

## Estimation of Kinetic Parameters during Polymer Degradation from Two DTA Traces

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### Synopsis

A method is presented for the estimation of kinetic parameters during polymer degradation from two DTA traces. By this method, changes in mechanism with conversion may be detected. The method is applied to polyethylene, polypropylene, polystyrene, and polytetrafluoroethylene (Teflon). The agreement between observed and reported values of kinetic parameters is good. Advantages and disadvantages of the method are discussed.

Recently, several communications<sup>1-3</sup> reported the estimation of kinetic parameters during polymer degradation by means of a single DTA trace. The values obtained represented overall values and because of this, it was difficult to ascertain whether or not any change in mechanism occurred during polymer pyrolysis. In order to overcome this shortcoming, a method has now been developed which will allow the estimation of reaction order  $n$  from two DTA traces at various degrees of polymer degradation. After  $n$  has been determined, activation energy  $E$  (and frequency factor  $Z$ ) may readily be evaluated. This method has been applied to polyethylene (PE), polypropylene (PPr), polystyrene (PSt) polytetrafluoroethylene (Teflon, TF), and benzenediazonium chloride (BDC). Advantages and disadvantages of the method are discussed.

### Experimental

The polymers investigated were of commercial grade. The DTA apparatus used was an Aminco thermoanalyzer. In general, 9-18 mg. of polymer sample was "sandwiched" between sufficient alumina (Fisher certified reagent grade) so that the total sample weight was 100 mg. and the sample was loosely packed. In order to obtain reproducible results for polytetrafluoroethylene, it was necessary to either use very small samples (about 9 mg.) or to disperse the sample throughout the alumina. The latter material (100 mg.) was also used as the inert reference. The constant heating rates (RH) employed for the various polymers ranged in value from 8.0 to 17.1°C./min., and nitrogen was passed over the sample and reference at a flow rate of 35-45 cc./min.

### Results and Discussion

By making the usual simplifying assumptions<sup>1-3</sup> that heat capacity terms may be neglected in comparison with other terms and that the cell constant is about equal for the reference and sample cells, we may write,

$$W_c \approx W_{0,c} (\bar{a}/A)$$

and

$$-dW_c/dT \approx W_{0,c} (\Delta T/A) \quad (1)$$

where,  $W_c$  and  $W_{0,c}$  denote active weight or weight fraction of polymer remaining and polymer initially present, respectively, during a pyrolysis;  $A$  represents the total area under the DTA curve; and

$$\bar{a} \approx A - \int_{T_0}^T \Delta T dT$$

where  $\Delta T$  denotes peak height.

We may also write, employing the Arrhenius equation,

$$-dW_c/dT = [Z/(RH)] e^{-E/RT} W_c^n \quad (2)$$

On substituting eq. (1) into eq. (2), there is obtained

$$W_{0,c} (\Delta T/A) \approx [Z/(RH)] e^{-E/RT} W_{0,c}^n (\bar{a}/A)^n \quad (3)$$

By employing two DTA traces for the same material at two different heating rates, eq. (3), becomes, for the same temperature range,

$$V_1 = nV_2 + \int_1^2 \log K dT \quad (4)$$

where

$$V_1 = \int_1^2 \log (\Delta T_1/\Delta T_2) dT$$

$$V_2 = \int_1^2 \log (\bar{a}_1/\bar{a}_2) dT$$

and

$$K = [(W_{0,c})_1 A_2 / (W_{0,c})_2 A_1] [(RH)_2 / (RH)_1]$$

From eq. (4), it can be seen that a plot of  $V_1$  versus  $V_2$  should afford a linear relationship whose slope should yield a value of  $n$  ( $\int_1^2 dT = \Delta T$ , which is maintained constant and, therefore, the last term in eq. (4) is constant). After  $n$  has been evaluated,  $E$  may be readily determined from a modified form of eq. (3), i.e.,

$$\log \Delta T - n \log \bar{a} \equiv V_3 = -E/2.3RT + \log \{ [Z/(RH)] (W_{0,c}/A)^{n-1} \} \quad (3a)$$

