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Bifunctional Initiators: Synthesis, Characterization, and Initiator Properties of Azo-Benzoin Initiators

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BIFUNCTIONAL INITIATORS: SYNTHESIS, CHARACTERIZATION, AND INITIATOR PROPERTIES OF AZO-BENZOIN INITIATORS

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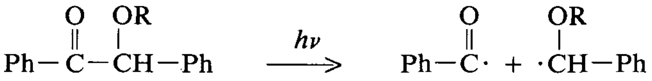
ABSTRACT

Two new azo-benzoin initiators were synthesized by the condensation of 4,4′-azo-bis-(4-cyanopentanoic acid chloride) (ACPC) with benzoin (B) and α-methylolbenzoin methyl ether. The initiator structures were confirmed by IR and NMR spectroscopy. The kinetics of the bulk polymerization of styrene initiated by the azo-benzoin initiator, obtained from ACPC and B, was investigated and the kinetic parameters evaluated. The initiation of polymerization of styrene by means of azo-benzoin initiators yields polymers with terminal photoactive benzoin groups.

INTRODUCTION

Bi- and polyfunctional initiators are of great interest because of their broad application in the synthesis of block copolymers [1]. This process involves the sequential decomposition of the functional groups introduced in the initiator. Azo peroxide initiators are suitable for this purpose but suffer from the thermal and photochemical sensitivity of both the azo and peroxide groups although at different rates [2].

Benzoin and its derivatives are well-known photoinitiators which find commercial application in UV curable coatings [3]. Upon irradiation, these molecules undergo Norrish Type I cleavage and yield radicals which are capable of initiating the free radical polymerization of vinyl monomers.



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle OR}{|}}{C}H{-}Ph} \xrightarrow{h\nu} \mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}\cdot} + \mathrm{\cdot\overset{\overset{\displaystyle OR}{|}}{C}H{-}Ph} \qquad (1)$$

The attachment of structurally related benzoin and its derivatives to the polymer main and side chains would afford a convenient procedure for block and graft copolymer formation, respectively, by a similar photo-induced decomposition. Smets [4, 5] described the incorporation of benzoin methyl ether in poly(bisphenol-A carbonate) which may contribute to the formation of a block copolymer by its photolysis in the presence of vinyl monomers. Recently, Yagci and Ledwith [6] prepared polytetrahydrofuran possessing terminal alkoxy acetophenone groups by degradative chain transfer to the photoinitiator in the cationic polymerization of tetrahydrofuran. Photopolymers containing side-chain benzoin and benzoin methyl ether choromophores, useful precursors for graft copolymers, have also been reported [7, 8].

In the present work we report the synthesis, characterization, and initiator properties of new azo-benzoin initiators which have appropriate functionality for two-stage polymerization, i.e., for block copolymer formation.

EXPERIMENTAL

Materials

4,4′-Azo-bis-(4-cyanopentanoic acid) (ACPA) (Fluka), benzoin, and benzoin methyl ether (Aldrich) were used without further purification. 4,4′-Azo-bis-(4-cyanopentanoyl chloride) [9] (ACPC) and α-methylolbenzoin methyl ether [8] (MBME) were prepared according to the described procedures. Styrene and solvents were purified by conventional drying and distillation procedures.

4,4′-Azo-bis-(4-cyanopentanoyl)-bis-benzoin (ACPB)

In a three-neck flask fitted with a stirrer, 2.75 g (12.72 mmol) benzoin in 50 mL chloroform was introduced and treated with 1.005 g (12.72 mmol) pyridine with cooling at 0°C. From a dropping funnel, 2.02 g

(6.36 mmol) ACPC dissolved in 25 mL chloroform was added under nitrogen at a temperature not exceeding 5°C. The mixture was stirred for another 5 h at this temperature and allowed to stand overnight. The solution was concentrated by evaporating the chloroform under vacuum, and the initiator was then precipitated in methanol at −70°C, giving white crystals of ACPB in a yield of 20%, mp 128°C. Elementary analysis: C, 68.97%; H, 5.65%; N, 8.54. Calculated: C, 71.85%; H, 5.38%; N, 8.39%

4,4′-Azo-bis-(4-cyanopentanoyl)-bis-(α-methylolbenzoin methyl ether) (ABME)

ABME was prepared by the reaction of α-methylolbenzoin methyl ether and ACPC as described above. Yellowish crystals were obtained with a yield of 18%, mp 44°C. Elementary analysis: C, 68.3%; H, 5.88%; N, 6.87%. Calculated: C, 69.84%; H, 5.82%; N, 7.40%

