Solvothermal Process for Grafting Dibutylmaleate Onto Poly(ethylene-*co*-1-octene)

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ABSTRACT: Solvothermal process was successfully developed to graft dibutylmaleate (DBM) onto poly(ethylene-*co*-1-octene) (POE) with dicumyl peroxide (DCP) as free radical-initiator. FTIR spectra demonstrate that DBM is successfully grafted onto the backbone of POE by this novel method. The influences of DBM content, DCP concentration, POE concentration, reaction temperature and reaction time on the grafting copolymerization have been investigated in detail through grafting degree (GD). It is worthy to indicate that high grafting degree (above 15%) can be achieved through the one-pot way when the graft reaction is carried out in 40 mL toluene at 150°C for 5 h with 1.6 g DBM, 6–8 g POE and 0.35 g DCP. This developed solvothermal process is becoming an effective way to prepare POE-*g*-DBM graft copolymers, and can be extended to other systems. In addition, TGA results show that the thermal properties of POE are enhanced after the grafting reaction. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 298–303, 2010

Key words: solvothermal process; poly(ethylene-*co*-1-octene); dibutylmaleate; grafting degree; graft copolymerization

INTRODUCTION

Poly(ethylene-*co*-1-octene) (POE) is a new family of polyolefin polymers which are produced by metallocene technology and have attracted much attention due to their high content (more than 18% octane) and unique uniform distribution of comonomer and narrow molecular weight distribution. POE exhibits outstanding thermal stability, weather resistance, aging resistance and excellent toughness. These properties make them wildly used as good toughening modifiers for polypropylene,[1-4] polycarbonate (PC),[5] and high-density polyethylene (HDPE).[6,7] However, POE is not effective to modify polar polymers such as poly(butylene terephthalate) (PBT) and nylon because of its poor polarity. To extend such applications of POE, it should be first functionalized or modified by grafting with some unsaturated low molecular compounds which contain polar functional groups. The as-formed POE reacts with PBT[8-11] or nylon[12,13] to effectively avoid a coarse and unstable phase morphology, poor interfacial adhesion along the inter phase or interfaces and improve the miscibility between polar and nonpolar polymers.[14] There are some frequently used functional monomers, such as maleic anhydride (MAH),[7,15-19] glycidyl methacrylate (GMA),[20,21] methacrylic acids and their derivatives,[22,23] dibutylmaleate (DBM),[24] epoxy resin.[25] DBM is also a useful monomer to modify the nonpolar polymers, and has a very low vapor pressure and is relatively nonvolatile. DBM has very low solubility in water and high affinity for organic substances.[26] Compared with MAH, DBM possesses weaker polarity, and thus be used in moderate reaction or compatibilization.

Solvothermal reactions due to their unique features such as very high self-generated pressure inside the sealed reaction vessel (autogenous pressure) and containment of volatile products are well suited for the preparation of nanopartiles or nanocomposites.[27,28] Our group have successfully prepared the ABS-*g*-MAH copolymers,[29] HDPE-*g*-MAH and POE-*g*-MAH via this method.[30,31] Different from the traditional solution grafting method, the grafting copolymerization can be carried out in both good solvents and poor solvents, and high grafting degree can be obtained in good solvents. Furthermore, the solvents and monomers are sealed in autoclave, and it can also avoid the evaporation of solvents and monomers, which benefits the environment and has high grafting yield.[32] Our previous works indicated that the solvothermal process could be a potential way for the graft-copolymerization because the solvents were sealed in the vessel, and the evaporation of the solvents and the monomer was inhibited, which are favorable for the environment. In this article, we give it a try to prepare POE-*g*-DBM
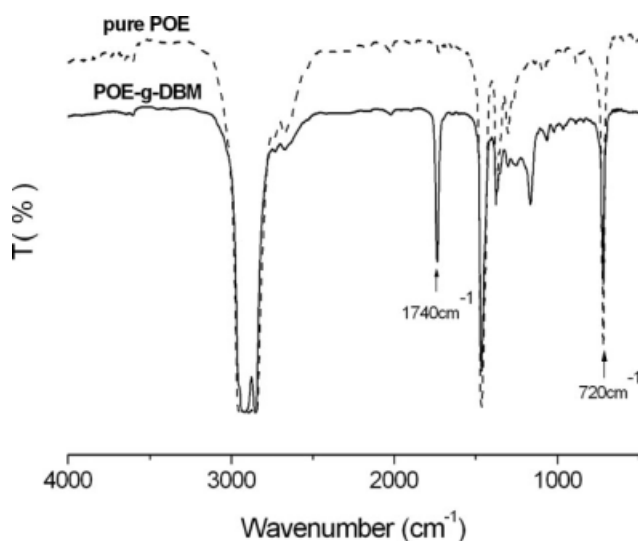
Figure 1 FTIR spectra of pure POE and POE-*g*-DBM.

