## Spontaneous Terpolymeritation of 1,3-Cycloalkadiene, Styrene, and Acrylonitrile in the Presence of Zinc Chloride

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## ABSTRACT

1,3-Cycloalkadienes of six- to eight-membered rings, such as 1,3-cyclohexadiene (1,3-CHD), 1,3-cycloheptadiene (1,3-$CH_pD$), and 1,3-cyclooctadiene (1,3-COD), underwent spontaneous terpolymerization with styrene (St) and acrylonitrile (AN) in the presence of $ZnCl_2$, which was accompanied by cycloaddition of the diene with AN when 1,3-CHD or 1,3-$CH_pD$ was used as the diene. In the system involving 1,3-CHD as diene, the increase in $ZnCl_2$ concentration increased both the rates of the two reactions and the terpolymer viscosity, while it scarcely affected the terpolymer composition. The terpolymers yielded in the terpolymerizations of 1,3-cycloalkadiene, St, and AN in the presence of $ZnCl_2$ were composed of ~50 mol% AN units and of ~50 mol% donor monomer units, 1,3-cycloalkadiene and St. The terpolymerization was regarded as a binary copolymerization between charge-transfer (CT) complexes of 1,3-cycloalkadiene and St with AN coordinated to $ZnCl_2$, $(AN)_c$, and the resulting monomer reactivity ratio for the 1,3-cycloalkadiene-$(AN)_c$ complex decreased in the order 1,3-CHD > 1,3-$CH_pD$ > 1,3-COD. Such a variation in the monomer reactivity ratios

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with the diene is explained in terms of two interactions in the propagation: one between the diene and $(AN)_c$ in the CT-complex and the other between the diene and a propagating radical having $(AN)_c$ as a terminal unit.

# INTRODUCTION

The physicochemical properties and the reactivities of cycloolefins are known to be dependent on the ring size [1]. It has been reported that the reactions of 1,3-cycloalkadienes of five- to eight-membered rings with acceptor monomers such as sulfur dioxide [2-5], maleic anhydride [4, 6-8], and acrylonitrile (AN) in the presence of $ZnCl_2$ [9-11] give rise to either cycloadduct or copolymer or both, and that the product ratio varies largely with the ring size of the dienes [9, 12].

Moreover, the alternating tendency of the copolymers obtained in the spontaneous copolymerizations of 1,3-cycloalkadienes of six- to eight-membered rings with AN in the presence of $ZnCl_2$ was observed to depend on the ring size of the diene [9-11]. Such a dependence was inferred to result from differences in the concentration and in the reactivity of charge-transfer (CT) complexes formed between the diene and AN coordinated to $ZnCl_2$, $(AN)_c$.

Styrene (St) copolymerizes with $(AN)_c$ to form a copolymer with an approximately alternating composition [13, 14], and its terpolymerization with butadiene and polar vinyl monomers in the presence of Lewis acids affords terpolymers consisting of ~50 mol% of polar monomer units and ~50 mol% of total monomer units of St and butadiene [15, 16]. It has been suggested that such a terpolymerization of two donor monomers and one acceptor monomer can be considered as a binary copolymerization between CT-complexes of the respective donor monomers with the acceptor monomer and that the apparent monomer reactivity ratios of the two CT-complexes can be estimated [17, 18].

The present study deals with the terpolymerizations of 1,3-cyclo-alkadiene of six- to eight-membered rings, St, and AN in the presence of $ZnCl_2$. The reactivity of the dienes in the terpolymerizations is discussed on the basis of the resulting monomer reactivity ratios of 1,3-cycloalkadiene-$(AN)_c$ complexes. Cyclopentadiene was not used for this work because of the lack of copolymerizability with AN [9].

## EXPERIMENTAL

### Materials

Syntheses and purifications of 1,3-CHD [10], 1,3-CH$_p$D [9], and 1,3-COD (commercial) [11] were carried out as reported previously. St and AN were purified by the usual methods. Zinc chloride, guaranteed reagent grade, was dried in the melt under vacuum.

### Spectral Measurements

IR measurements were carried out on a Shimadzu IR-400 infrared spectrometer. NMR spectra were obtained by using a Hitachi R-24B high resolution NMR spectrometer.