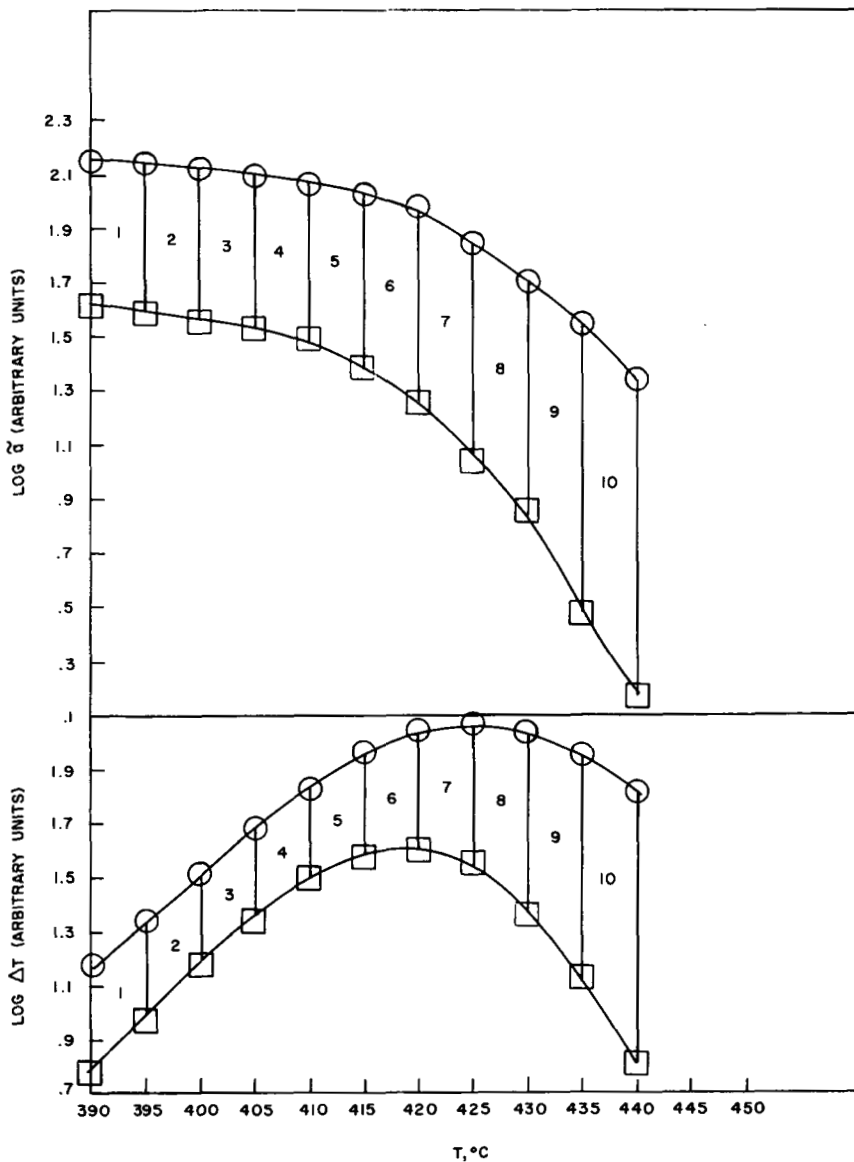


Fig. 1. Evaluation of  $V_1$  and  $V_2$  for PSt from plots of  $\log \Delta T$  and  $\log \bar{a}$  vs. temperature (O) 15.2°C./min.; (□) 8.6°C./min.

In Figure 1 are seen typical plots of  $\log \Delta T$  and  $\log \bar{a}$  versus temperature in the case of polystyrene ( $\Delta T = \text{constant} = 5^\circ\text{C}.$ ). From such plots, corresponding values of  $V_1$  and  $V_2$  may be determined by measuring areas (the same numbered areas are used in such a determination). Then, from eq. (4), a plot of  $V_1$  versus  $V_2$  should provide a value of  $n$  (and  $K$ ). Such plots are shown in Figure 2 for the various polymers. After  $n$  has been

evaluated, a value of  $E$  for each polymer may now be obtained from a plot of  $V_3$  versus  $1/T$  [see eq. (3a)]. In Figures 3 and 4 are shown such plots (in the latter figure  $n = 0$ ). In Table I are summarized values of  $n$ ,  $E$ , and  $K$  obtained for various polymers by the method already outlined. The values of the first two parameters are compared with values reported in