copolymers and purposely study the effect of the various factors such as DBM concentration, the initiator's content, reaction temperature, reacting time and POE concentration on the grafting copolymerization. Moreover, the effect of the grafting degree on the thermal properties of POE-*g*-DBM has been discussed. It can be found that POE-*g*-DBM can reach higher grafting degree than those of the samples through conventional methods.

EXPERIMENTAL

Materials

POE with 1-octene contents 18% (Engage 8003) was purchased from Dupont Dow Elastomer (Shanghai, China). The free-radical initiator dicumyl peroxide (DCP) (Shanghai Lingfeng Chemical Solvent, Shanghai, China) was recrystallized in anhydrous ethanol. DBM (Sinopharm Chemical Reagent, Shanghai, China), acetone and toluene (Shanghai Chemical Solvent Factory, Shanghai, China) were used as received.

Synthesis of the grafted copolymers

The grafting reactions were performed in a sealed vessel with solvents under various process conditions. In a typical process, appropriate amount of POE, DBM, DCP, and toluene (as a solvent) were introduced into the sealed autoclave. Then the sealed vessel was put into a constant temperature oven. After a certain time, the products were taken away from the vessel and precipitated in acetone, and then the solid residue was washed several times with acetone to remove the unreacted DBM before measuring the grafting degree. The purified polymer

was collected and dried in a vacuum oven at 60°C for 24 h to a constant weight.
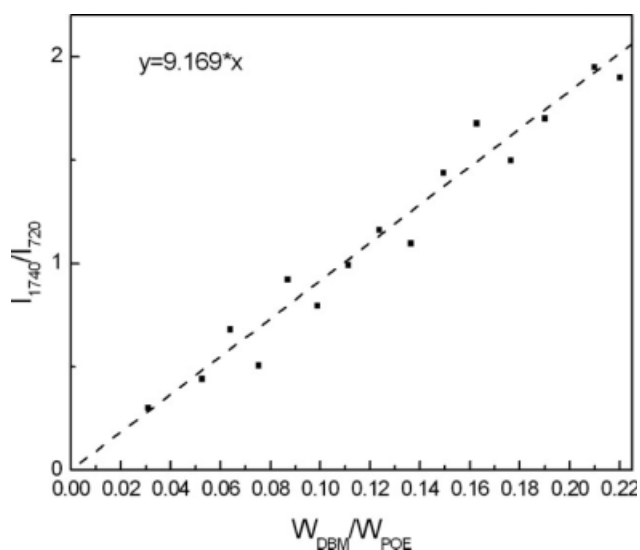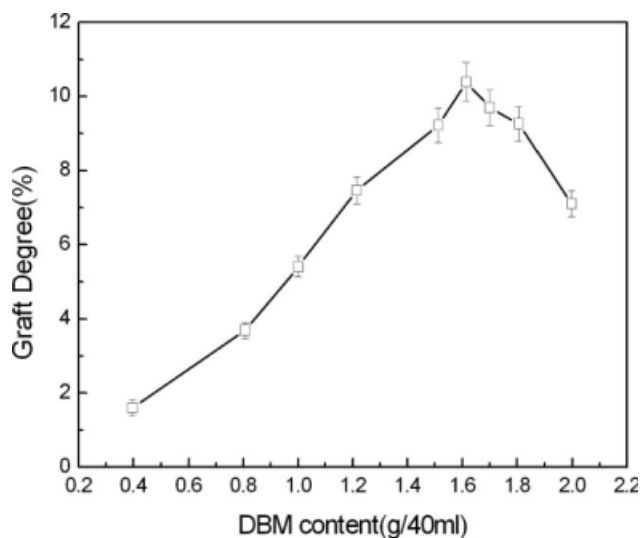
Characterization

FTIR

The purified products were compression molded into thin films with a thickness of less than 0.100 mm for Fourier transform infrared (FTIR) characterization. IR spectroscopy information was obtained on a Perkin–Elmer Paragon 1000 Fourier transform infrared spectrophotometer. The grafting degree could be calculated through the standard curve (the known different ratio of POE to DBM were prepared and characterized by FTIR).

