Preparation and Characterization of Biscyanamide Resins Containing o-Substituted Groups or Phenyl–Ether Linkage

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SYNOPSIS

New biscyanamides containing o-substituted groups or a phenyl–ether linkage were synthesized. The curing reaction behaviors of the biscyanamides were investigated. All the prepared biscyanamides began to polymerize as soon as they melted after being put on a heated plate beyond a certain temperature. The cured resins of each biscyanamides were prepared on the optimal conditions. Optimal conditions for cured resins were obtained from the curing reaction behaviors of each biscyanamide by differential scanning calorimetry (DSC). The effect of chemical structures of the biscyanamides on the thermal and mechanical properties of the cured resins such as seen by thermal gravimetric analysis (TGA), density, and flexural strength were studied. The introduction of alkyl groups into the ortho position decreased intermolecular interactions. The introduction of a long phenyl–ether linkage into the structure gave a broad exothermal peak in the DSC and good workability for the preparation of the cured resins. Moreover, the extension between cross-linkings improved the flexibility of the cured resins. The cured resins with fluorine-containing substituent groups also had better thermal stability in the air compared with hydrocarbon group resins.

INTRODUCTION

Aromatic cyanamides are well known as heat-resistant compounds that undergo a cyclotrimerization reaction to form isomelamine rings.[1] Accordingly, biscyanamides are expected to yield cured resins with excellent thermal and mechanical properties through the formation of ring structure linkages and high cross-linking density.

Several biscyanamides that have different structures have been synthesized and investigated.[2–5] These aromatic biscyanamides polymerize without melting because of their high reactivity. This curing behavior has made it difficult to mold them and to investigate their thermal and mechanical properties. Therefore, correlations between chemical structures and properties of the cured resins have not been investigated much; especially important would be the introduction of alkyl groups into the ortho po-

sition of the cyanamide groups or a long phenyl–ether linkage.

This paper reports on the preparation and curing of new aromatic biscyanamides that have o-substituted groups or phenyl–ether linkage and the investigation of mechanical properties for the cured biscyanamide resins. The structural effects of these aromatic biscyanamides on thermal and mechanical properties of the cured resins are discussed.

EXPERIMENTAL

Materials

Diamines starting materials were obtained commercially and were used without further purification. 4,4'-Diaminodiphenylmethane, 4,4'-diaminodiphenylether, 4,4'-diamino-3,3'-dimethyldiphenylmethane, and 4,4'-diamino-3,3'-diethyldiphenylmethane were obtained from Nihonkayaku. 2,2-bis[4-(4-aminophenoxy)phenyl]propane was ob-

tained from Wakayama Seika Kogyo. 2,2-Bis[4-(4-aminophenoxyphenyl] - 1,1,1,3,3,3 - hexafluoropropane and 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane were obtained from Central Glass Co., Ltd.

Preparation of Biscyanamides

Biscyanamides were prepared from the corresponding diamines and cyanogen bromide following published procedures.[6,7] In general, the preparation of biscyanamides was as follows: A 100 mL four-necked flask was charged with water (250 mL) and cyanogen bromide (0.9 mol) and then cooled at 0–5°C. N,N-Dimethylacetoamide (120 mL) and sodium hydrogencarbonate (0.68 mol) were added to the flask. Then, a solution of diamine (0.3 mol) in N,N-dimethylacetoamide (165 mL) was added dropwise at 0–10°C. The mixture in the flask was then stirred for 12 h while being kept at 0–10°C. The insoluble portion was removed by filtration, and the filtrate was added to cold water (3.2 L). The precipitate was collected, washed with water, and dried *in vacuo*. The product was recrystallized from a 2-methoxyethanol and water mixture (weight ratio: 1 : 1).

4,4'-Biscyanamidediphenylmethane (BCDP)

Recrystallization of the product gave a light yellow solid in 91.5% yield.

ANAL: Calcd for $C_{15}H_{12}N_4$: C, 72.8%; H, 4.5%; N, 22.7%. Found: C, 71.1%; H, 5.2%; N, 22.3%. IR(KBr) (cm^{-1}): 3170 (N—H); 2950 (C—H); 2220 (C≡N). ^{1}H-NMR (DMSO-d_6) (ppm): 9.75 (s, 2H, —NHCN); 7.5–6.56 (m, 8H, aromatic); 3.82 (s, 2H, olefinic).