### Reaction

The reaction of 1,3-cycloalkadiene, St, and AN in the presence of ZnCl$_2$ and the isolation of the products, terpolymer and cycloadduct (when 1,3-CHD or 1,3-CH$_p$D was used as the diene), were conducted by procedures similar to those shown for the copolymerizations of 1,3-cycloalkadiene with AN in the presence of ZnCl$_2$ [9-11], except additions of 1,3-cycloalkadiene and St to the solution of ZnCl$_2$ in AN were done by using their mixture at a fixed composition.

### Characterization of Terpolymers

The terpolymer composition was determined from the area ratio of peaks due to methylene-methyne, olefinic, and aromatic protons which appeared in the discrete region in NMR spectra measured in CDCl$_3$ as solvent (see Fig. 2). The viscosity of the terpolymer composed of 1,3-CHD, St, and AN units was determined at a concentration of 0.5 g/dL in nitrobenzene as solvent at 25°C with an Ubbelhode viscometer.

## RESULTS AND DISCUSSION

### The Terpolymerization of 1,3-CHD, St, and AN in the Presence of ZnCl$_2$

As reported previously [10], when 1,3-CHD is mixed with AN in the presence of ZnCl$_2$, cycloaddition and copolymerization take place simultaneously. Similarly, both the cycloadduct of 1,3-CHD with AN
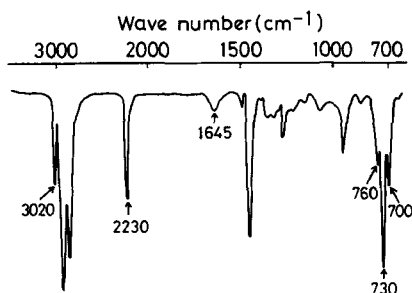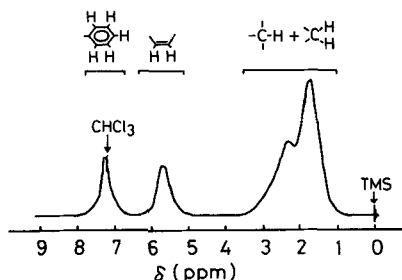
FIG. 1.  IR spectrum of 1,3-CHD-St-AN terpolymer.



FIG. 2.  NMR spectrum of 1,3-CHD-St-AN terpolymer.  Solvent: CDCl₃; temperature: 35°C; internal reference:  tetramethylsilane (TMS).

and the terpolymer are yielded in the system involving 1,3-CHD, St, and AN in the presence of $ZnCl_2$ (see Fig. 3).  IR and NMR spectra of the resulting terpolymer are illustrated in Figs. 1 and 2, respectively.  The terpolymer involving 1,3-CH$_p$D or 1,3-COD as the diene unit affords similar IR and NMR spectra.  The IR spectrum shows peaks of the carbon-carbon double bond at 730 (cis), 1645, and 3020 $cm^{-1}$, of the phenyl group at 700 and 760 $cm^{-1}$, and of the nitrile group at 2230 $cm^{-1}$, indicative of the co-presence of 1,3-CHD, St, and AN units in the terpolymer.  In the NMR spectrum, two peaks at 6.8-7.8 and 5.3-6.4 ppm are assignable to aromatic protons of the St unit and to olefinic ones of the 1,3-CHD unit, respectively.  The peak at 0.9-3.6 ppm is considered to be due to methylene and methyne protons resulting from monomer units of 1,3-CHD, St, and AN in the terpolymer.  Accordingly, the terpolymer composition can be determined from the ratio of areas of the respective peaks in the NMR spectrum.  For example, the contents of 1,3-CHD, St, and AN units in the terpolymer obtained at a $ZnCl_2$ concentration of 1.5 mol/L in
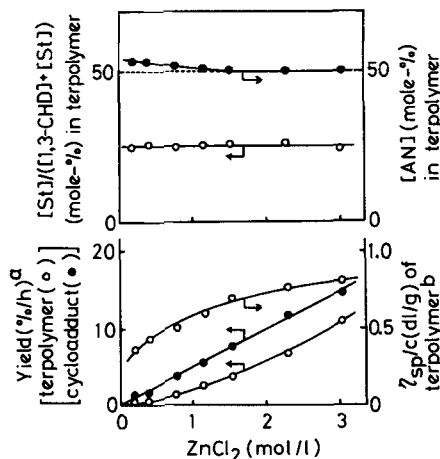
FIG. 3.  Effect of ZnCl₂ concentration on the reaction of 1,3-CHD, St, and AN in the presence of ZnCl₂.  Feed: [ 1,3-CHD] = [ St] = 1.50 mol/L; temperature: 40°C; [a]terpolymer yield (%) was calculated on the ratio of (1,3-CHD + St) units/AN units = 1 in the terpolymer; [b]determined in nitrobenzene, c = 0.5 g/dL at 25°C.

