Study on poly(oxybenzoate-*p*-trimethylene terephthalate) copolymer

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Abstract

This study examined copolymers synthesized from poly(trimethylene terephthalate) (PTT) and *p*-acetoxybenzoic acid using solution proton nuclear magnetic resonance (NMR) spectroscopy. Proton NMR spectra showed that these *p*-oxybenzoate (POB)/PTT copolyesters were almost random copolymers because the preference factor of POB bonded to another POB unit in these copolyesters is close to 1.0 with a POB content between 20 and 80 mol%.

The melting and crystallization behaviors of these copolyesters were studied by differential scanning calorimetry (DSC). In the heating DSC scan of the POB rich composition, the endothermic peak is weaker because the enthalpy of fusion decreased due to a melting transition from a crystalline to anisotropy liquid state. Thermogravimetric analysis results indicated that the decomposition temperature (T_d) increased with POB content. The crystalline morphology of the copolyester was further investigated with a polarized optical microscope, indicating that the POB/PTT copolyesters with 60 mol% POB are highly anisotropic in the liquid state.
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1. Introduction

Poly(trimethylene terephthalate) (PTT) is a terephthalic polyester. Such polyesters are commonly used in engineering thermoplastics. Recently, PTTs have attracted interest for their applications in the textile industry due to a great reduction in the manufacturing cost of 1,3-propanediol, the monomer used in PTT synthesis [1]. Accordingly, several studies of PTT, on the synthetic technique [2–6], molecular and crystalline structure [7–10], spinning technology [11–13], and crystallization behaviors [14,15], have been published. Several researchers have investigated the structure and properties of a series of copolyesters, based upon poly(ethylene terephthalate) (PET) that has been copolymerized with *p*-acetoxyben-

zoic acid (PAB) or *p*-hydroxybenzoic acid (PHB) [16–25]. The co[poly(oxybenzoate-*p*-ethylene terephthalate)] copolyesters (POB/PET) have been demonstrated to exhibit liquid crystallinity at or above 35 mol% POB. Our previous research on blends of PET with POB/PET, investigated the crystallization kinetics by differential scanning calorimetry (DSC) [26,27], morphologic observation by polarized light microscopy [28], compatibility by scanning electron microscopy (SEM) [29], and also the interchange reaction between PET and POB/ PET, elucidated by proton nuclear magnetic resonance (NMR) [30,31]. We also previously studied a series of copolyesters, based upon another member of the terephthalic polyesters, poly(butylene terephthalate) (PBT) using composition analysis to elucidate sequence distribution, thermal behavior, and crystalline morphology [32,33].

PTT has a structure similar to that of PET and PBT. Moreover, poly(*p*-oxybenzoate) into which has been incorporated in PTT would be expected to exhibit liquid

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crystalline behavior at certain compositions. The series of POB/PTT copolyesters has not been investigated as extensively as POB/PET copolyesters. In this study, POB/PTT copolyesters are prepared by melt polycondensation of PTT with PAB. The compositions of the copolyesters, and their sequence distribution, thermal behavior, thermal stability, and crystalline morphology are also considered.

2. Experimental

2.1. Materials

PTT resin was kindly donated by Shin Koung Textile Co. (Taoyuan, Taiwan). The resin has an intrinsic viscosity of 0.794 (dl/g) in 60/40 (w/w) phenol/tetrachloroethane at 30 °C. PAB was supplied by BASF. Sb_2O_3 (Merck, reagent grade) and was used to catalyze melt condensation. Trifluoroacetic acid (TFA, Aldrich Chemical Co.) was used as a solvent for proton NMR analysis.

POB/PTT copolymers were synthesized following the method presented by Kuhfuss and Jackson [16], in which a mixture of the PAB, PTT, and 1 wt.% catalyst is placed in a flask equipped with a stirrer and a short head with an inlet and an outlet for nitrogen. The nitrogen outlet was connected to a glass tube distillation column, which led to a receiver, with provision for creating a vacuum. After the reaction flask was evacuated and purged with nitrogen three times to remove all air, it was heated to 250 °C and held for 1 h in a nitrogen atmosphere in a eutectic salt bath of sodium nitrite and potassium nitrate. After the initial polymer fragmentation reaction was completed, a vacuum of about 0.5 mmHg was slowly applied to execute the polymerization reaction for 6 h at 250 °C.