The grafting reactions were performed in a sealed vessel with solvent under various process conditions. The FTIR spectra of pure POE and the modified products using solvothermal process are compared in Figure 1. It can be seen that all the characteristic peaks of POE at 1465 and 720 cm^{-1} appear in both polymers.[33] These two bands are the characteristic peaks of $-CH_3$ asymmetric, and long ethylene sequence $-(CH_2)_n-(n \geq 5)$ respectively. But in the grafted polymer, the peak at 1465 cm^{-1} is a little stronger than in the pure POE, because DBM also has $-CH_3$ which contributes to the absorbance at 1465 cm^{-1}. Besides the characteristic peaks of POE, other peaks at 1740 and 1165 cm^{-1} are also clearly found in the grafted copolymers, which are attributed to the symmetric stretching of carbonyl group from DBM. This result indicates that DBM has been grafted onto the POE successfully.

Because the peak at 1165 cm^{-1} is small but wide, it is often used as the characteristic peak to estimate whether DBM is grafted onto POE, but not sensitive for calculating grafting degree. Because both POE

Figure 2 Calibration curve for FTIR analysis.

Figure 3 Effect of the DBM concentration on the GD.

and DBM are solvable in toluene, so solutions with known different ratio of POE to DBM are prepared and characterized by FTIR. Because most of the characteristic peak of POE at 720 cm^{-1} remains constant, so it is chosen to be the fiducial peak. The intensity of the characteristic peak at 1740 cm^{-1} for DBM is calculated as I_1, and the intensity of the peak at about 720 cm^{-1} is calculated as I_2. Then the ratio of I_1 and I_2 is in direct proportion to the content of DBM in the mixtures. As shown in Figure 2, good correlation among the data and linear relationship were achieved. Then the grafting degree (GD) of POE-g-DBM was calculated by using the FTIR spectra according to the following eq. (1):

$$GD\,(\%) = (I_1/I_2)/9.169 \times 100\% \tag{1}$$

TGA

The high grafting degree will lead to the changement of the chain structure, and resulting in the thermal properties. So the effects of grafting degree on the thermal properties of products have been studied on a thermogravimetric analysis (TGA 7, Perkin–Elmer,) at a heating rate of 20°C /min under nitrogen atmosphere.

RESULTS AND DISCUSSION
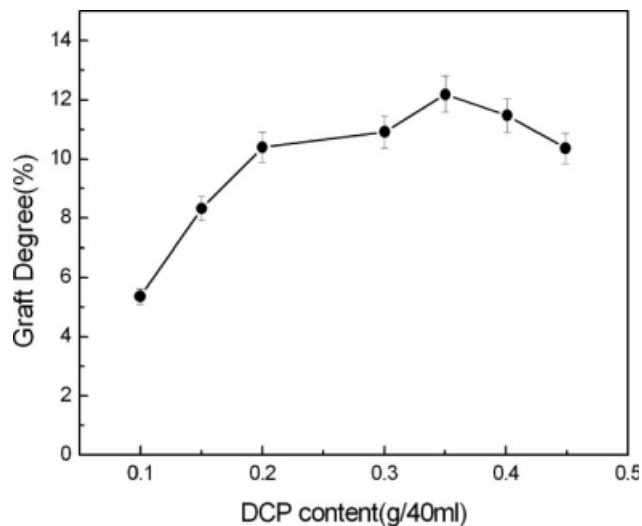
Effect of DBM concentration

The grafting copolymerization depends strongly on the synthesis conditions. So it is important to investigate the effect of the various factors, including DBM content, initiator concentration, POE concentration, reaction temperature and time on the grafting reaction.