Fig. 3 was estimated to be 37.0, 12.7, and 50.3 mol%, respectively, and the content of the AN unit is nearly equal to the total contents of donor monomer units, 1,3-CHD and St.  Thus the terpolymer containing ~50 mol% of an AN unit can be represented as $+ 1,3\text{-}CHD\cdot AN)_m (St\cdot AN)_n$.

The effect of ZnCl₂ concentration on the rates of cycloaddition and of terpolymerization, the composition, and the viscosity of the resulting terpolymer at fixed concentrations of both 1,3-CHD and St in AN is presented in Fig. 3.  Under the present conditions, all the ZnCl₂ added is considered to be present in the form of the (AN)₂ZnCl₂ complex, which further forms CT-complexes with both 1,3-CHD [ 9] and St [ 14].  A linear dependence of the rate of cycloaddition on ZnCl₂ concentration indicates that $(AN)_c$ acts as a dienophile.  The rate constant of the cycloaddition was found to be ~0.065 L/mol·h from the results shown in Fig. 3, which is comparable to that (~0.071 L/mol·h [ 10]) for the system composed of 1,3-CHD and AN in the presence of ZnCl₂.  Therefore, St appears to have only a slight affect on the cycloaddition of 1,3-CHD with $(AN)_c$.  The increase in the rate of termpolymerization and in the viscosity of the terpolymer with increasing ZnCl₂ concentration can be explained by considering the formation of initiating radicals and the propagation through the CT-complexes of donor monomers, 1,3-CHD and St, with $(AN)_c$ for the
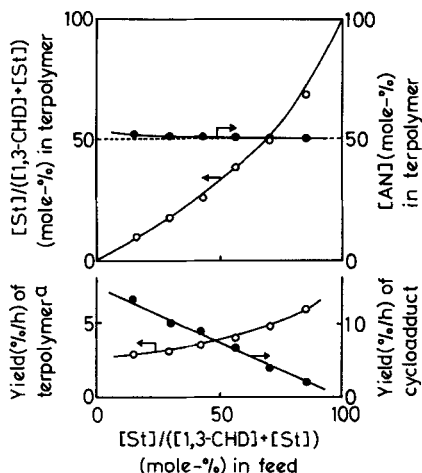
FIG. 4. Effect of feed composition of donor monomers, 1,3-CHD and St, on the reaction of 1,3-CHD, St, and AN in the presence of ZnCl$_2$. Feed: [1,3-CHD] + [St] = 2[ZnCl$_2$] = 2.94 mol/L; temperature: 40°C; [a]terpolymer yield (%) was determined on the ratio of (1,3-CHD + St) units/AN units = 1 in the terpolymer; the curve representing the ratio of St to 1,3-CHD units in the terpolymer was calculated on the apparent monomer reactivity ratios shown in Table 1.

terpolymerization in a similar manner as suggested for alternating copolymerizations of donor and acceptor monomers [10, 11, 13, 19].

The ratio of monomer units of 1,3-CHD to St in the resulting terpolymers is scarcely dependent on the ZnCl$_2$ concentration. Furthermore, the content of AN units in the terpolymer shows a value very close to 50 mol%. However, it increases slightly at lower ZnCl$_2$ concentration, probably because of some participation of free AN in the propagation through the CT-complexes.