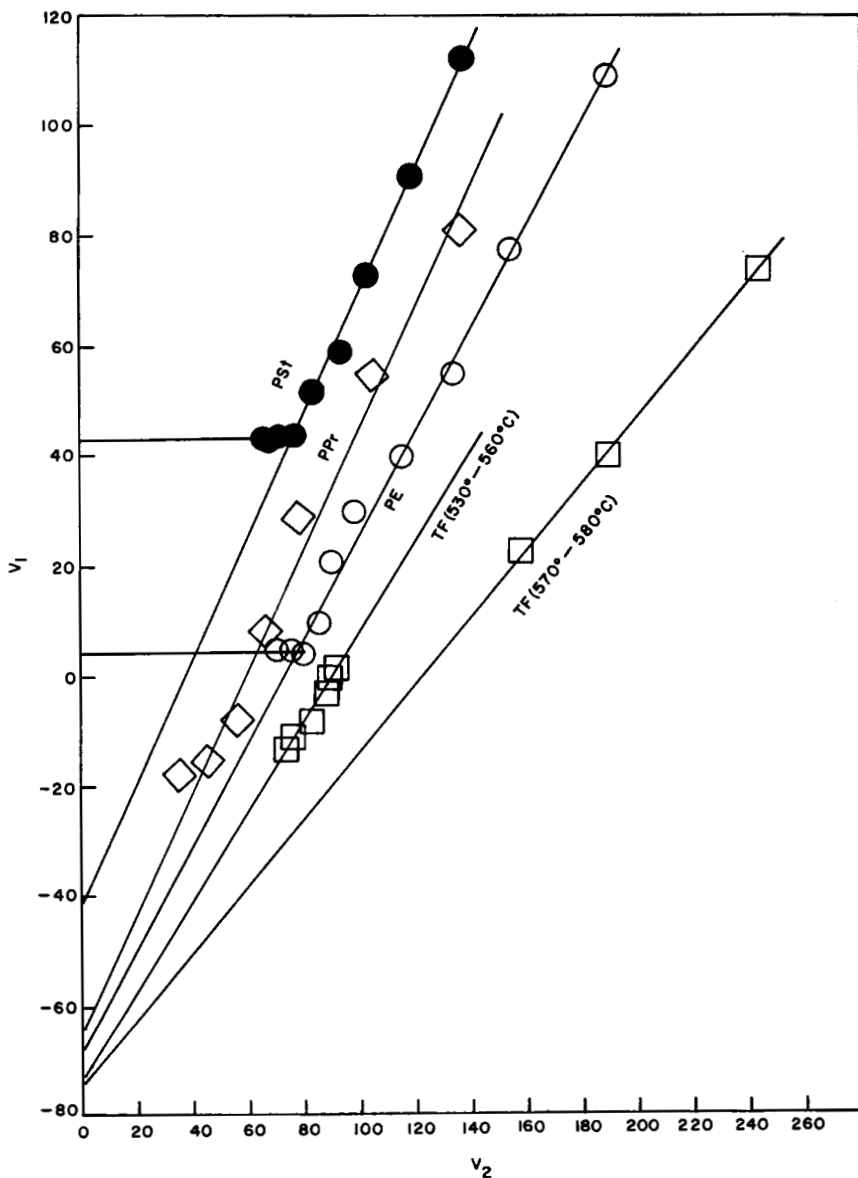


Fig. 2. Estimation of  $n$  and  $K$  from a plot of  $V_1$  vs.  $V_2$  for several polymers [eq. (4)]: (O) 8.7 and 16.1°C./min.; ( $\diamond$ ) 10.4 and 17.1°C./min.; ( $\square$ ) 8.0 and 15.3°C./min.; ( $\bullet$ ) 8.6 and 15.2°C./min.