2.2. Copolymer composition analyses and sequence distribution

Proton NMR analysis was performed to determine the compositions of the POB/PTT copolyesters. For the NMR spectra, 5–10 wt.% solutions of copolyester in cold (room temperature) deuterated TFA were prepared. The spectra were obtained using a Varian Unity Inova 600-MHz FT proton NMR spectrometer, operating at 600 MHz under the standard conditions with tetramethylsilane (TMS) as the internal standard. The dyads fractions or the mol% of POB bonded to PTT unit were determined from the NMR spectra by integrating the specific peak areas, as described by Lenz et al. [34] and Nicely et al. [35] and the authors [29, 30].

2.3. Differential scanning calorimetry measurement

Thermal analysis was conducted using TA 2010 Thermal Analyzer. The weight of all samples was maintained between 10 and 11 mg. The reference material was a blank aluminum pan. All powder samples were pretreated by heating to 280 °C and holding for 3 min to destroy anisotropy. They were then cooled, cooling at 10 °C/min to 30 °C, and finally analyzed at a heating rate of 10 °C/min to 280 °C. T_m was taken as the maximum of the endothermic melting peak from the heating scans and T_c was that of the exothermic peak from the cooling scans that was associated with crystallization. The heat of fusion (ΔH_f) and the crystallization heats (ΔH_c) were obtained from the areas under the melting peaks and the crystallization peaks. ΔH_f and ΔH_c refer to the entire sample. All results were averages across the three samples.

2.4. Polarized optical microscopy

All samples were observed using a Olympus BX-51 polarized microscope. The specimens held between two thin microscope cover slips were prepared on the hot stage by preheating at 200–300 °C. Once melted, the samples were pressed on the upper cover slip and then immediately quenched in liquid nitrogen. The sequence of heating, pressing, and quenching was always performed in under 30 s. The films were photographed at room temperature.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed by TA 951 TGA system. The TGA was used to measure the weight change of a material as a function of temperature, at a heating rate of 10 °C/min under an atmosphere of nitrogen.

3. Results and discussion

3.1. Copolyester composition analysis and sequence distribution

Table 1 presents the codes for each sample synthesized. Fig. 1(a) shows the Varian Unity Inova 600 MHz FT proton NMR spectrum of T64 in TFA solution, and is dominated by four peaks. The first is at 2.33 ppm and represents the two central aliphatic protons. The second is at 4.60 ppm and corresponds to the four aliphatic protons adjacent to the ester group. The third is at 7.25 and 7.35 ppm and is associated with the POB–PTT dyad and the POB–POB dyad, respectively. The dyad fraction or the molar fraction of POB bonded to other POB units was determined by integrating the two peaks. The fourth

Table 1
The code, composition and characteristic of POB/PTT

POB/PTT (molar ratio)	Code	X_{POB}	$f_{POB-POB}$	a	m
20/80	T28	0.185	0.114	0.102	1.12
40/60	T46	0.376	0.253	0.232	1.09
60/40	T64	0.563	0.412	0.392	1.05
70/30	T73	0.648	0.493	0.479	1.03
80/20	T82	0.736	0.570	0.582	0.98