Polymerization Procedures

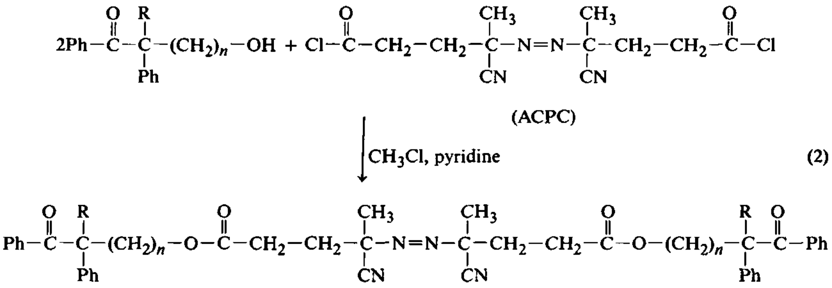
Bulk styrene containing a known amount of ACPB or ABME was outgassed in the usual manner and placed in a constant temperature bath at a given temperature. At the end of a given time the reaction mixtures were poured into a tenfold excess of methanol, and the precipitated polymers then filtered and dried.

Analysis

^{1}H-NMR spectra were recorded on JEOL FX-100 and JEOL GX-500 spectrometers in the pulse Fourier Transform (FT) mode using TMS as internal standard. IR spectra were recorded on a JASCO FT/IR-3 spectrometer. Elemental analysis was carried out with a Yanaco-CHN MT3 instrument. UV spectra were recorded on a Perkin-Elmer 550S UV-Vis spectrophotometer. The $\overline{P}_n$ values were calculated from g.p.c. chromatograms according to standard polystyrene samples using a Knauer M-64 instrument and THF as the eluent at a flow rate of 1 mL/min.

RESULTS AND DISCUSSION

This paper presents the synthesis of new azo-benzoin initiators by reactions of benzoin (B) or α-methylolbenzoin methyl ether (MBME) and the diacid chloride (ACPC) as shown by



$$2\,\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle Ph}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}{-}(CH_2)_n{-}OH} + \mathrm{Cl{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}N{=}N{-}\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl}$$

(ACPC)

$$\xrightarrow{\mathrm{CH_3Cl,\ pyridine}} \qquad (2)$$

$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle Ph}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}{-}(CH_2)_n{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}N{=}N{-}\underset{\underset{\displaystyle CN}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}(CH_2)_n{-}\underset{\underset{\displaystyle Ph}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Ph}$$

(ABME)

(ACPB: R = H, n = 0; ABME: R = $-OCH_3$, n = 1).

The structure of the new azo-benzoin initiators was confirmed by elemental analysis as well as spectroscopic investigations. The IR spectra contain the characteristic CO ester band and the CO keto group of benzoin at 1725 and 1680 cm^{-1}, respectively (Fig. 1). The ^1H-NMR spectra, recorded in $CDCl_3$ evidenced resonance signals of the phenyl, OH, CH_2-O, OCH_3, CH_2, and CH_3 protons of relative intensities corresponding to the number and type of protons (Figs. 2 and 3).

ACPB was used as a free radical initiator for the polymerization of styrene in bulk. Typical results are shown in Table 1. The conversion versus time plots of polymerizations at 60, 70, and 80°C are presented in Fig. 4. The logarithm of the rates of polymerization is plotted against the reciprocal of the absolute temperature, and an Arrhenius-type diagram (Fig. 5) is obtained in which an activation energy of 75.89 kJ/mol is obtained in the 60–80°C range. For free radical polymerization the inverse degree of polymerization ($1/\bar{P}_n$) is related to the rate of polymerization (R_p) by [10]

$$1/\bar{P}_n = (fkd[\mathrm{I}])/R_p) + C_\mathrm{M} + C_\mathrm{I}([\mathrm{I}]/[\mathrm{M}]), \qquad (3)$$

in which C_I and C_M are transfer constants to initiator and monomer, respectively; k_d is the thermal decomposition rate constant; and f is the initiator efficiency. A plot of the reciprocal number-average degree of polymerization ($1/\bar{P}_n$) against [I]/[M] is shown in Fig. 6. The C_I value for ACPB in styrene was calculated from the slope of the straight line and was found to be C_I = 0.416. Azo initiators are commonly preferred over other types of initiators due to their negligible participation in transfer reactions. However, in our case the benzoin groups attached to the azo