4,4'-Biscyanamidediphenylether (BCDE)

The product was treated in the same way as was BCDP. A white solid was obtained in 90.6% yield.

ANAL: Calcd for $C_{14}H_{10}N_4O$: C, 67.2%; H, 4.0%; N, 22.4%. Found: C, 65.3%; H, 4.5%; N, 21.8%. IR(KBr) (cm^{-1}): 3160 (N—H); 2223 (C≡N); 1245 (—O—). ^{1}H-NMR (DMSO-d_6) (ppm): 9.75 (s, 1H, —NHCN); 7.20–6.70 (m, 8H, aromatic).

Bis[4-(4-cyanamide-3-methylphenyl)]methane (BCMM)

The product was treated in the same way as was BCDP. The white solid was obtained in 86.7% yield.

ANAL: Calcd for $C_{17}H_{16}N_4$: C, 73.9%; H, 5.8%; N, 20.3%. Found: C, 68.5%; H, 6.0%; N, 19.7%. IR(KBr) (cm^{-1}): 3176 (N—H); 2924 (C—H); 2236 (C≡N); ^{1}H-NMR (DMSO-d_6) (ppm): 9.20 (s, 1H, —NHCN); 7.45–6.64 (m, 6H, aromatic); 3.72 (s, 2H, olefinic); 2.12 (s, 6H, methyl).

Bis[4-(4-cyanamide-3-ethylphenyl)]methane (BCEM)

The product was treated in the same way as was BCDP. A white solid was obtained in 75.2% yield.

ANAL: Calcd for $C_{19}H_{20}N_4$: C, 75.0%; H, 6.6%; N, 18.4%. Found: C, 71.4%; H, 6.7%; N, 18.0%. IR(KBr) (cm^{-1}): 3192 (N—H); 2964 (C—H); 2232 (C≡N); ^{1}H-NMR (DMSO-d_6) (ppm): 9.17 (s, 2H, —NHCN); 7.45–6.50 (m, 6H, aromatic); 3.79 (s, 2H, olefinic); 2.50 (q, 4H, methylene); 1.09 (t, 6H, methyl).

Bis[4-(4-cyanamide-3,5-dimethylphenyl)]methane (BCDM)

This compound was synthesized in the same way as was BCDP, except a mixed solution of N,N-dimethylacetamide/ethylene dicloride/water (weight ratio: 1 : 1 : 1) was used when the diamine was added to the reaction flask. A white solid was obtained in 53.0% yield.

ANAL: Calcd for $C_{19}H_{20}N_4$: C, 75.0%; H, 6.6%; N, 18.4%. Found: C, 71.2%; H, 6.8%; N, 17.3%. IR(KBr) (cm^{-1}): 3190 (N—H); 2910 (C—H); 2232 (C≡N). ^{1}H-NMR (DMSO-d_6) (ppm): 8.70 (s, 2H, —NHCN); 6.92 (s, 4H, aromatic); 3.70 (s, 2H, olefinic); 2.23 (s, 6H, methyl).

2,2-Bis[4-(4-cyanamidephenoxy)phenyl]propane (BCPP)

The product was treated in the same way as was BCDP. A white solid was obtained in 96.5% yield.

ANAL: Calcd for $C_{29}H_{24}N_4O_2$: C, 75.6%; H, 5.3%; N, 12.2%. Found: C, 72.3%; H, 5.8%; N, 11.6%. IR(KBr) (cm^{-1}): 3128 (N—H); 2950 (C—H); 2232 (C≡N); 1246 (—O—). ^{1}H-NMR (DMSO-d_6) (ppm): 9.80 (s, 2H, —NHCN); 7.36–6.50 (m, 16H, aromatic); 1.60 (s, 6H, methyl).

2,2-Bis[4-(4-cyanamidephenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (BCPF)

The product was treated in the same way as was BCPP. A white solid was obtained in 86.0% yield.

ANAL: Calcd for $C_{29}H_{18}N_4O_2F_6$: C, 61.3%; H, 3.2%; N, 9.9%; F, 20.1%.