peak at 8.06 and 8.25 ppm corresponds to the tere-phthalate proton of PTT and POB. Each resulting peak was taken integrated to determine molar fraction of POB units in the copolyester, as described below. Following the assignment of various protons in the POB/PTT copolyesters in Fig. 1(a), the integrations of the peaks at 8.06 and 8.25 ppm are indicated as A_1 and A_2. The peaks at 7.25 and 7.35 ppm are designated as B_1 and B_2, respectively. The peaks at 2.33 and 4.60 ppm are
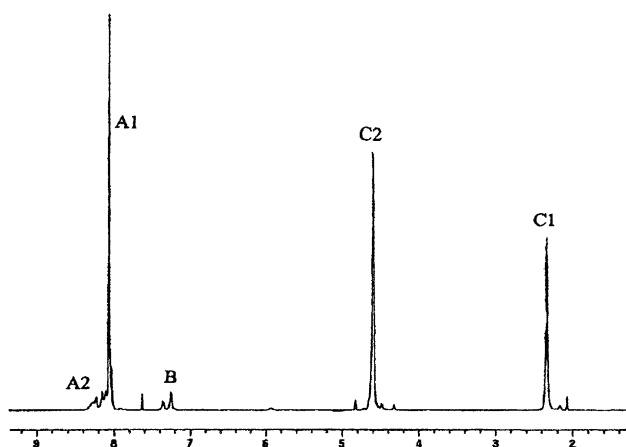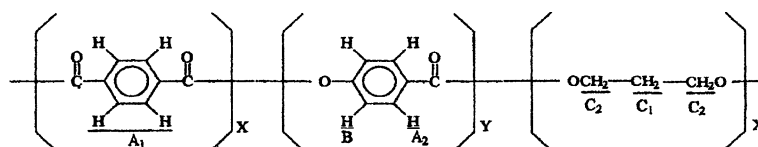
(a)
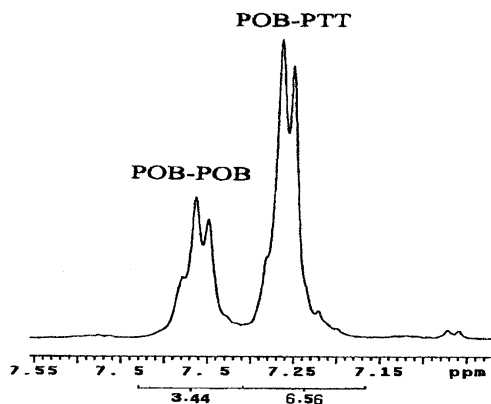
(b)

Fig. 1. (a) Proton 600 MHz NMR spectrum of the T64 copolymer (b) Peak integrals of POB–POB and POB–PTT peaks.

designated as C_1 and C_2, respectively. The composition of the POB/PTT copolyester was determined using the following equation from the data in Fig. 1(a).

$$X_{POB} = \frac{\frac{B}{2}}{\frac{A_1}{4} + \frac{A_2}{2}} = \frac{2B}{A_1 + 2A_2} = \frac{2B}{(A_1 + A_2) + A_2} = \frac{2B}{A + B} \tag{1}$$

where X_{POB} is the molar fraction of POB units in the copolyester; $A = A_1 + A_2$, and $B = B_1 + B_2$.

Table 1 presents the compositions of the copolyesters, as determined by NMR analysis. The POB contents were always lower than calculated from the monomer amounts in the copolymerizations. The result is similar to the data for POB/PET copolyesters, presented by Nicely et al. [35] and to the data for POB/PBT copolyesters synthesized by the authors [32]. Two causes appear to explain: (1) PAB is lost by hydrolysis and sublimation during copolymerization, and (2) PAB monomer forms an insoluble, infusible polymer by homopolymerization during copolymerization.

The fraction of the POB–POB peak area over both the sum of the POB–POB and POB–PTT peak areas can be determined by integrating the two peaks at 7.25 (B_1) and 7.35 ppm (B_2), shown in Fig. 1(b).

$$f_{POB-POB} = \frac{B_2}{B_1 + B_2} \tag{2}$$

where $f_{POB-POB}$ is the fraction of POB units which are connected directly to other POB units in a copolyester with a X_{POB} molar fraction of POB units.

In the non-random copolymer, if the POB has a composition-independent preference for bonding to itself, then [36]

$$f_{POB-POB} = ma \tag{3}$$

where m is the preference factor, which is unity, for a purely random copolymer, and a is the probability of a POB being bonded to another POB in a purely random copolymer and is determined from X_{POB} [36].

Table 1 lists the values of X_{POB}, $f_{POB-POB}$, a, and m. Based on a probability calculation [36], the value of m should be unity for a fully random copolymer. Although the values of m of these POB/PTT copolyesters are slightly smaller or larger than 1.0, the deviations are small compared to that predicted by the random model. Consequently, these POB/PTT copolyesters are very close to fully random copolymers. The value of m of 1.3 was obtained for the POB/PET copolyesters in an earlier report of Lenz et al. [34]. The values of m obtained here for the POB/PTT copolyesters are always below 1.3. This finding suggests that POB/PTT copolyesters here are more nearly random copolymers than those POB/PET copolyesters synthesized by Lenz et al. [34]. Restated, the POB sequence length of POB/PET copolyesters should exceed that of POB/PTT copolyesters.