The effect of DBM concentration on grafting degree has been studied when the other conditions were fixed as follows: POE = 4 g; DCP = 0.2 g; toluene = 40 mL; temperature = 150°C; time = 5 h. In these reactions, the quantities of DBM changed from 0.4 to 2.0 g/40 mL, and the results are shown in Figure 3, showing that the grafting degree initially increases with the increase of the DBM concentration, and reaches up to the maximum when the DBM concentration is 1.6 g/40 mL. However, the GD decreases with the further increase of DBM concentration.

Because the reactions are radical polymerizations, the free radicals of the monomer are diffused more easily than those of polymer, so the grafting reactions mainly depend on the diffusion of the DBM free radicals throughout the reaction medium and reach the polymers to form the grafting copolymers. More DBM free radicals lead to higher grafting degree. It is worth mentioning that the DBM also acts as the trap for free radicals. In other word, more DBM results in less polymer radicals and more homopolymerization of DBM if the DBM concentration is too high. This fact results in the difficulty of the grafting reaction, and that is why the grafting degree decreases with the increasing DBM concentration at last.

Effect of initiator concentration

The effect of DCP concentration on the grafting polymerization is shown in Figure 4. The conditions were fixed (POE = 4 g; DBM = 1.6 g; toluene = 40 mL; temperature = 150°C; time = 5 h). From Figure 4, it can be shown that the grafting degree also reaches the maximum value (at 12%) when DCP is 0.35 g/40 mL, and then decreases with the increase

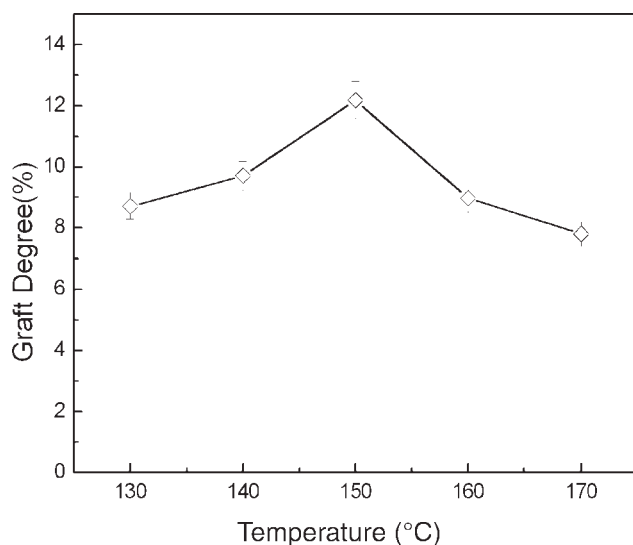**Figure 4** Effect of the DCP concentration on the GD.

Figure 5 Effect of the reactive temperature on the GD.

Figure 7 Effect of the POE concentration on the GD.

of DCP. This phenomenon can be explained from dual function of DCP. The free radicals initiated from DCP can induce both grafting and crosslinking reactions simultaneously during the solvothermal process. The grafting and crosslinking reactions are competitive radical polymerization. For the grafting degree, it rapidly increases when the content of DCP increases in the first place, but when the content of DCP becomes too high, the crosslinking will dominantly take place, leading to the high viscosity of the solution and inhibiting the diffusion of monomers and the dissolvation of polymers, the grafting reaction will be weakened and thus leads to the grafting degree slightly decreasing with the increase of DCP concentration (over 0.35 g/40 mL). The product with the highest grafting degree was obtained when the amount of DCP was 0.35 g/40 mL.
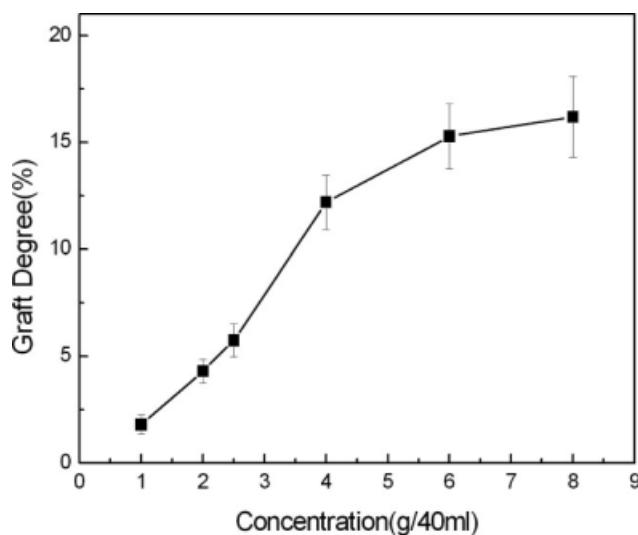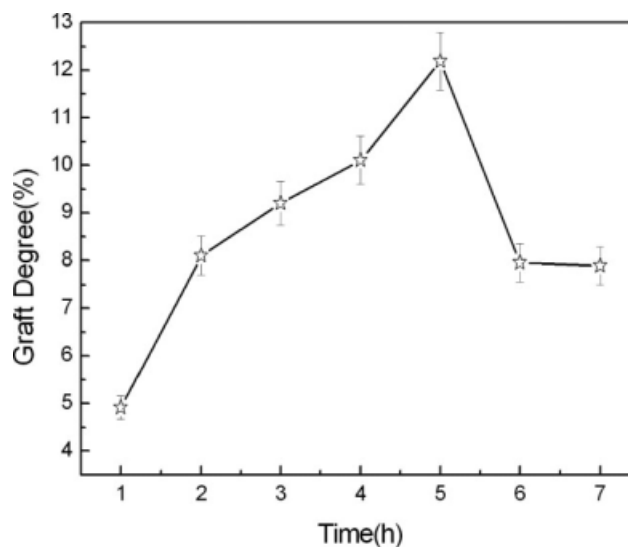
Effect of reaction temperature

