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Polymeric photoinitiators containing in-chain benzophenone and coinitiators amine: Effect of the structure of coinitiator amine on photopolymerization

Xuesong Jiang, Xiaowei Luo, Jie Yin*

Research Institute of Polymer Materials, School of Chemistry and Chemical Technology, State Key Laboratory for Composite Materials, Shanghai Jiao Tong University, Shanghai 200240, PR China

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Abstract

Through introducing of benzophenone and different coinitiator amines, three kinds of polymeric photoinitiator, PBPB, PBPE and PBPP, were synthesized. The UV–vis spectra of these polymeric photoinitiators are similar to the parent benzophenone. The photopolymerization of two monomers, methyl methacrylate (MMA) and poly(propylene glycol) diacrylate (PPGDA), initiated by these three types of polymeric photoinitiators was studied by dilatometer and photo-DSC. The results show that the structure of coinitiator amine has important influence on photopolymerization and different photoinitiators exhibit different behavior towards different monomers: PBPP is the most efficient for MMA, and PBPE is the most efficient for PPGDA.

Keywords: Polymeric photoinitiator; Photopolymerization; Benzophenone; Coinitiator amine

1. Introduction

Compared with low molecular weight analogues, polymeric photoinitiators have some advantages and obtained much attention recently [1–9]. Through introducing the photoinitiator chromophore into side-chain of polyacrylates, a large amount of polymeric photoinitiators have been synthesized. These polymeric photoinitiators have two kinds of radical photoinitiator: photofragmentation (type I photoinitiators) and hydrogen abstracting chromophores (type II photoinitiators). Among them, benzophenone is one of the most widely used bimolecular photoinitiators in photopolymerization and its photoinitiation activity can be promoted by the presence of hydrogen donor amines [10–14].

The interaction between the benzophenone and coinitiator amine, which involves an electron and proton transfer process, plays a very important role in the process of generation of active radicals. Therefore, the yield of the primary photochemical process is strongly dependent on the structure of the amine, which has an important effect on the production of radicals [15,16].

The dependence of the photopolymerization on the structure of amine has been reported [15,17,18]. However, there are few studies about the effect of coinitiator amine contained in polymeric photoinitiator on photopolymerization. Recently, we studied the effect of the structure of coinitiator amine in polymeric thioxanthone photoinitiator on photopolymerization [19,20]. In this context, a series of polymeric benzophenone photoinitiator were synthesized using step-growth polymerization by the introduction of benzophenone and different coinitiator amine monomers. We choose two representative types of monomer with different functionality, a monofunctional monomer methyl methacrylate (MMA) and a difunctional monomer poly(propylene glycol) diacrylate (PPGDA) to be initiated by these polymeric photoinitiators, in order to obtain some

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* Corresponding author. Tel.: +86 21 54746215; fax: +86 21 54741297.
E-mail address: jyin@sjtu.edu.cn (J. Yin).

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useful information about the effect of the structure of coinitiator amine in these polymeric benzophenone photoinitiator on the photopolymerizaton of different multifunctional monomers.

2. Experimental

2.1. Materials

Piperazine, *N*,*N*′-dimethylethylenediamine, *N*,*N*′-diethyl-2-butene-1,4-diamine (from Acros), 4,4′-dihydroxyl benzophenone (DHBP, from Xiangfan Yuchang Fine Chemical Company). PPGDA (from Adrich), methyl metharylate (from Chinese Medicine Group) was washed with 5% aqueous NaOH solution, dried over anhydrous Na_2CO_3 and distilled. Epichlorohydrin was purified by refluxing with calcium hydroxide and redistilled. Other chemicals are of analytical grade except as noted.