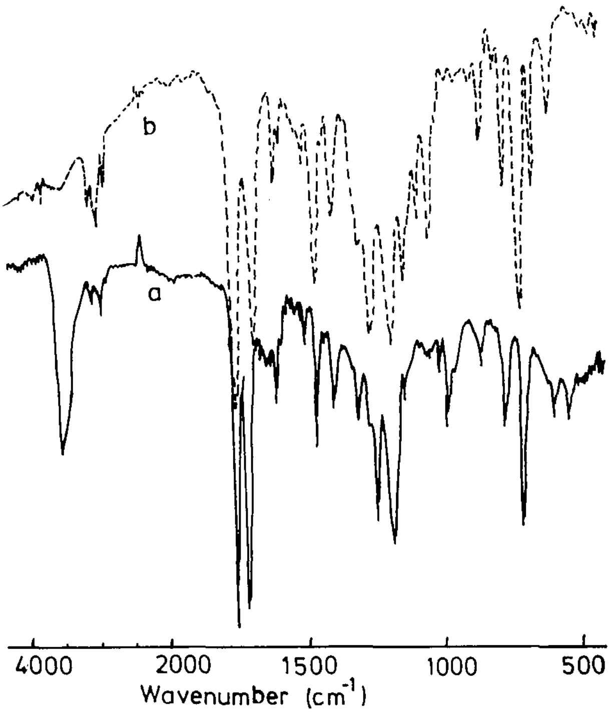


FIG. 1. IR spectra of (a) ACPB (——) and (b) ABME (- - -).

initiator may contribute to the relatively higher value of C_I. Figure 7 shows a plot of $(1/\bar{P}_n)$ against $([I]/R_p)$, from which the value of fk_d for ACPB was calculated to be 2.44×10^{-6} s^{-1}. In this connection it is interesting to note that a similar value, $fk_d = 8.07 \times 10^{-6}$ s^{-1}, was reported by George and Ward [11] for the polymerization of styrene in DMF initiated by ACPA. The slightly lower value found in our case might be due to the cage effect resulting from the limited diffusion of the higher molar mass radical fragments.

The initiation of polymerization by means of azo-benzoin initiators yields polymers with one or two benzoin end groups according to the termination mode of the polymerization of the particular monomer involved. The following reactions may be written for styrene polymerization since styrene-derived radicals terminate almost exclusively by combination [12].

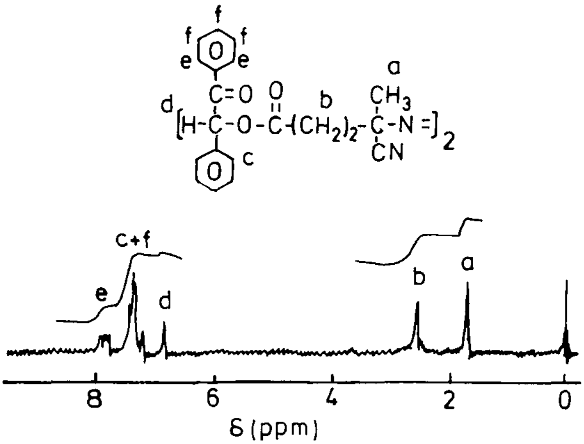


FIG. 2. ^{1}H-NMR spectrum of ACPB.

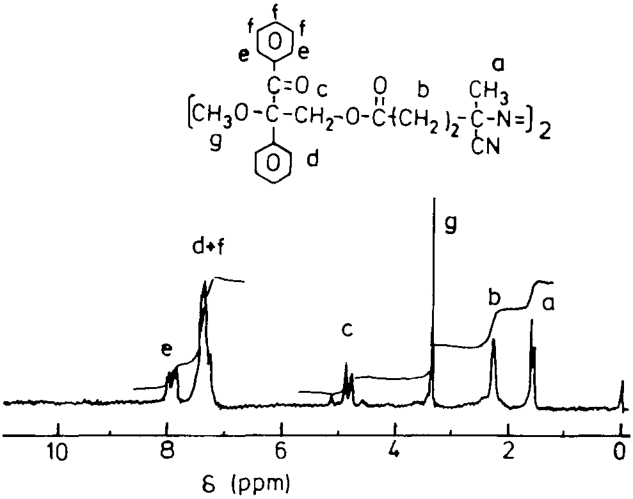


FIG. 3. ^{1}H-NMR spectrum of ABME.