The solvothermal process requires high temperature and pressure. The reaction temperature was set above the boiling temperature of toluene. The results shown in Figure 5 are based on the reaction temperature varying from 130 to 170°C. And the detail conditions were given as follows: POE = 4 g; DBM = 1.6 g; DCP = 0.35 g; toluene = 40 mL; time = 5 h.

As seen from Figure 5, relatively low grafting degrees (less than 9%) were observed at 130 and 170°C, while the highest grafting degree of 12% was obtained at 150°C. With the temperature increasing, the mobility of the reagent and the sealed vessel's pressure increased while the solution viscosity decreased. This was favorable for the grafting copolymerization and would cause the increase in the GD. On the other hand, the initiator half-life decreases with the increase of temperature.[29] In
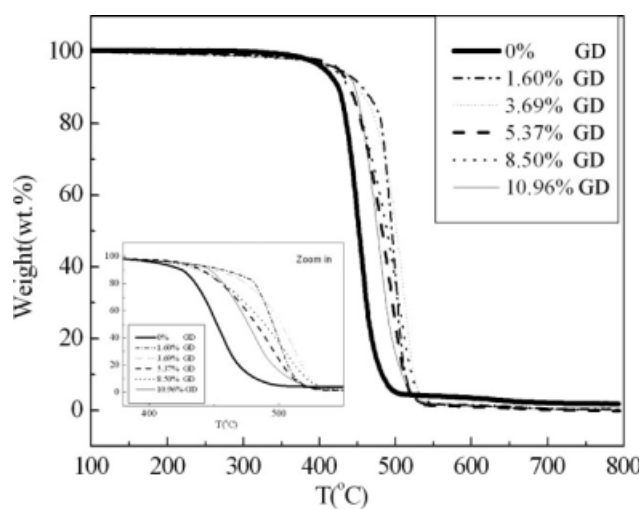

Figure 6 Effect of the reactive time on the GD.

Figure 8 TGA curves of POE and POE-*g*-DBM.

TABLE I
Degradation Temperature of the Grafted Copolymers

	1	2	3	4	5	6
Graft degree	0.00%	1.60%	3.69%	5.37%	8.50%	10.96%
T_d (°C)	428.67	476.94	477.26	452.51	453.24	450.41
$T_{5\%}$ (°C)	407.91	427.02	425.28	419.68	427.62	425.35
$T_{25\%}$ (°C)	439.20	484.39	480.66	462.85	460.50	460.61
$T_{50\%}$ (°C)	452.57	495.85	501.26	488.95	476.76	482.39
$T_{75\%}$ (°C)	465.40	504.41	515.24	508.98	491.06	499.50

general, the half-life of the initiator DCP extremely decreases from about 400 min at 120°C to nearly one minute at 170°C. At low temperature, especially at 130°C, the incomplete decomposition of DCP during the reactions limited the grafting reaction and the low GD of the copolymers were obtained. While the reaction was carried out at high temperature, a shorter half-life of initiator would cause a higher transient radical concentration for the same concentration of initiator,[34] which may lead to lower graft efficiency because of the increase of radical-radical combination. So the GD decreased with the increase of the temperature beyond 150°C.