2.2. Synthesis of 4,4′-di (2,3-epoxypropyloxy) benzophenone (DEBP)

A mixture of 4,4′-dihydroxyl benzophenone (10.5 g, 0.05 mol), epichlorohydrin (30 ml, 0.36 mol), anhydrous potassium carbonate powder (15 g, 0.1 mol), butanone (80 ml), and polyethylene glycol (PEG-400, 1 ml), was stirred for 12 h at 80 °C and then refluxed for 6 h at 120 °C in oil bath. The organic layer was poured out after cooling, and the inorganic residue was washed with butanone until the solution became colorless. The combined organic solution was distilled to remove the solvent and excess epichlorohydrin, and the residue was dissolved in dimethyl sulfoxide (DMSO). The solution was poured with stirring into 10-fold water, and filtered. The residue was recrystallized from ethanol.

m.p.: 142 °C. EIMS (70 eV) *m/e*: 326. $C_{19}H_{18}O_5$ ($326\,g\,mol^{-1}$): Calcd. C 69.93, H 5.52; Found: C 69.12, H 5.63. ^1H NMR ([-d_6] DMSO, 400 MHz): $\delta = 7.68$, 7.09 (8H, aromatic), 4.54, 3.96 (4H, OCH_2–), 3.36 (2H, –CH, epoxide), 2.86, 2.71 (4H, –CH_2, epoxide). FT-IR (KBr, cm^{-1}): 1640(C=O), 1296, 1040 (Ar–O–C), 1268, 909 (epoxy group).

2.3. Synthesis of polymeric photoinititiators

The polymeric photoinitiators were synthesized according to Scheme 1. 4,4′-Di (2,3-epoxypropyloxy) benzophenone (0.0112 mol) was dissolved in DMSO (8 ml), and then 0.0113 mol diamine monomer (piperazine, *N*,*N*′-dimethylethylenediamine, *N*,*N*′-diethyl-2-butene-1,4-diamine) was added into the stirred solution. The mixture was stirred at 80 °C for 12 h, and then poured into 10-fold diluted aqueous solution of NaOH. The solution was filtered to give product, which was dried in vacuo to obtain polymeric photoinitiator.

PBPP: $Mn = 5.9 \times 10^3$, $Mw/Mn = 1.30$ (determined by GPC using DMF as an eluent). ^1H NMR ([-d_6] DMSO, 400 MHz): $\delta = 7.67$–7.08 (8H, aromatic), 4.93 (2H, –OH), 4.22–3.95 (6H, –OCH_2, –OCH), 2.52–2.33 (12H, –NCH_2). FT-IR (KBr, cm^{-1}): 3396 (O–H), 2923, 2813 (C–H), 1640 (C=O).

PBPE: $Mn = 4.4 \times 10^3$, $Mw/Mn = 1.2$ (determined by GPC using DMF as an eluent). ^1H NMR ([-d_6] DMSO, 400 MHz): $\delta = 7.68$, 7.09 (8H, aromatic), 4.98 (2H, –OH), 4.21–3.93 (6H, –OCH_2, –OCH), 2.48–2.41 (14H, –NCH_2, –NCH_3). FT-IR (KBr, cm^{-1}): 3395 (O–H), 2927, 2808 (C–H), 1640 (C=O).

PBPB: $Mn = 4.5 \times 10^3$, $Mw/Mn = 1.2$ (determined by GPC using DMF as an eluent). ^1H NMR ([-d_6] DMSO, 400 MHz): $\delta = 7.68$, 7.09 (8H, aromatic), 5.55 (2H, –CH=CH–), 4.90 (2H, –OH), 4.21–3.91 (6H, –OCH_2, –OCH), 3.05–2.49 (12H, –NCH_2), 0.96–0.87 (6H, –CH_3). FT-IR (KBr, cm^{-1}): 3396 (O–H), 2927, 2827 (C–H), 1640 (C=O).

2.4. Measurement

2.4.1. Physicochemical measurements

Molecular weights were determined by gel permeation chromatography (GPC) on a Perkin-Elmer Series 200 apparatus on the basis of linear polystyrene (PS) standards. Both THF and DMF were used as eluents.

^1H NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer with DMSO-d_6 as solvent.

FT-IR spectra were recorded on a Perkin-Elmer Paragon1000 FTIR spectrometer. The samples were prepared as KBr disc.

UV–vis spectra were recorded in ethanol solution on Perkin-Elmer Lambda 20 UV–vis spectrophotometer.

Differential scanning calorimetric (DSC) analysis was conducted on a Perkin-Elmer Pyris 1 DSC.