Figure 4 depicts the influence of feed composition of donor monomers, 1,3-CHD and St, on the reaction with AN in the presence of ZnCl$_2$, both total donor monomer and ZnCl$_2$ concentrations being kept constant. The terpolymerization is enhanced to some extent with an increase in the feed composition of St. The resulting terpolymer consists of ~50 mol% of AN units, though a slight increment of AN content takes place at a lower feed composition of St. On the other hand, the ratio of 1,3-CHD to St units in the terpolymer varies profoundly with the feed composition, and the content of 1,3-CHD units in the terpolymer is higher than that in the feed over a whole range of feed composition.
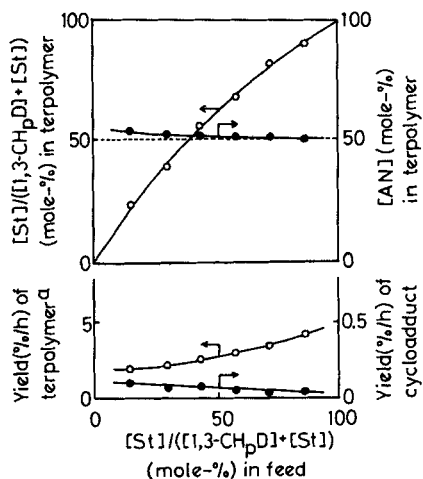
FIG. 5. Effect of feed composition of donor monomers, $1,3\text{-CH}_p\text{D}$ and St, on the reaction of $1,3\text{-CH}_p\text{D}$, St, and AN in the presence of $\text{ZnCl}_2$. Feed: $[1,3\text{-CH}_p\text{D}] + [\text{St}] = 2[\text{ZnCl}_2] = 2.91$ mol/L; temperature: $40°\text{C}$; [a]terpolymer yield (%) was determined on the ratio of $(1,3\text{-CH}_p\text{D} + \text{St})$ units/AN units = 1 in the terpolymer; the curve representing the ratio of St to $1,3\text{-CH}_p\text{D}$ units in the terpolymer was calculated on the apparent monomer reactivity ratios shown in Table 1.

## The Terpolymerization of $1,3\text{-CH}_p\text{D}$, St, and AN in the Presence of $\text{ZnCl}_2$

As presented in Fig. 5, when $1,3\text{-CH}_p\text{D}$ is used as the diene the terpolymerization is exceedingly predominant compared to the cycloaddition, similar to the relationship between copolymerization and cycloaddition for the system without St [9]. Although the resulting terpolymer has a composition close to 50 mol% of AN units, an increment of AN content in the terpolymer at lower feed composition of St is slightly larger than that in the system involving 1,3-CHD as diene. Moreover, the composition of St units in the terpolymer is higher than that in the feed.
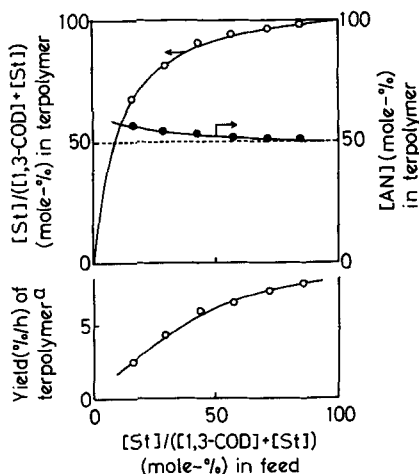
FIG. 6.  Effect of feed composition of donor monomers, 1,3-COD and St, on the reaction of 1,3-COD, St, and AN in the presence of $ZnCl_2$.  Feed: $[1,3\text{-COD}] + [St] = 2[ZnCl_2] = 2.87$ mol/L; temperature:  40°C; [a]terpolymer yield (%) was determined on the ratio of (1,3-COD + St) units/AN units = 1 in the terpolymer; the curve representing the ratio of St to 1,3-COD units in the terpolymer was calculated on the apparent monomer reactivity ratios shown in Table 1.

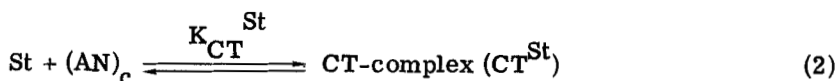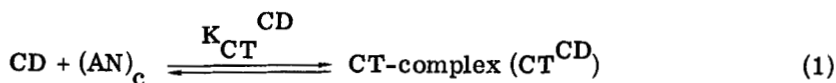## The Terpolymerization of 1,3-COD, St, and AN in the Presence of $ZnCl_2$

1,3-COD undergoes only a spontaneous copolymerization with AN in the presence of $ZnCl_2$ [11].  Similarly, only a terpolymer is obtained in the system involving 1,3-COD as diene.  As illustrated in Fig. 6, the deviation of AN content in the resulting terpolymer from 50 mol% at a lower feed composition of St becomes more pronounced compared to that observed for the system containing 1,3-CHD or 1,3-CH$_p$D as diene.  Furthermore, the ratio of 1,3-COD to St units in the terpolymer is considerably low over a wide range of feed composition.  These results correspond to the lower alternating tendency of the copolymer obtained in the copolymerization of 1,3-COD with AN in the presence of $ZnCl_2$ [11].