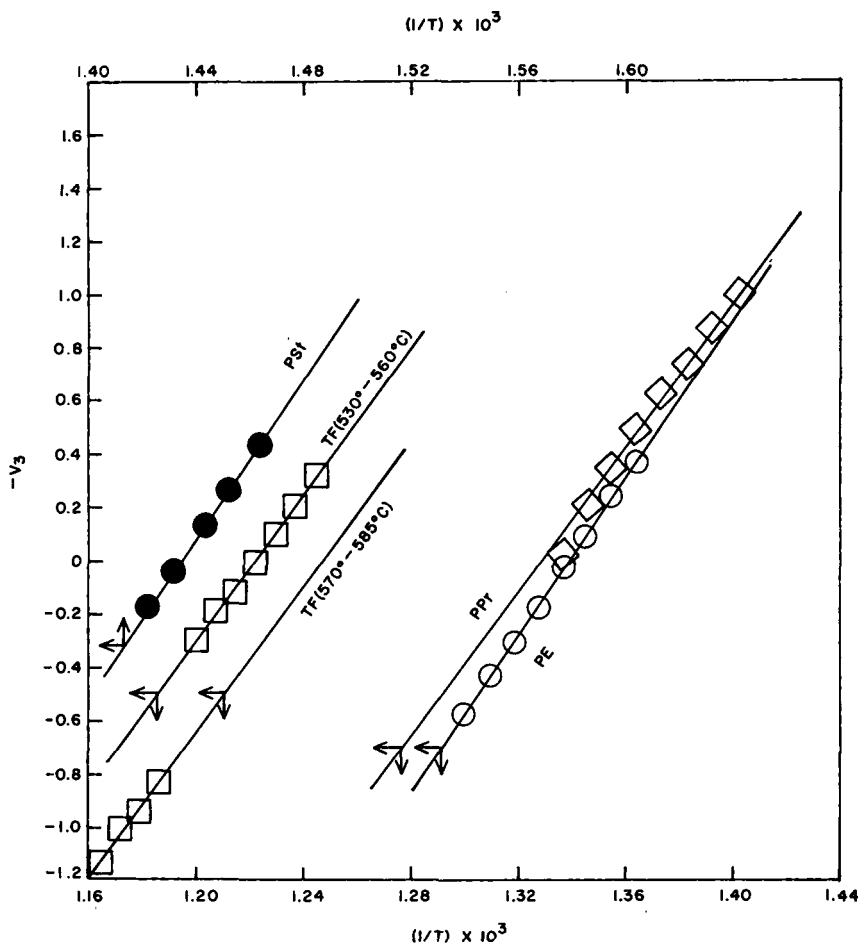


Fig. 3. Estimation of  $E$  from a plot of  $V_3$  vs. reciprocal temperature [eq. (3a)]: (●) 15.2°C./min.; (□) 8.0°C./min.; (◇) 17.1°C./min.; (○) 16.1°C./min.

the literature, whereas the observed value of  $K$  is compared with the calculated value. (Values for BDC are also included, since this case represents an almost ideal situation in which cell constants, heat capacities, and volume terms are almost identical for the sample and reference cells.)

From Table I, it can be seen that observed and calculated values of  $K$  are in good agreement. This strengthens the validity of the assumptions made in obtaining eq. (1). In general, there is also good agreement between observed and reported values of  $E$  and  $n$ . In connection with the latter two parameters, it can be observed from Table I and Figures 2-4 that  $E$  and  $n$  changed with conversion for PE, PSt, and TF. Thus, between a conversion range of  $8 \pm 2$  to  $23 \pm 7\%$ ,  $n = 0$  and  $E = 60$  kcal./mole for PE, while for a conversion range of  $23 \pm 7$  to  $85 \pm 9\%$ ,  $n = 0.94$  and  $E = 68$  kcal./mole. Anderson and Freeman<sup>6</sup> reported that in the thermal