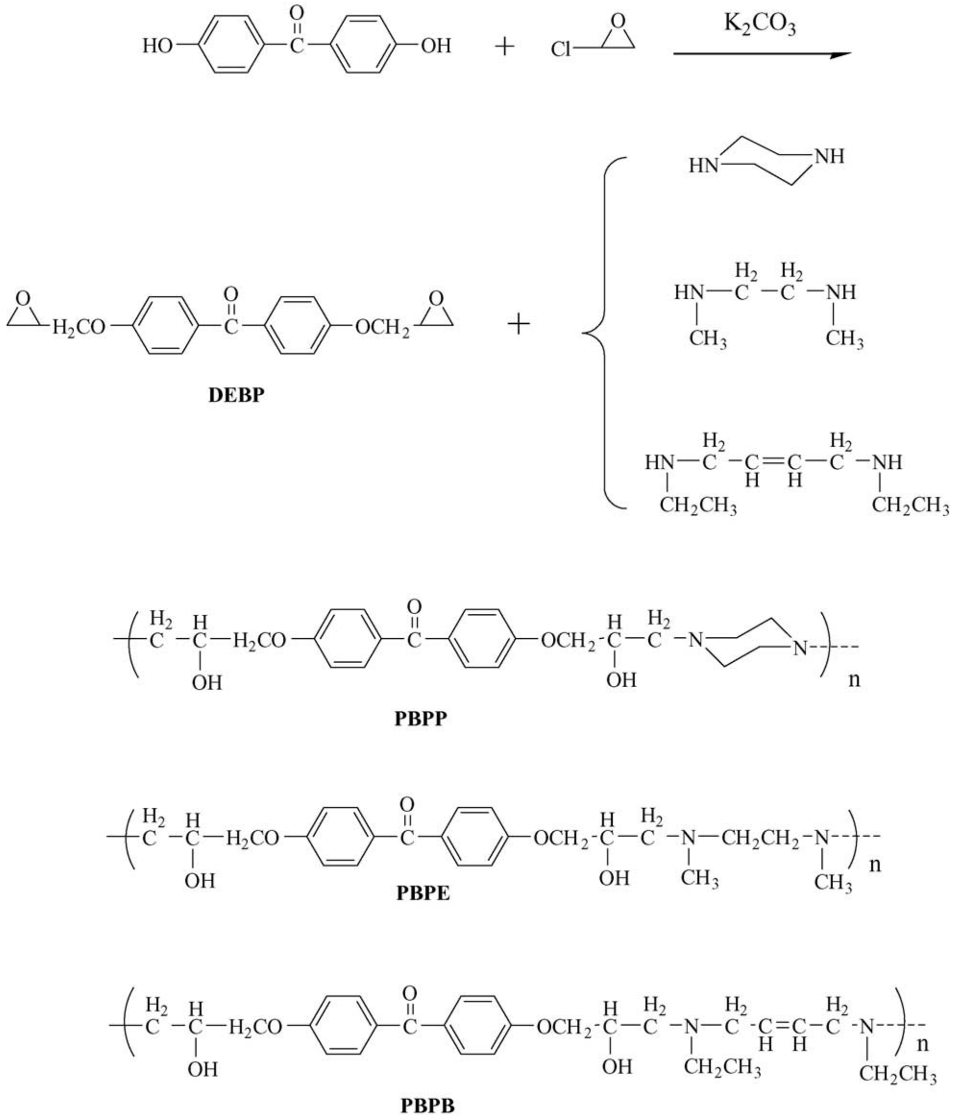
2.4.2. Photopolymerization

The studies of photopolymerization kinetics for MMA were performed dilatometerically on a recording dilatometer by irradiating about 12 ml of 3.0 M MMA solution in DMF at 30 °C (according to [19]). The concentration of photoinitiator is 0.001 M. The light source was a high-pressure Hg lamp (400 W), set at a distance of 40 cm from the sample. The polymerization rate (R_p) was determined below 10% conversion where R_p is almost independent of the conversion.

2.4.3. Photocalorimetry (photo-DSC)

The photopolymerization of PPGDA was carried out by DSC 6200 (Seiko Instrument Inc.) photo-DSC according to [21]. Approximately 2 mg sample mixture was placed in the aluminum DSC pan.

Heat flow versus time (DSC thermogram) curves were recorded in an isothermal mode under a nitrogen flow of



Scheme 1.

