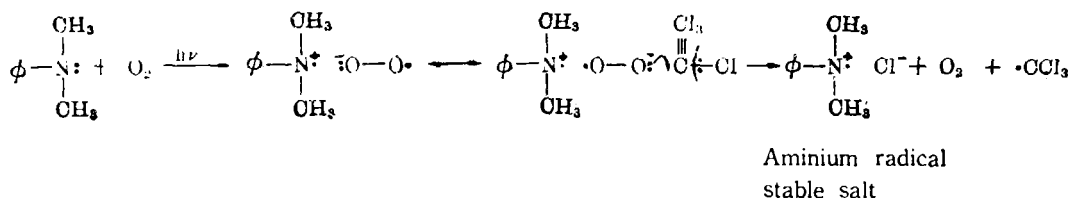


FORMATION OF AMINIUM RADICAL STABLE SALT THROUGH AMINE-O₂ SYSTEM

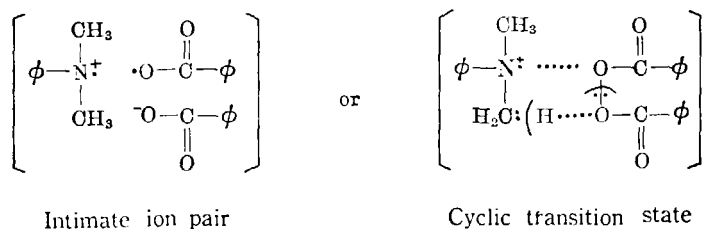
Latowski^[14] reported that DMT would react with CCl₄ under light to form purple colored substances which he supposed to be aminium radical. We repeated this reaction and discovered^[15] that the presence of O₂ is necessary, otherwise no purple colored product will be formed. We performed the elementary analysis of the products and characterized by UV and NMR with the results corresponding to aminium radical chloride which is water soluble and persists its purple color as stable salt.

We have observed and verified the formation of DMT-O₂ CCT which may serve as an effective electron donor to CCl₄ molecule while the photosensitized DMT alone is unable. Since the UV light was filtered i.e. cut off all <300 nm to ensure that it will not photolyze the CCl₄,

molecule, so we propose the following displacement mechanism:



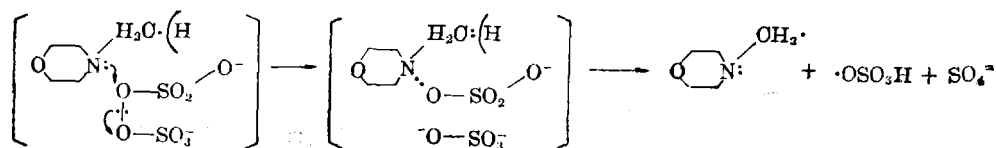
This aminium radical salt in aqueous solution is rather stable and will not polymerize acrylonitrile (AN) even with $\text{C}_6\text{H}_5\text{COONa}$ which was usually supposed to extract H^+ from the aminium radical to form the amino-methyl radical. So we^[10] incline to believe that the solvated aminium radical will not be deprotonated by $\text{C}_6\text{H}_5\text{COO}^-$ anion, and only the intimate ion pair or in the form of cyclic transition state will proceed the deprotonation as follows:



We^[15] have also discovered that this aminium radical chloride is rather reactive toward thiophenol as H abstractor to form $\text{C}_6\text{H}_5\text{S} \cdot$ radical which then polymerizes AN monomer as usual.

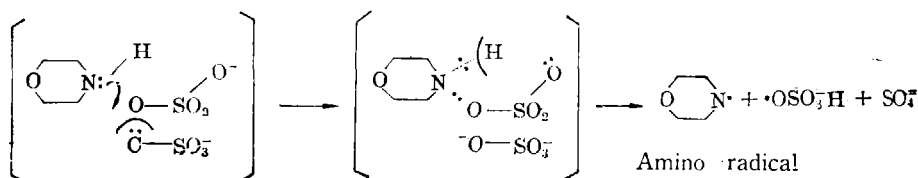
AMINIUM RADICAL IN PERSULFATE-AMINE SYSTEM

We^[17] have investigated the persulfate-amine system in the initiation of vinyl polymerization and verified that all kinds of aliphatic or cyclic amine will form redox system with $\text{K}_2\text{S}_2\text{O}_8$ in aqueous solution in which diethylamine, piperidine and N-methyl morpholine show the best results in their corresponding homologue amines. The E_a value were determined to be around 30 KJ/mole with molecular weights showing no serious chain transfer in the polymerization. Therefore we propose the following reaction mechanism which involves the formation of aminium radical as the intermediate step. In case of morpholine this secondary amine would form amino radical instead of methyl radical as follows:



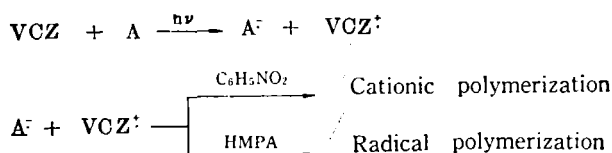
Cyclic transition state

Intimate ion pair

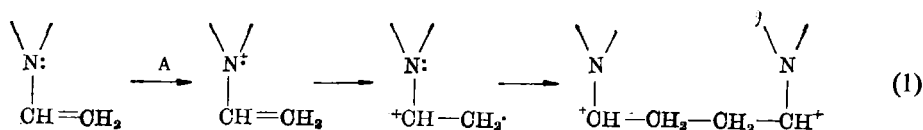


FORMATION OF AMINIUM RADICAL THROUGH TERTIARY AMINE CTC OR EXCIPLEX

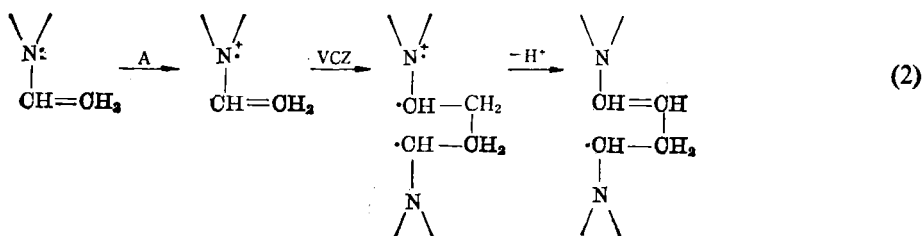
A substantial number of photoinduced charge transfer polymerization has been known to proceed through N-vinylcarbazole (VCZ) as an electron donating monomer with some electron-acceptor (A), such as tetracyanoethene (TCNE) or fumaronitrile (FN). It can be summarized^[18] as follows:



The first step is the formation of exciplex between VCZ and A under irradiation, then cationic polymerization will proceed in the presence of less basic solvent such as nitrobenzene as equation (1), while radical polymerization will take place predominantly in strong basic solvent such as hexamethyl phosphoric triamide (HMPA) as equation (2):



Cationic polymerization
in nitrobenzene

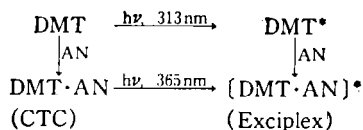


Radical polymerization in HMPA

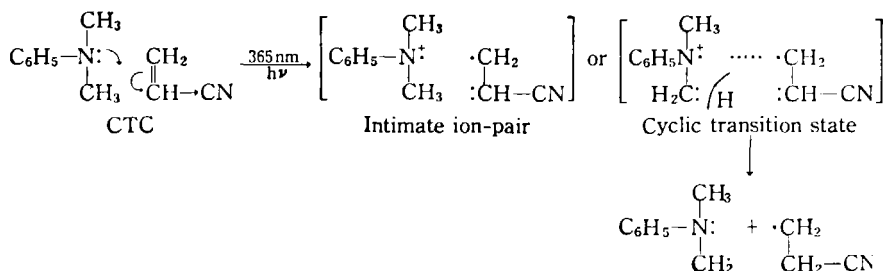
The last step of equation (2) shows the deprotonation of the aminium radical to form an alkyl radical as reactive species for free radical initiation of polymerization.

But much less attention was paid to the polymerization of acrylic monomers as electron-acceptor in the presence of amine as a donor. The photoinduced charge transfer polymerization of electron-attracting monomer such as methyl acrylate (MA)^[19] and acrylonitrile (AN)^[20] has been studied recently in our laboratory^[21].

Through UV spectra we have verified the formation of charge transfer complex (CTC) from AN and DMT and this CTC was then photoactivated with 365 nm light to form exciplex. If 313 nm light was used, DMT will be activated at first and then form exciplex directly with the ground state AN molecule as follows:

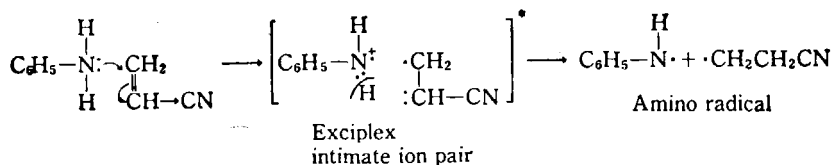


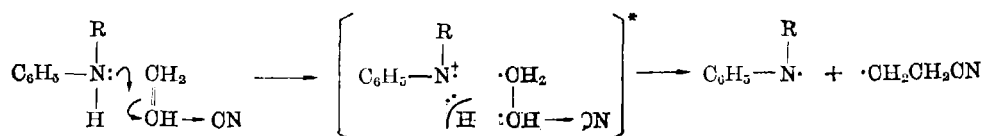
Feng^[16] proposed the formation of aminium radical as the active state of the exciplex either in the form of an intimate ion-pair or cyclic transition state which then will undergo proton transfer process of deprotonation leading to the formation of active radical species for initiation as follows:



FORMATION OF AMINIUM RADICAL THROUGH AROMATIC SECONDARY OR PRIMARY AMINE CTC OR EXCIPLEX

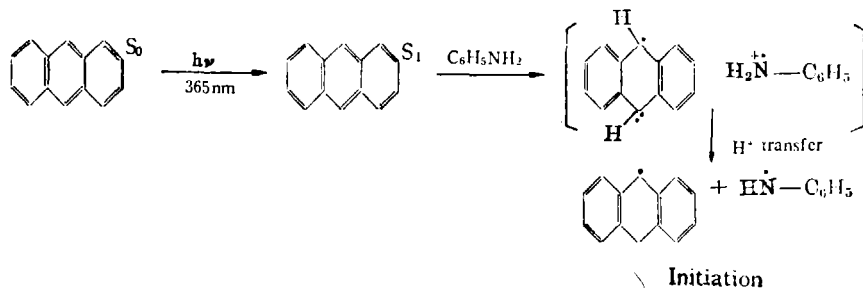
In our laboratory, Li^[22] found that aniline alone will proceed the photopolymerization of AN either in DMF solution or in bulk with fair rate of polymerization only next to DMT. From UV spectra it is proved that aniline will form CTC with AN. Using 313 nm the CTC is then excited to exciplex and polymerization proceeds. N-methyl aniline will polymerize AN similarly. The following mechanism was proposed:





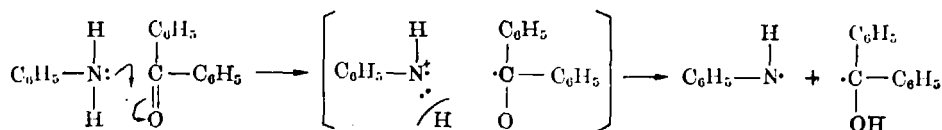
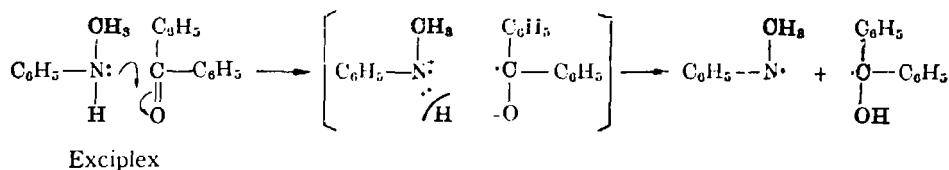
Thus deprotonation of the aminium radical from secondary or primary amine will at last form amino radical instead of amino-alkyl radical as well as the $\cdot\text{CH}_2\text{CH}_2\text{CN}$ radicals. This amino radical will then serve as the active species for initiation of polymerization.

Barton^[23] reported that condensed aromatic hydrocarbon (CAH) alone will act as photoinitiator and also will form exciplex with amine. However, Kubota^[24] pointed out that aniline or N-methylaniline (NMA) will inhibit this CAH initiated photopolymerization of vinyl monomers. Li^[25] et al. have studied CAH-aniline system and detected the radical intermediate produced by photoreaction between anthracene and aniline with ESR spectra. The initiation of polymerization involves the formation of exciplex from the excited singlet state of CAH and the ground state of aniline molecule as the first step and then followed by proton transfer leading to the generation of two kinds of radical species. From the end group analysis of the polymer obtained it is verified that both species are involved in the initiation process. So we propose the reaction mechanism as follows:



FORMATION OF AMINIUM RADICAL THROUGH BENZOPHENONE AND PRIMARY OR SECONDARY AROMATIC AMINE

The well known photopolymerization of acrylic monomers is usually involved in the charge transfer system with carbonyl compound as an acceptor and aliphatic tertiary amine say triethylamine (TEA) as a donor. Instead of tertiary amine such as TEA or DMT, Li^[26] et al. investigated the photopolymerization of AN in the presence of benzophenone (BP) and aniline (A) or N-methylaniline (NMA) and found that BP-A or BP-NMA system will give higher rate of polymerization than that of the well known system of BP-TEA. Still we know that secondary aromatic amine would be deprotonated the H-atom mostly on N-atom so we propose the mechanism as follows:



Thus aminium radical from primary or secondary amine will at last form amino radical instead of amino-methyl radical. This amino radical will then serve as the only active radical species to initiate the vinyl polymerization.

The end groups of the polymers, photoinitiated with aromatic amine with or without the presence of carbonyl compound BP, have been detected with absorption spectrophotometry and fluorescence spectrophotometry^[26]. The spectra showed the presence of secondary amino end group in the polymers initiated with primary amine such as aniline and the presence of tertiary amino end group in the polymer initiated with secondary amine such as NMA. These results show that the amino radicals, formed through the deprotonation of the aminium radical in the active state of exciplex from the primary or secondary aromatic amine molecule, are responsible for the initiation of the polymerization.

CONCLUSION

The above survey is concerned with some generalization with emphasis on the reaction mechanism regarding to the role of aminium radical in the initiation of vinyl polymerization. Most of the amines including primary, secondary and tertiary amine with active H atom either on the N atom or on the α -carbon atom appear to initiate the vinyl polymerization either in the form of redox system or in the form of exciplex through the common intermediate of aminium radical which serves as the precursor of the reactive species for initiation such as the amino alkyl radical from tertiary amine or the amino radical from secondary or primary amine.

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