## Comparison of the Monomer Reactivity Ratios of 1,3-Cycloalkadiene-(AN)$_c$ Complexes

As described above, the AN content in the terpolymers obtained here was found to be ~50 mol% in higher feed composition of St.  This

indicates that the terpolymerization can be regarded as a binary co-polymerization of two CT-complexes, 1,3-cycloalkadiene-$(AN)_c$ and St-$(AN)_c$.

The equilibria of CT-complex formations can be represented as

$$CD + (AN)_c \xrightleftharpoons{K_{CT}^{CD}} \text{CT-complex } (CT^{CD}) \tag{1}$$

$$St + (AN)_c \xrightleftharpoons{K_{CT}^{St}} \text{CT-complex } (CT^{St}) \tag{2}$$

where $K_{CT}^{CD}$ and $K_{CT}^{St}$ are the equilibrium constants of CT-complex formation and CD is 1,3-cycloalkadiene. Since $K_{CT}$ values have been found to be small for the CT-complex formation of 1,3-cyclo-alkadienes of six- to eight-membered rings and of St with $(AN)_c$ [9, 11, 14], the concentrations of CT complexes, $[CT^{CD}]$ and $[CT^{St}]$, can be expressed as

$$[CT^{CD}] = K_{CT}^{CD}[CD][(AN)_c] \tag{3}$$

$$[CT^{St}] = K_{CT}^{St}[St][(AN)_c] \tag{4}$$

where $[CD]$, $[St]$, and $[(AN)_c]$ are the concentrations of 1,3-cyclo-alkadiene, St, and $(AN)_c$, respectively. Thus the monomer unit ratio of 1,3-cyclodiene to St in the terpolymers can be derived from the composition equation for a binary copolymerization between $CT^{CD}$ and $CT^{St}$:

$$\frac{(CD \text{ unit})}{(St \text{ unit})} = \frac{[CD]}{[St]} \frac{r_{CD}(K_{CT}^{CD}/K_{CT}^{St})([CD]/[St]) + 1}{([CD]/[St]) + r_{St}(K_{CT}^{St}/K_{CT}^{CD})} \tag{5}$$

where $r_{CD}(K_{CT}^{CD}/K_{CT}^{St})$ and $r_{St}(K_{CT}^{St}/K_{CT}^{CD})$ are considered to imply the apparent monomer reactivity ratios of the CT complexes of 1,3-cycloalkadiene and St with $(AN)_c$, respectively, and they can be evaluated from the dependence of (CD unit)/(St unit) in the terpolymers on $[CD]/[St]$ in the feed.

TABLE 1. The Apparent Monomer Reactivity Ratios, $r_{CD}(K_{CT}{}^{CD}/K_{CT}{}^{St})$ and $r_{St}(K_{CT}{}^{St}/K_{St}{}^{CD})$, and the Equilibrium Constants of the Formation, $K_{CT}{}^{CD}$ and $K_{CT}{}^{St}$, of 1,3-Cycloalkadiene-(AN)$_c$ Complex and St-(AN)$_c$ Complex, Respectively, the Ionization Potential (I.P.), and the Interplanar Angle ($\theta$) of Two Double Bond Planes of 1,3-Cycloalkadienes