$50\,\text{ml}\,\text{min}^{-1}$. The reaction heat liberated in the polymerization was directly proportional to the number of vinyl groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of reaction could be determined according to:

$$C = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}} \tag{1}$$

where ΔH_t is the reaction heat evolved at time t, and $\Delta H_0^{\text{theor}}$ is the theoretical heat for complete conversion. $\Delta H_0^{\text{theor}} = 86\,\text{kJ}\,\text{mol}^{-1}$ for an acrylic double bond [22]. The rate of polymerization (R_p) is directly related to the heat flow ($\text{d}H/\text{d}t$) by the following equation:

$$R_\text{p} = \frac{\text{d}C}{\text{d}t} = \frac{\text{d}H/\text{d}t}{\Delta H_0^{\text{theor}}} \tag{2}$$

3. Results and discussions

3.1. Synthesis

Polymeric photoinitiators containing in-chain benzophenone and coinitiator amines with different structure were synthesized according to Scheme 1. By FT-IR, ^{1}H NMR and GPC spectra, their structures were confirmed. Compared with DEBP and amine monomer, the disappearance of signals related to the epoxy and secondary amine groups, accompanied by the occurrence of the hydroxyl signal in the IR and ^{1}H NMR spectra of polymeric photoinitiators, were considered as an evidence of the completion of reaction. The molecular weight of polymeric photoinitiator determined by GPC also confirmed this result. Some physical and chemical properties of three kinds of polymeric photoinitiators are shown in Table 1.

Table 1
Some properties of three kinds of polymeric photoinitiators

Photoinitiator	PBPP	PBPE	PBPB
λ_{max} (nm)[a]	295	295	295
$\varepsilon \times 10^{-4}$ (L mol^{-1} cm^{-1})[a]	1.24	1.40	1.30
T_g (°C)	39.0	28.5	−7.6

[a] The photoinitiator concentration is 5×10^{-5} M in terms of benzophenone moieties in ethanol.

3.2. UV–vis spectra

UV–vis spectra of the three polymeric photoinitiators in ethanol are shown in Fig. 1. PBPP, PBPE and PBPB exhibit the usual characteristic absorption of benzophenone with a maximum at 295 nm, which shows that the macromolecular structure and coinitiator amine have no significant influence on the UV–vis absorption of benzophenone moieties in polymeric photoinitiators. Because of the efficient light absorption, the high molar absorption makes these polymeric photoinitiators attractive as photoinitiators.

3.3. Photopolymerization of MMA

In the presence of coinitiators such as amines, the photolysis of benzophenone leads to the formation of radicals produced from a carbonyl compound (ketyl-type radical) and the other radicals derived from the coinitiator amines through the proton and hydrogen transfer between benzophenone and amines. Because the ketyl radicals are not reactive towards vinyl monomers due to the steric hindrance and the delocalization of unpaired electron, the polymerization of vinyl monomers is usually almost initiated by amine radicals [10,23]. The overall mechanism of the photoinitiation is represented in Scheme 2, from which we can know that the quantity and activity of amine radicals determine the photopolymerization rate. Fig. 2 shows conversion of MMA versus time for three polymeric photoinitiators. As can be seen, the polymerization rate of MMA initiated by PBPP is the largest and that initiated by PBPB is the smallest, which is also shown in Table 2. This result may be addressed to the most-effective energy transition along the PBPP chain between the excited state of benzophenone and the amine. In order to make the proton and hydrogen transfer fast, both benzaophenone and amine group must get as close as possible. Compared with PBPE and PBPB, the absence of side-group (methyl group in PBPE and ethyl group in PBPB) connected to amine in macromolecular chain could lead to the least steric hindrance, which may result in the highest efficiency for the quenching of the excited benzophenone by amine group, and the fastest proton and hydrogen transition [20,24]. Therefore, the largest amount of amine radicals are generated in PBPP photoinitiator systems, which determined the highest efficiency of photoinitiation of MMA. Compared with ethyl