3.2. Differential scanning calorimetry analysis

Fig. 2(a) and (b) shows DSC thermograms of the POB/PTT copolyesters, respectively, obtained from heating and cooling scans. Table 2 presents various thermal and crystallization parameters obtained from the DSC thermograms. As shown in Fig. 2(a), the melting point declines from 228 °C for pure PTT to 149 °C for T82 (80% POB) as POB content increases. The values of T_m reveal that melting is due to the incorporation of POB segments in the PTT regions, causing a diluting effect. However, the extent of broadening of the melting peak is observed to increase with the POB content. Taking T28 as an example, its T_m was found to be 214 °C and its melting peak was broader than that of pure PTT. The higher content of POB reduced the sequence length of PTT blocks. Thus, a lower T_m and a broad peak were observed for T46, T64, T73 and T82.

T64 showed broad and obscurely small two melting peaks at 160 and 180 °C. The small value of ΔH_f is determined by its crystal–nematic mesophase transition. The mesophase of T64, observed using polarized optical
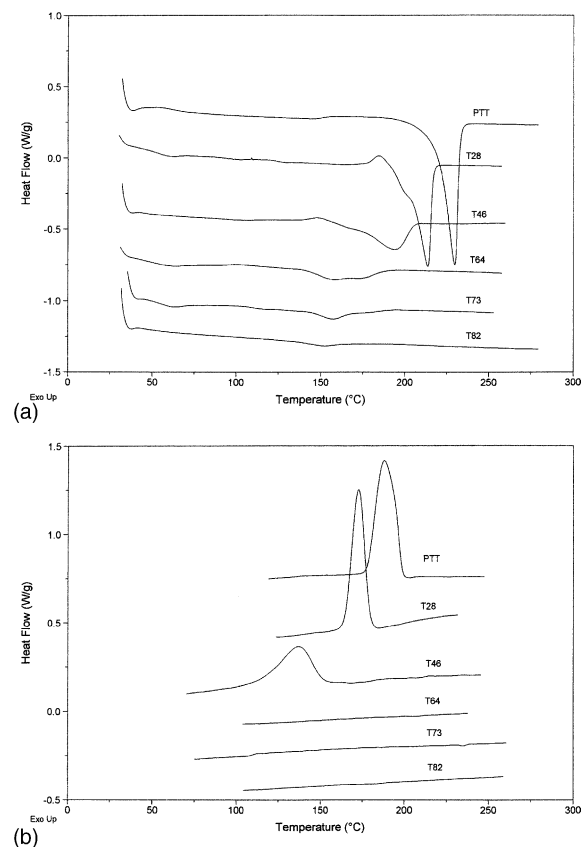

Fig. 2. DSC thermogram of POB/PTT: (a) heating scans; (b) cooling scans.

Table 2
DSC data of PTT and POB/PTT copolyesters

Composition	Melting (from heating scans)				Crystallization (from cooling scans)			
	Onset (°C)	T_m (°C)	ΔT_m (°C)[a]	ΔH_f (J/g)	Onset (°C)	T_c (°C)	ΔT_c (°C)[b]	ΔH_c (J/g)
PTT	214	228	24	54.3	202	188	30	52.4
T28	185	214	36	52.2	184	173	34	44.6
T46	149	194	60	38.3	161	137	64	32.1
T64	139	160	50	13.7	No crystallization			
T73	138	157	54	7.3	No crystallization			
T82	133	149	34	1.5	No crystallization			

[a] ΔT_m: melting peak width.
[b] ΔT_c: crystallization peak width.

microscopy (POM), becomes the continuous liquid crystalline phase during the thermal process, yielding a broad peak, because the heating softens the rigid chain of the liquid crystalline polymer. T73 and T82, rich in POB, exhibit very low values of ΔH_f similar to that of T64.

The cooling scans clearly show a distinct exothermic crystallization peak for T28 and T46. However no distinct crystallization peak is observed for T64, T73 or T82. The crystallization peak temperature (T_c) and the crystallization peak width (ΔT_c) of PTT are 188 and 30 °C, respectively. T_c of T28 and T46 are always lower than that of pure PTT and decrease as the POB content increases between 20 and 40 mol%. These changes in the crystallization peak width (ΔT_c) are related to the crystallite size distribution and/or defects in the crystallites.