Effect of reaction time

Figure 6 shows that the grafting degree increased as reaction time increased from 1 h all the way to 5 h, and decreased with further extending reaction duration. And other conditions were POE = 4 g, DBM = 1.6 g; DCP = 0.35 g; toluene = 40 mL; temperature = 150°C. The reasonable explanation for this phenomenon comes from the fact that the short lifetime of free radical initiated from DCP. The grafting reaction depends on the decomposition of initiator. However, a certain period of time is needed for the dissolution of polymers and for the reaction system to reach the reaction temperature. So low grafting degree was obtained at the initial stage, and high grafting degree achieved with prolonging time (less than 5 hours). As mentioned earlier, the crosslinking also take place simultaneously caused by the POE radicals and POE-g-DBM radicals as immediates. However, the diffusion of monomer-radicals was easier than that of macro-radicals which leaded to crosslinking reaction being kept in inactive and the graft reaction being the dominant reaction.

Effect of POE concentration

The concentration of POE also has great effects on the grafting polymerization. In these reactions, the quantities of POE were changed from 1.0 g to 8.0 g/40 mL toluene (DBM = 1.6 g; DCP = 0.35 g; toluene = 40 mL; temperature = 150°C, time = 5h).

As shown in Figure 7 the grafting degree steadily increased when the POE increased. Because POE and DBM compete each other for initiator radical, when the concentration of initiator is fixed, more POE will increase the chance to catch initiator radical and get more POE radicals, which further results in enhancing the reaction probability of collide among the POE radicals, DBM radicals, or other radicals during the sealed reaction, and copolymers with high grafting degree (16%) was obtained when the concentration of POE was 8.0 g/40 mL. On the other hand, too high POE concentration makes DBM radical movement become more difficult which will decrease the DBM oligomer. Because of the limitation of the sealed vessel, more amount of POE could not be studied.

Effect of grafting degree on the thermal properties

It is well-known that the thermal stability of materials is related to their molecular chemical bond strength, structural rigidity and regularity, cross-link density, molecular imperfection and so on.[35] When DBM is grafted onto a POE backbone, its structural regularity (such as degree of branching) will be changed and thus leads to the differing thermal stability of POE. Figure 8 shows mass percentage versus temperature plots for POE and POE-g-DBM.

It can be seen that the thermal stability of grafted POE is remarkably improved compared with neat POE. The degradation temperature of grafted POE is higher than that of the pure POE. These results indicate that the crosslinking and the grafting reactions of POE raise its upper temperature limit of application. The data of TGA further confirm that DBM had grafted onto the POE successfully, and the copolymers are much steadier than the pure POE.[36] Because DBM's polarity can improve the interaction between the molecules, which makes the chains of copolymers become rigid, and the degradation temperature of copolymers are improved. Furthermore, DBM is a low volatility compound, it will continue to react with POE once it has degraded from POE, so the degradation temperature is a little lower when grafting degree is higher, which can be seen in Table I.

CONCLUSION

In general, DBM is difficult to graft onto polymers to form copolymers with high grafting degree (>5%) by the traditional grafting ways. In this article, the solvothermal process has successfully been developed to graft dibutyl maleate onto ethylene 1-octene copolymers, and POE-*g*-DBM copolymer with high graft degree above 15% has been obtained, indicating that solvothermal process is a useful way to prepare POE-*g*-DBM. The influence of reaction parameters on the grafting degree was also investigated. The important results are summarized as follows:

1. The grafting degree initially increased with the increase of DBM content, DCP concentration, reaction temperature and reaction time, and reached to a maximum value, and then decreased.
2. The grafting degree increased with the POE concentration increasing.
3. POE-*g*-DBM copolymer with highest grafting degree of about 16% can be obtained when the reaction is carried out at 150°C for 5 h with the optimal ratio of POE/DBM/DCP at 8.0 g/1.6 g/0.35 g in 40 mL toluene.
4. The thermal stability of grafted POE is remarkably improved compared to that of original POE.

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