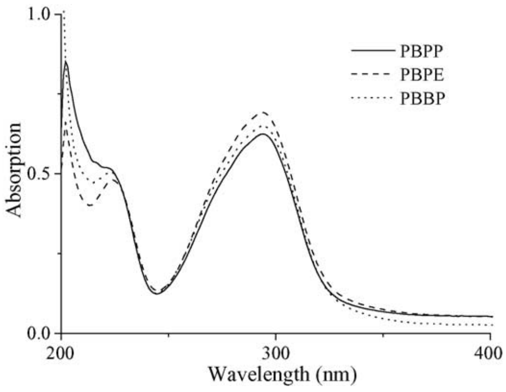
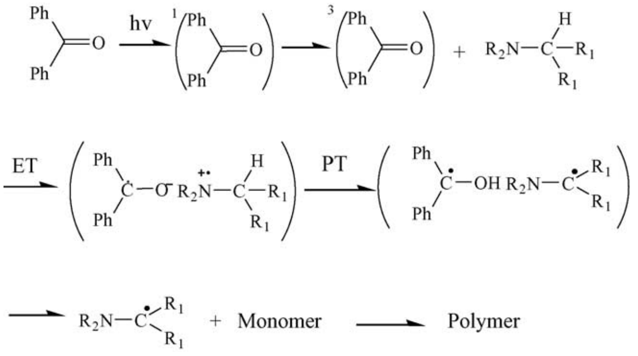


Fig. 1. UV–vis absorption spectra of PBPP, PBPE and PBPB in ethanol (the concentration is 5×10^{-5} M in term of benzophenone moieties).



Scheme 2.

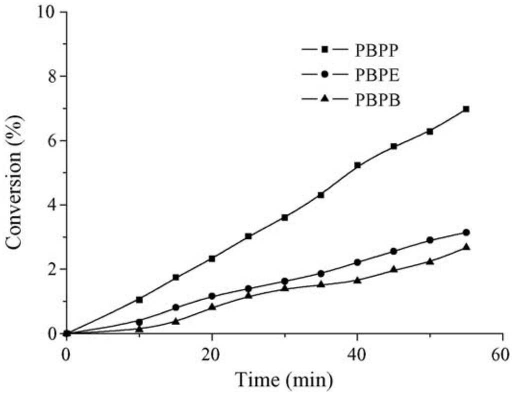


Fig. 2. Conversion vs. time curves for the polymerization of MMA in DMF photoinitiated by PBPP, PBPE and PBPB. The photoinitiator concentration is 0.001 M in terms of benzophenone moieties and the MMA concentration is 3 M.

Table 2
Polymerization[a] of MMA photoinitiated by PBPP, PBPE and PBPB in DMF at 30 °C

Photoinitiator	R_p ($\times 10^5$ mol L^{-1} s^{-1})	Mn[b] ($\times 10^{-4}$ g mol^{-1})	Mw/Mn
PBPP	19.5	4.94	2.10
PBPE	8.9	4.24	2.04
PBPB	7.4	4.32	2.16

[a] The photoinitiator concentration is 0.001 M in terms of BP moieties and [MMA] is 3 M.

[b] Determined by GPC using THF as an eluent.

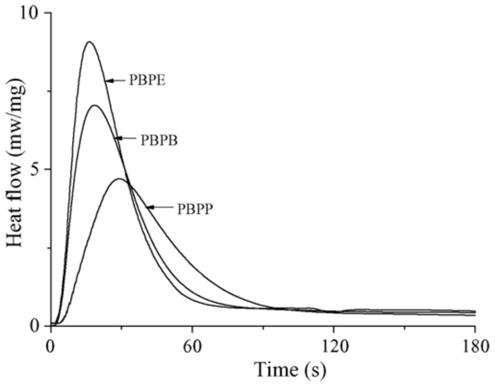


Fig. 3. Photo-DSC profiles for polymerization of PPGDA initiated by PBPP, PBPE and PBPB, cured at 25 °C by UV light with an intensity of 50 mW cm^{-2} (the photoinitiator concentration is 0.001 M in term of benzophenone moieties).

group in PBPB, the steric hindrance of methyl group in PBPE may be smaller, resulting in the higher polymerization rate of MMA.