The heat of crystallization (ΔH_c) is related to the degree of crystallinity. Moreover, ΔT_c and ΔH_c for the T28 and T46 are smaller than those of pure PTT. These results are expected since the observed crystallization is due to PTT and, as the PTT content is lowered, the overall degree of crystallinity is reduced.

3.3. Morphological studies

A polarized optical microscope was used to observe the crystalline texture of the copolymers. Fig. 3(a) shows the spherulitic texture of pure PTT. Many spherulites impinge on each other and some large spherulites are dispersed among small spherulites. As shown in Fig. 3(b) for T28, the perfection of the spherulite is less than that of PTT and some anisotropic phases, indicated by a
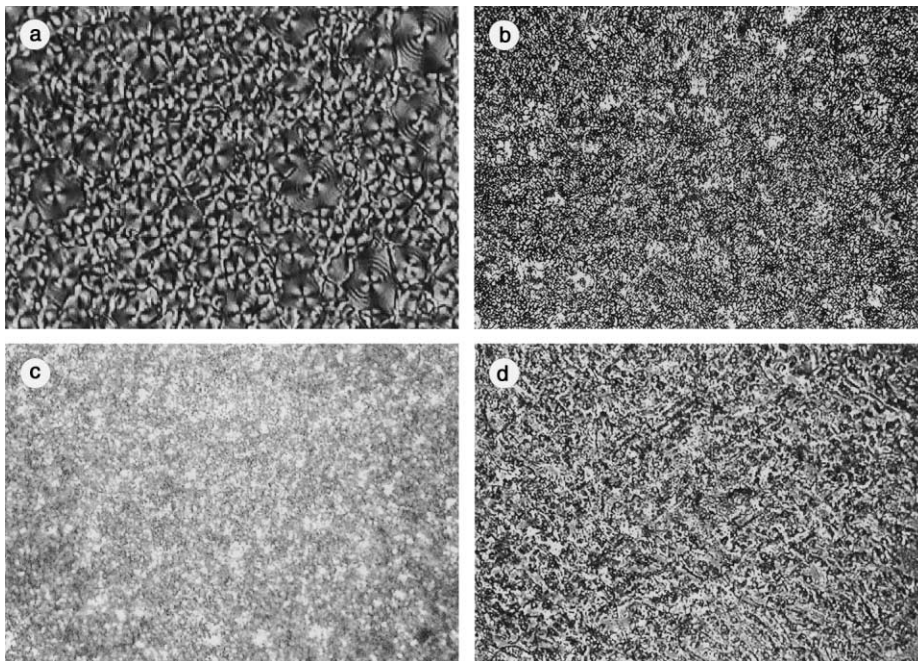

Fig. 3. Polarized light micrographs of samples: (a) PTT; (b) T28; (c) T46; (d) T64.

brown color, are scattered among the isotropic matrix phase. The pattern for T46 (Fig. 3(a)) is a dispersed anisotropic phase in a continuous isotropic phase, while maintaining isotropic and anisotropic biphases. Compared with T28, the pattern for T46 (Fig. 3(a)) shows more anisotropic phase and a less perfect crystal. This result shows that the POB reduces the perfection of the crystal and increases the extent of the anisotropic phase. As shown in Fig. 3(c) for T64, the mesophase becomes continuous and the patterns show the typical threaded texture, which result is consistent with the presence of a nematic phase. Although T73 and T82 showed melting peaks in the DSC thermograms, they did neither melted nor became liquid-like on the hot stage. Their crystalline morphology could not be observed using a polarized optical microscope.

3.4. Thermogravimetric analysis

TGA experiments on PTT and POB/PTT copolyesters were performed to determine the effect of POB content on thermal stability. Fig. 4 plots the thermogravimetric curves for PTT and POB/PTT copolyesters. Table 3 lists the characteristic temperatures, including the decomposition temperature (T_d), the lower decomposition temperature (T_l) and the upper decomposition temperature (T_u). Table 3 and Fig. 4 clearly show that the decomposition temperature of POB/PTT copolyesters depends mainly on the POB content. The decomposition temperature increases with POB content. Hence, the thermal stability of POB/PTT copolyesters increases with POB content, which result may be explained by the fact that the decomposition temperature of poly(p-oxybenzoate) (515 °C) [37] exceeds that of PTT (399 °C).