TABLE 1. Bulk Polymerization of Styrene Initiated by ACPB at 60°C[a]

Run	[I] × 10^3 mol/L	Time, min	Yield, %	$R_p \times 10^5$ mol · L^{-1} · s^{-1}	$(1/\overline{P}_n) \times 10^4$
1	7	120	4.44	5.34	5.80
2	5	180	5.22	4.18	3.90
3	3	240	5.61	3.38	3.16
4	1	360	5.75	2.30	1.98
5	0.5	480	5.08	1.54	1.82

[a] [M] = 8.71 mol/L.

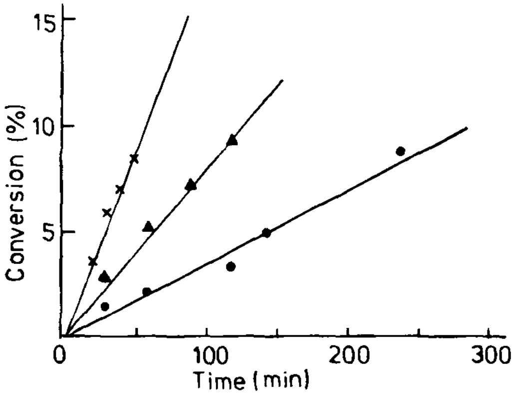


FIG. 4. Time-conversion curves for the bulk polymerization of styrene at various temperatures. ACPB = 5 × 10^{-3} mol/L: (●) 60°C, (▲) 70°C, (×) 80°C.

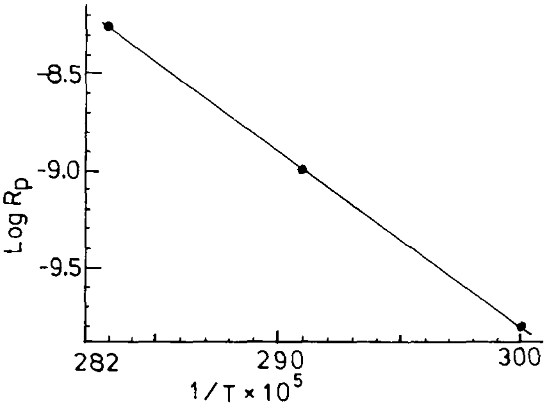


FIG. 5. Plot of log R_p versus $1/T$ for the bulk polymerization of styrene initiated by ACPB.

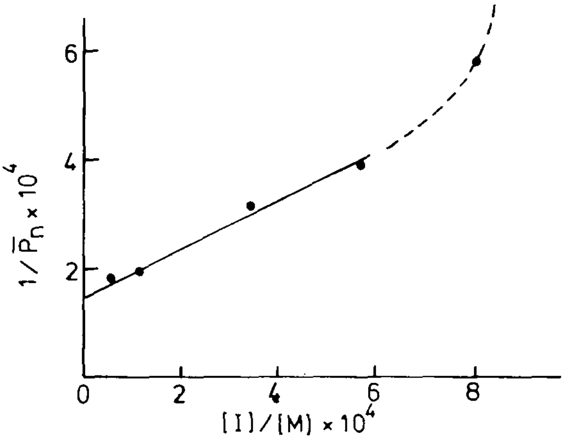


FIG. 6. Plot of the reciprocal degree of polymerization ($1/\overline{P}_n$) versus [I]/[M] for styrene polymerization in bulk at 60°C by ACPB.