Found: C, 59.9%; H, 3.1%; N, 9.7%; F, 20.1%. IR(KBr) (cm^{-1}): 3128 (N—H); 2950 (C—H); 2232 (C≡N); 1246 (—O—); 1204, 1188 (C—F). ^{1}H-NMR (DMSO-d_6) (ppm): 9.80 (s, 2H, —NHCN); 7.40–6.65 (m, 16H, aromatic).

2,2-Bis[4-(4-cyanamide-3-trifluoromethylphenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (BCFP)

The product was treated in the same way as was BCPP. A white solid was obtained in 96.5% yield.

ANAL: Calcd for C$_{31}$H$_{16}$N$_4$O$_2$F$_{12}$: C, 52.8%; H, 2.3%; N, 8.0%; F, 32.4%.
Found: C, 51.8%; H, 3.0%; N, 9.0%; F, 29.0%. IR(KBr) (cm^{-1}): 2232 (C≡N); 1244 (—O—); 1168, 1134 (C—F). ^{1}H-NMR (DMSO-d_6) (ppm): 10.42 (s, 2H, —NHCN); 7.53–6.85 (m, 16H, aromatic).

Curing Method of Biscyanamides

Biscyanamides were placed in a heated molding press with a 1 mm spacer and cured under a pressure of 100 kgf/cm^2. The initial temperature (T_i) depends on each biscyanamide and was determined by measuring the thermal properties of each biscyanamide. Details are described below. The values are listed in Table I. After curing 1 h at T_i, the temperature was raised to 250°C and held for 1 h.

Measurement of Thermal and Mechanical Properties

Differential scanning calorimetry (DSC) was carried out on a Rigaku Denki thermal analyzer (Model TAS-100) equipped with a DSC module (Model 8240) at a heating rate of 5°C/min in air. Thermal gravimetric analysis (TGA) was done with a Shinku-Riko TGD (Model 7000RH) in air at a heating rate of 5°C/min. Dynamic mechanical analysis (DMA) was done using an Iwamoto Seisakusho device (Model RPX-706) between −180 to 350°C at a heating rate of 5°C/min. The sample was a rectangular strip, 40 × 4 × 1 mm. Flexural testing (JIS-K6911) was conducted on a Shimazu Autograph (Model DDS-5000).

The densities of the cured products were evaluated using a bromoform (d: 2.9)–toluene (d: 0.86) mixture of the same density at 25°C. The density of the corresponding mixture was measured on an Anton Parr precision density meter (Model DMA-02C).

RESULTS AND DISCUSSION

Syntheses and Curing Reaction Behaviors of Biscyanamides

The chemical structures of the prepared biscyanamides are shown in Figure 1. These were synthesized from the corresponding diamines and cyanogen bromide.

The DSC curves of the alkyl-substituted biscyanamides and the biscyanamides containing ether linkage are shown in Figures 2 and 3, respectively. All biscyanamides had no melting points, and most of them had one exothermal peak attributed to the curing reaction, except BCDP and BCPP. BCDP and BCPP had two exothermal peaks that were attributed to a complex curing reaction. The exother-

Table I   Thermal Properties of Biscyanamides

Biscyanamides	T_1^a (°C)	T_{exo}^b (°C)	T_2^b (°C)	$T_m'^d$ (°C)	T_i^e (°C)
BCDP	103	139, 151	198	> 150	160
BCMM	191	213	234	—	220
BCEM	106	134	190	> 150	170
BCDM	157	177	196	> 200	220
BCDE	110	153	192	> 155	160
BCPP	106	143, 190	199	> 150	170
BCPF	96	138	197	> 140	170
BCFP	107	153	217	> 140	170

[a] Onset temperature for curing reaction by DSC.
[b] Exothermal peak temperature by DSC.
[c] Temperature for completion of reaction by DSC.
[d] Melting temperature measured on a heated plate.
[e] Initial temperature for curing biscyanamide.