3.4. Photopolymerization of PPGDA

The photo-DSC profiles of the polymerization of PPGDA for three polymeric photoinitiators are shown in Fig. 3. The polymerization behavior appears similar to other multifunctional monomers [25–29]. Fig. 4(a) shows that the conversion corresponding to the maximum of polymerization (R_{rmax}) is dependent on photoinitiaitor. Fig. 4(b) shows that the final conversion of polymerization for PBPE is the largest. The data for R_{pmax} and final conversion of polymerization of PPGDA is also shown in Table 3. From Fig. 4 and Table 3, PBPP is the least efficient photoinitiator for the polymerization of PPGDA, which is in contrast to the polymerization of MMA. This may be attributed to the different structures of the three macrophotoinitiators and vinyl monomers. Compared with PBPB and PBPE, the macromolecular chain of PBPP is the most rigid, and cannot move freely during the polymerization process of PPGDA because of the high viscosity of PPGDA, leading to very small conversion. The major differences between PBPE and PBPB photoinitiation systems were that the polymerization rate of PBPE is higher than that of PBPB at early stage, but slower at later stage. At early stage, the steric hindrance of methyl group in PBPE is smaller than that of ethyl group in PBPB, leading to more active radicals and the higher polymerization rate of PPGDA for PBPE. As the polymerization goes on, the increasing crosslinking level limits the mobility of monomers. At this stage, the mobility of macromolecular radicals is the most important factor to polymerization rate. Compared with PBPE, the longer side group and double bond in PBPB make its mobility higher (can be also seen in Table 1), which leads to the faster polymerization rate of PPGDA for PBPB at the later stage.

Table 3
Phtopolymerization[a] of PPGDA initiated by PBPP, PBPE and PBPB, cured at 25 °C by UV light with an intensity of 50 mw cm^{-2}

Photoinitiator	R_{pmax}[b] × 10^2 (s^{-1})	Final conversion[c] (%)
PBPP	1.47	65.8
PBPE	2.85	76.2
PBPB	2.21	72.4

[a] The photoinitiator concentration is 0.01 M in term of benzophenone moieties.

[b] R_{pmax} is obtained from Fig. 4(a) and corresponding to the maxim of conversion rate of double bonds.

[c] Final conversion is the final double bond (C=C) conversion.

4. Conclusions

In this article, we synthesized three kinds of polymeric photoinitiator by step-polymerization of benzophenone and different amino monomers, then studied the photopolymerization of monofunctional monomer MMA and difunctional monomer PPGDA initiated by the three macrophotoinitiators through dilatometer and photo-DSC. It is found that the structure of coinitiator amine has important effect on photopolymerization: PBPP is the most efficient for MMA, PBPE is the most efficient for PPGDA.

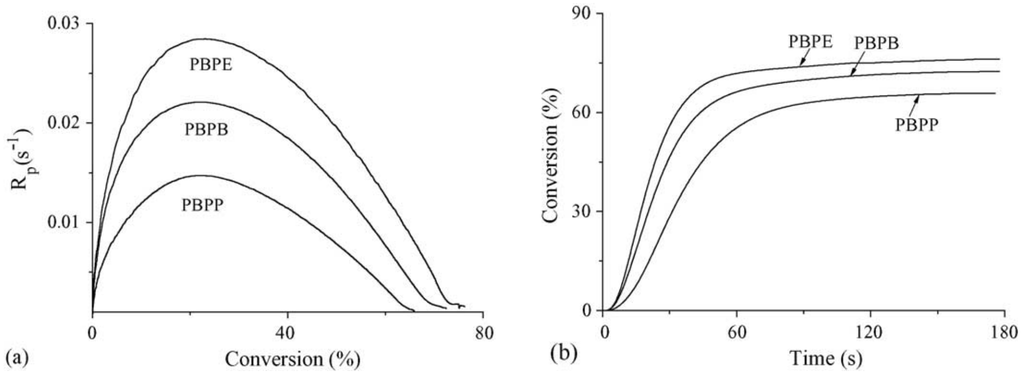


Fig. 4. (a) Rate vs. conversion and (b) conversion vs. time for polymerization of PPGDA for PBPP, PBPE and PBPB systems, cured at 25 °C by UV light with an intensity of 50 mW cm^{-2} (the photoinitiator concentration is 0.001 M in term of benzophenone moieties).

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