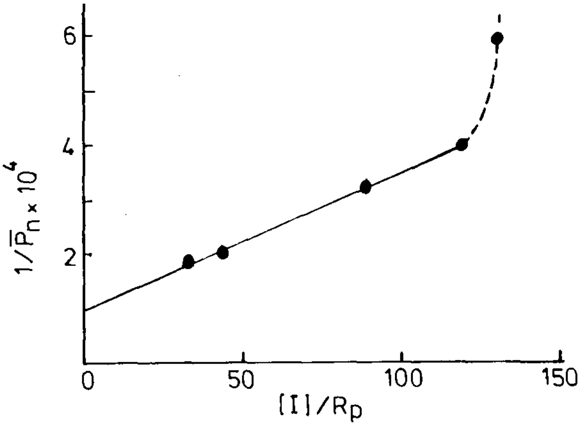
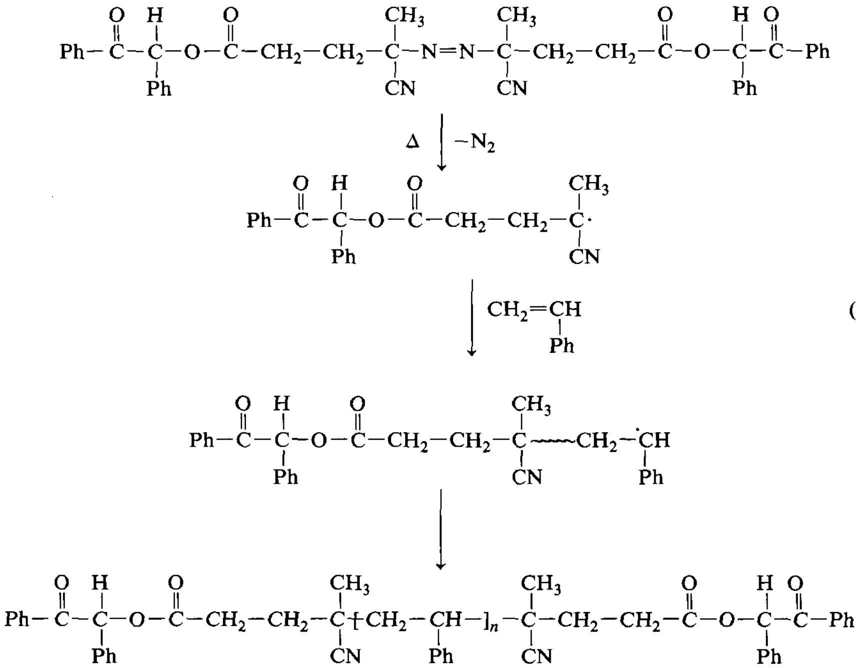


FIG. 7. ($1/\overline{P}_n$) as a function of ($[\mathrm{I}]/R_p$) for the polymerization of styrene in bulk at 60°C.



$$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{Ph}{\overset{H}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-\underset{Ph}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-Ph}$$

$$\Delta \Big\downarrow -N_2$$

$$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{Ph}{\overset{H}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}\cdot}$$

$$\Big\downarrow \mathrm{CH_2{=}\underset{Ph}{CH}} \qquad (4)$$

$$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{Ph}{\overset{H}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}\sim\!\sim CH_2-\underset{Ph}{\dot{C}H}}$$

$$\Big\downarrow$$

$$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{Ph}{\overset{H}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}\!+\!CH_2-\underset{Ph}{CH}-]_n-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-\underset{Ph}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-Ph}$$

The incorporation of benzoin groups into the polymer was evidenced in the case of polystyrene. Figure 8 shows the absorption spectra of ACPB and ABME together with the absorption spectra of polystyrenes obtained by initiation with these initiators. It can be seen that both spectra contain an absorption band characteristic of the precursor benzoin group.

Further studies on the use of these polymers as photoinitiator are now in progress and will be published elsewhere.

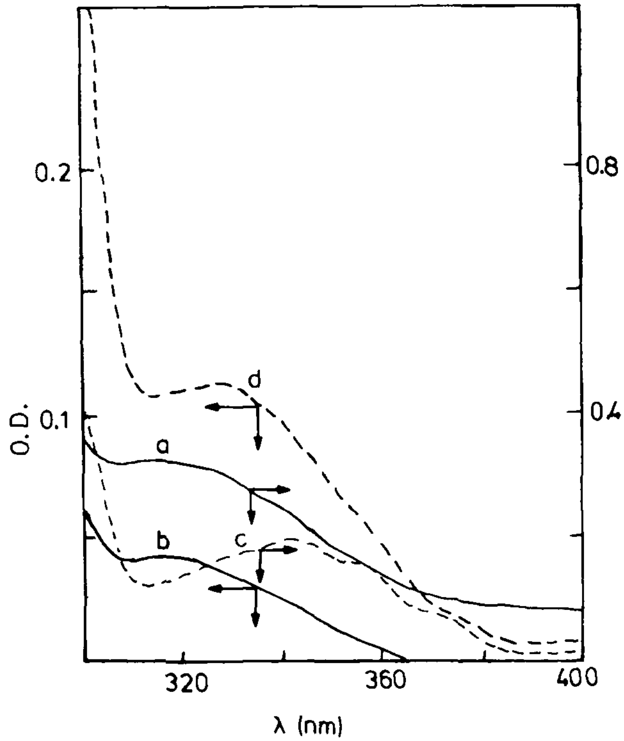


FIG. 8. UV absorption spectra of THF solutions containing (a) ACPB (2.98×10^{-4} mol/L), (b) polystyrene (2.18 g/L) initiated with ACPB, (c) ABME (4.41×10^{-4} mol/L), (d) polystyrene (8.04 g/L) initiated with ABME.

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