Name

BCDP   NCHN-⟨◯⟩- CH₂-⟨◯⟩-NHCN

BCMM   NCHN-⟨◯⟩- CH₂-⟨◯⟩-NHCN (with H₃C and CH₃ substituents)

BCEM   NCHN-⟨◯⟩- CH₂-⟨◯⟩-NHCN (with H₅C₂ and C₂H₅ substituents)

BCDM   NCHN-⟨◯⟩- CH₂-⟨◯⟩-NHCN (with H₃C, CH₃ substituents)

BCDE   NCHN -⟨◯⟩- O -⟨◯⟩-NHCN

BCPP   NCHN-⟨◯⟩-O-⟨◯⟩-C(CH₃)(CH₃)-⟨◯⟩-O-⟨◯⟩-NHCN

BCPF   NCHN-⟨◯⟩-O-⟨◯⟩-C(CF₃)(CF₃)-⟨◯⟩-O-⟨◯⟩-NHCN

BCFP   NCHN-⟨◯⟩-O-⟨◯⟩-C(CF₃)(CF₃)-⟨◯⟩-O-⟨◯⟩-NHCN (with F₃C)
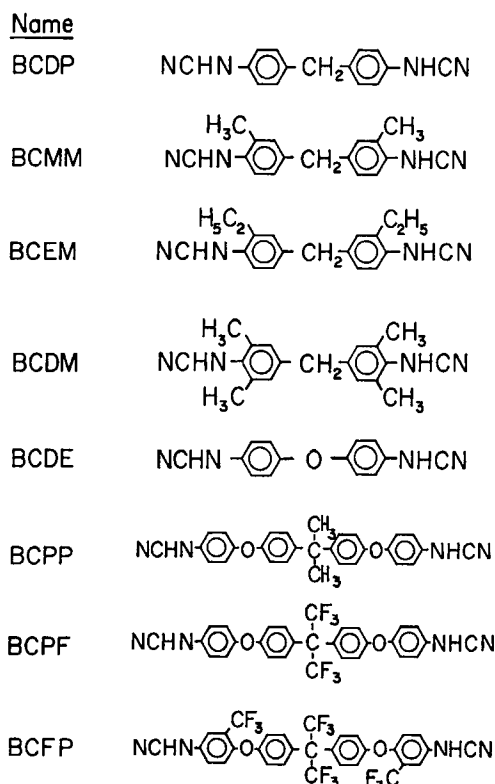
Figure 1   Structures of the prepared biscyanamides.

mal peak was broadened by the introduction of a long phenyl–ether linkage as shown in the cases of BCPP, BCPF, and BCFP.
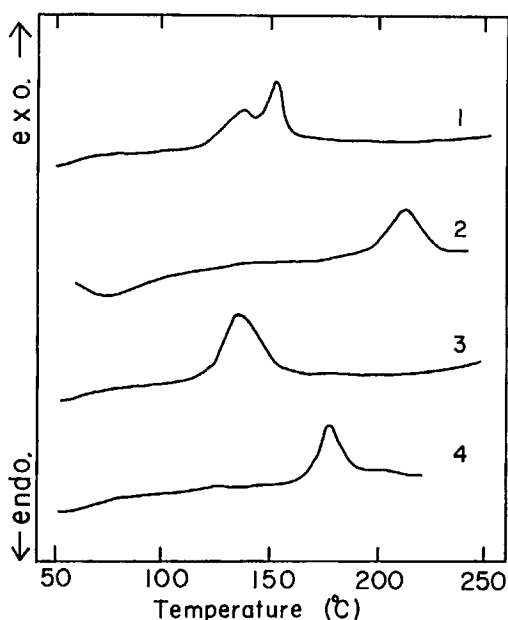

Figure 2   DSC curves of the alkyl-substituted biscyanamides: (1) BCDP, (2) BCMM, (3) BCEM, (4) BCDM.
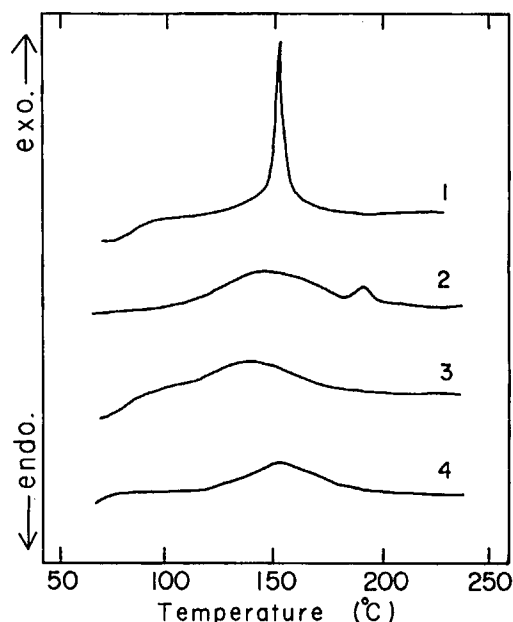

Figure 3   DSC curves of the biscyanamides containing ether linkage: (1) BCDE, (2) BCPP, (3) BCPF, (4) BCFP.