Table 3
TGA data of PTT and POB/PTT copolyesters

Composition	T_l (°C)	T_d (°C)	T_u (°C)	ΔT (°C)[a]
PTT	377	399	420	43
T28	378	399	421	43
T46	385	408	431	46
T64	381	412	442	61
T73	382	415	448	66
T82	379	428	474	95

[a] $\Delta T = T_u - T_l$.

From the results published elsewhere [37], a higher degree of polymerization of the same chemical segment may result in lower stability under the thermal decomposition temperature of POB/PET copolyesters. For POB/PTT copolyesters, the lower decomposition temperature is related to the PTT moiety and the upper decomposition temperature is related to the POB moiety, which is a hard segment. The lower decomposition temperature of POB/PTT copolyesters is higher than that of pure PTT (377 °C) by 1–8 °C. This result implies that the chain of the PTT unit in the POB/PTT copolyesters is shorter than that of pure PTT. In contrast, the upper decomposition temperatures of POB/PTT copolyesters, except T28, significantly exceeds that of PTT (420 °C). Introducing POB moiety into the structure increases the upper decomposition temperature of the POB/PTT copolyesters. Similar phenomena have been observed in POB/PET [37] and POB/PBT [33] copolyesters. Furthermore, the difference between the upper decomposition temperature and the lower decomposition temperature (ΔT) of POB/PTT copolyesters exceeds that of pure PTT (43 °C). Accordingly, the
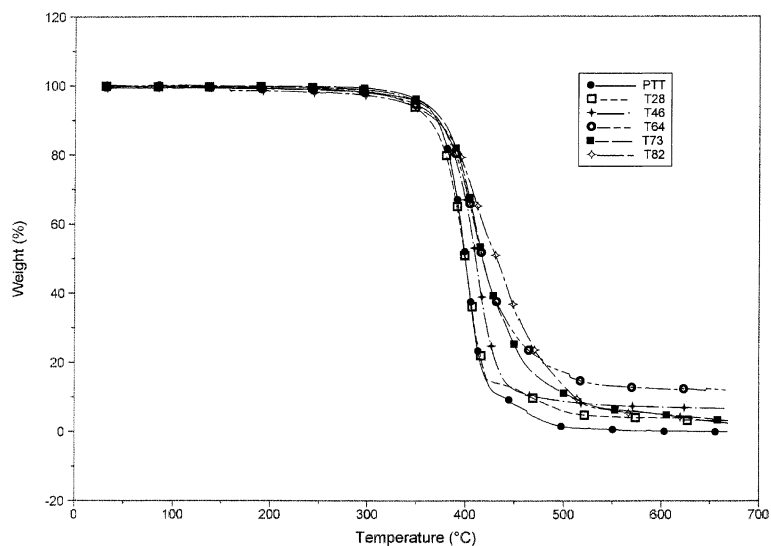

Fig. 4. TGA curves for PTT and POB/PTT.

POB/PTT copolyesters have more uniform thermal characteristics over a broad heating temperature interval. T82 has the most uniform thermal characteristics of all the POB/PTT copolyesters because it has the highest ΔT.

POB/PTT copolyesters were formed from the hard segment of POB moiety and soft segment of PTT moiety. Introducing POB moiety into the structure increases the decomposition temperature and the upper decomposition temperature.

4. Conclusions

Proton NMR spectra of solutions have shown that the sequence distributions of POB/PTT copolyesters can be expressed by a probability model in which POB has an almost arbitrary probability which of being bonded to another POB unit.

The thermal and crystallization behavior results reveal that the inclusion of the rigid POB unit in the PTT chain destroys the PTT isotropic crystal domain and reduces the crystallizable segment length of PTT. Under polarized light, T28 melt showed no explicit melt birefringence. T64 exhibits the typical threaded texture of nematic liquid crystalline.

The decomposition temperature and the upper decomposition temperature of POB/PTT copolyesters increase with POB content. Consequently, the thermal stability of POB/PTT copolyesters increases with POB content.

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