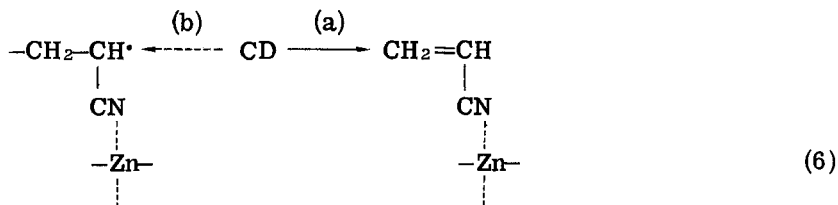| 1,3-Cycloalkadiene (CD) | 1,3-CHD | 1,3-CH$_p$D | 1,3-COD |
|---|---|---|---|
| $r_{CD}$ $(K_{CT}{}^{CD}/K_{CT}{}^{St})$ | 1.78 | 0.71 | 0.15 |
| $r_{St}$ $(K_{CT}{}^{St}/K_{CT}{}^{CD})$ | 0.32 | 1.80 | 12.0 |
| $K_{CT}{}^{CD}$ (L/mol)[a] | 0.109[b] | 0.101[b] | 0.071[c] |
| I.P. (eV)[d] | 8.25 | 8.30 | 8.68 |
| $\theta$[e] | 17° | 52° | 68° |

[a]In AN at 25°C.
[b]Cf. Ref. [9].
[c]Cf. Ref. [11].
[d]Chemical Society of Japan (ed.), Kagaku Binran, Fundamental Edition, 2nd ed., Maruzen, Tokyo, 1975, pp. 1279-1282.
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Equation (5) indicates that the ratio of donor monomer units, (CD unit)/(St unit), in the terpolymers does not depend on the feed composition of (AN)$_c$, the ZnCl$_2$ concentration, but only on the feed ratio of 1,3-cycloalkadiene to St. These dependencies are evidenced by the results shown here. However, Eq. (5), at the same time, requires the AN content in the terpolymers to be 50 mol%. Therefore, the apparent monomer reactivity ratios were estimated in the range of feed composition where the resulting terpolymers show an AN content relatively close to 50 mol%. The monomer reactivity ratios determined in this manner are summarized in Table 1, together with the equilibrium constants of CT-complex formation and physicochemical properties of the dienes. The curves representing the proportion of St units in donor monomer units in the terpolymers, shown in Figs. 4-6, are calculated from the values for the monomer reactivity ratios presented in Table 1. Thus the monomer reactivity ratios for 1,3-cycloalkadiene-(AN)$_c$ complexes decrease with increasing ring size of the dienes.

The variation in the monomer reactivity ratios with the 1,3-cyclo-alkadiene used can be interpreted by considering two factors related to the interaction in the propagation:

$$
\begin{array}{ccc}
& \text{(b)} & \text{(a)} \\
-CH_2-CH\cdot & \xleftarrow{\text{------}} \quad CD \quad \xrightarrow{\hspace{1cm}} & CH_2=CH \\
| & & | \\
CN & & CN \\
\vdots & & \vdots \\
-Zn- & & -Zn- \\
\vdots & & \vdots
\end{array}
\qquad (6)
$$

Besides a CT-interaction (a) between 1,3-cyclodiene and $(AN)_c$, the diene in the CT-complex should bear an interaction (b) with a propagating radical having $(AN)_c$ as a terminal unit, as suggested by Ikegami et al. [20].

The donor property of 1,3-cycloalkadiene affecting these interactions decreases in the order $1,3\text{-CHD} > 1,3\text{-CH}_pD > 1,3\text{-COD}$ (see ionization potential in Table 1). Increasing the donor property of the dienes should increase the CT interaction (a) in the complex, as shown by $K_{CT}^{CD}$ values, as well as the intercomplex interaction (b), resulting in enhanced reactivity of the CT complexes as a result of a lowering of activation energy for the propagation caused by these interactions.

The increase in the ring size of the dienes, at the same time, leads to a decrease in the coplanarity of two double bond planes, as shown by the interplanar angle $(\theta)$ in Table 1. The conformation of the dienes is considered to exert a steric effect on these interactions, which may also be responsible for the variation in the apparent monomer reactivity ratios of the CT complexes.

The deviation of the AN content in the terpolymer from 50 mol% at lower feed composition of St becomes more pronounced as the monomer reactivity ratio for the 1,3-cycloalkadiene-$(AN)_c$ complex decreases, and hence it can be attributed to additional participation of $(AN)_c$ and/or free AN in propagation via the CT complexes, as reported for the copolymerization of the 1,3-cycloalkadienes with AN in the presence of $ZnCl_2$ [9-11].

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