Although most of the biscyanamides had no exothermic peaks in the DSC, they melted when placed on the heated plate above a certain temperature (T'_m) and immediately began to polymerize. Therefore, to obtain a homogeneous cured product, the biscyanamides must be heated above T'_m and immediately pressed. The initial molding temperature (T_i) for curing was determined from T'_m and T_{exo}. The curing reaction behaviors and molding conditions of the biscyanamides are summarized in Table I. Each of them was placed in a molding press heated at T_i under 100 kgf/cm² for 1 h. Then, the temperature was raised to 250°C and held for 1 h. Most of them, except BCMM, yielded yellowish or brownish transparent cured products. After curing, the peak assigned to the nitrile group in the IR spectra and the exothermal peak in the DSC curves disappeared. Therefore, the curing reaction was completed.

Physical and Thermal Properties of Cured Biscyanamide Resins

Table II shows physical properties of cured biscyanamide resins. The flexural strength of BCEM, which has ethyl groups at the *ortho* position of the cyanamide groups, was smaller than that of BCDP, which has no alkyl-substituted groups. Generally, it is thought that flexural strength is effected by cross-linking density. The cross-linking density in the rubber region of BCEM obtained from dynamic me-

Table II   Physical Properties of Cured Biscyanamide Resins

Biscyanamides	Flexural Strength (MPa)	Flexural Modulus (MPa)	Density (g/cm^9)
BCDP	198	4240	1.17
BCEM	90.6	4220	1.14
BCDM	—	—	1.10
BCDE	110	4720	1.25
BCPP	187	3190	1.15
BCPF	143	3590	1.21
BCPF	—	—	1.31

chanical analysis (DMA) data (Fig. 4) following Nielsen's method[8] was almost as good as that of BCDP (5.23×10^{-3} mol/cm^3 and 5.99×10^3 mol/cm^3, respectively). Consequently, it seemed that lowering of the flexural strength of BCEM was not due to reduction of the cross-linking density by the hindrance of ethyl groups, but due to decreasing intermolecular interactions by the existence of ethyl groups. In this case, the existence of polar C=NH groups in the isomelamine rings caused intermolecular interactions, dipole–dipole interactions, or hydrogen bonds. Such intermolecular interactions were reported in the case of polyisocyanurates that were produced by cyclotrimerization of diisocyanates[9] (in this case, the intermolecular interactions were a di-
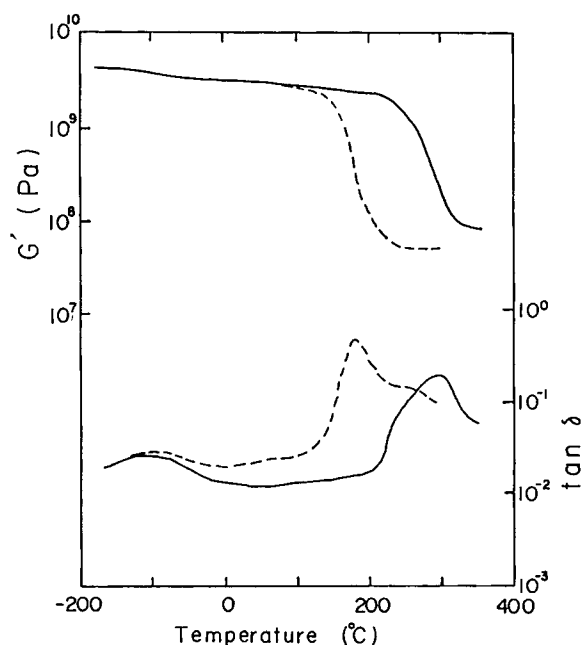
Figure 4   DMA curves of the cured biscyanamide resins: (———) BCDP; (- - - - -) BCEM.

pole–dipole type due to the C=O groups in the isocyanurate rings). Although flexural testing and DMA of BCMM and BCDM could not be done, similar results should be obtained for them. This reduction of the intermolecular interaction was responsible for the reduction in density of cured biscyanamide resins that have alkyl-substituted groups.

In addition, the flexural modulus of BCDE, which has a phenyl–ether (ph—O) linkage, was higher than that of BCDP, which has phenyl–methylene (ph—CH$_2$) linkage, and the flexural strength of the former resin was smaller than that of the latter. The cured product of BCDE was more brittle than that of BCDE, although the flexibility of the phenyl–ether linkage of BCDE was higher than that of the phenyl–methylene linkage of BCDP. By contrast, BCPP and BCPF, which both have a long phenyl–ether linkage, showed the most flexibility.

Table III shows the thermal properties of cured biscyanamide resins. The relative thermal stability of cured resins was assessed by comparing the initial decomposition temperature (IDT), which was defined as the 5% weight loss temperature, the temperature with the maximum rate of weight loss (T_{max}), and char yields at 500°C (Y_c). The glass transition temperature (T_g) was obtained from DMA data.

Thermal stability of alkyl-substituted biscyanamide (BCMM, BCEM, BCDM) resins was slightly lower than BCDP, which has no substituted groups. These results were caused not only by the existence of steric hindrance after the curing reaction that decreased their cross-linking densities, but also by an ability to break more easily the phenyl-methyl (ph—CH$_3$) or phenyl-ethyl (ph—C$_2$H$_5$)

Table III   Thermal Properties of Cured Biscyanamide Resins

Biscyanamides	IDT[a] (°C)	T_{max}[b] (°C)	Y_c[c] (%)	T_g[d] (°C)
BCDP	369	522	62.0	290
BCMM	368	552	64.1	—
BCEM	344	508	44.7	180
BCDM	337	513	43.6	—
BCDE	295	490	40.6	250
BCPP	299	509	43.1	200
BCPF	376	523	73.9	180
BCFP	322	516	64.4	—

[a] 5% wt loss temperature.
[b] Temperature of maximum rate of weight loss.
[c] Char yield at 500°C.
[d] The glass transition temperature measured by DMA.

linkage compared with the phenyl–hydrogen linkage. Moreover, it was also considered that the lowered thermal stability was due to the reduced intermolecular interactions between C=NH groups in the isomelamine rings due to steric hindrance of alkyl-substituted groups.

Similarly, the thermal stability of the resins containing aromatic ether bonds (BCDE, BCPP) was less than that of BCDP. Generally, the presence of flexible chain is known to facilitate the cyclotrimerization with a large conversion and to enhance the thermal stability of the cross-linked resin.[8] But the decomposition temperatures of BCDE and BCPP were lower than that of BCDP. This result was attributed to an easier breaking of the phenyl–ether linkage in comparison with the phenyl–methylene linkage. But the resins containing trifluoromethyl groups (BCPF, BCFP) were more thermal stable than was BCDP, even if they had the phenyl–ether linkage. This thermal stability was due to oxidation by the electron-withdrawing substituents of perfluoro groups.

In addition, the T_g of biscyanamides containing phenyl–ether bonds (BCPP, BCPF) was lower than that of BCDP and BCDE. This was caused by flexibility of phenyl–ether bonds and by decreasing the cross-linking density with a long distance between cross-linking units.

CONCLUSIONS

The homogeneous transparent cured products of several biscyanamides were obtained by optimal molding conditions after investigating their curing reaction behaviors. The introduction of alkyl groups into the ortho position of the cyanamide groups did not affect the cross-linking density, but it decreased intermolecular interactions between isomelamine rings in the case of 4,4'-biscyanamidediphenylmethane (BCDP) and bis[4-(4-cyanamide-3-ethyl-phenyl)]methane (BCEM). This was regarded as one of main reasons why thermal and mechanical properties of the cured resin were lowered. Lengthening the distance between cross-linking joints by introducing long phenoxy chains increased flexibility of cured resin, but the introduction of ether linkages decreased their heat resistance. In order to increase thermal stability, introduction of perfluoromethyl groups was effective and mechanical properties were not lowered.

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