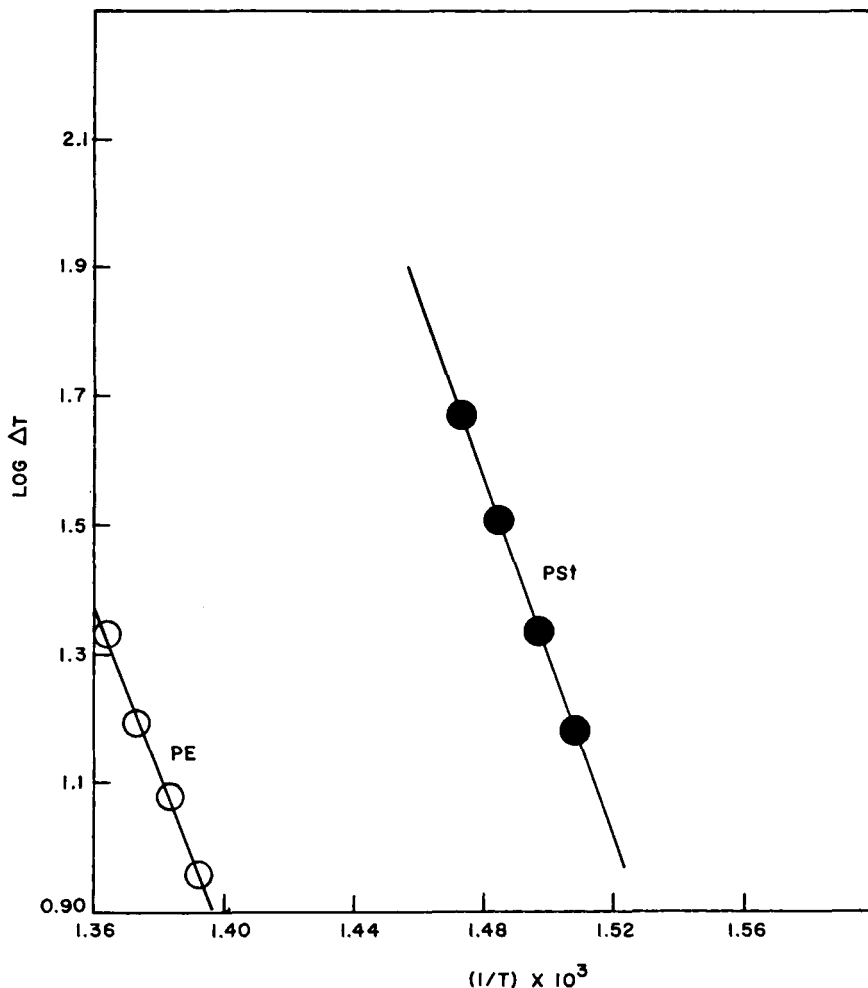


Fig. 4. Estimation of  $E$  for  $n = 0$  from plots of  $\log \Delta T$  vs. reciprocal temperature: (O) 16.1°C./min.; (●) 15.2°C./min.

decomposition of PE in vacuum the value of  $n$  was essentially unity and  $E = 67 \pm 5$  kcal./mole over a conversion range of 35–95% (thermogravimetric experiments were performed). However, in the range of 3–15% reaction, a value of  $E = 61$  kcal./mole was obtained, and this region appeared to involve a transition from zero- to first-order kinetics. The latter stage of PE pyrolysis (3–15%) was ascribed to end chain cleavage, whereas the 35–95% stage was attributed to random rupture of carbon-carbon bonds (an energy of 66 kcal./mole is required).

In the case of PSt, it can also be observed that values of  $E$  and  $n$  change with conversion. Thus, over a range of 3–22 ± 3%, values of  $E$  and  $n$  were found to be 64 and 0, respectively; over a conversion range of 22 ± 3 to 90 ± 5%, these values were 70 and 1.1, respectively. Anderson and Freeman<sup>6</sup> also observed a similar behavior when they degraded PSt

TABLE I  
 Values of  $E$ ,  $n$ , and  $K$  for Various Polymers

Material pyrolyzed	Reaction order $n$		Activation energy $E$ , kcal./mole		$K$	
	Obsd.	Reptd.	Obsd.	Reptd.	Obsd.	Calcd.
BDC (aq. soln.)	1.1	1.0 <sup>a</sup>	29.3	28.3 <sup>a</sup> , 28.7 <sup>b</sup>	0.47	0.49
PE	0.94	1.18 (35–95% conversion) <sup>c</sup>	68	67 ± 5 <sup>c</sup>	0.54	0.54
	0.0	>0 (3–15% conver- sion) <sup>c</sup>	60	61 <sup>c</sup>	1.04	0.98
PPr	1.1	1 (over a limited con- version range) <sup>d</sup>	62	58 <sup>d</sup> , 65 <sup>e</sup>	0.56	0.59
PSt	1.1	1 (15–95% conver- sion) <sup>c</sup>	70	60 ± 5 <sup>c</sup>	0.47	0.49
	0.0	0 (up to 10% version) <sup>c</sup>	64	46 <sup>c</sup>	2.2 0.51	2.1 0.53
TF	0.82	0.85–1.16 <sup>f</sup>	65	66–74 <sup>f</sup>		
	0.61		64		0.51	0.53

<sup>a</sup> Data of Borchardt.<sup>4</sup>

<sup>b</sup> Data of Reed et al.<sup>5</sup>

<sup>c</sup> Data of Anderson and Freeman.<sup>6</sup>

<sup>d</sup> Data of Madorsky.<sup>7</sup>

<sup>e</sup> Data of Davis et al.<sup>8</sup>

<sup>f</sup> Data of Reich et al.<sup>9</sup>

by means of thermogravimetric techniques. Thus, over 15–95% reaction, the value of  $n$  was found to be unity and  $E = 60 \pm 5$  kcal./mole; over a conversion range up to about 10%, the values of  $E$  and  $n$  were 46 kcal./mole and zero, respectively. The lower conversion stage was attributed to the splitting off of styrene monomer. These results indicated that there were two degradation mechanisms, one predominant over low temperatures and the other at high temperatures.

From Table I and Figures 2–4, it can be observed that values of  $E$  and  $n$  for TF also change with conversion. Thus, over a conversion range of 7 to  $36 \pm 9\%$ , the values of  $E$  and  $n$  were 65 kcal./mole and 0.82, respectively; at higher conversions ( $52 \pm 13$  to  $77 \pm 17\%$ ), these values were 64 kcal./mole and 0.61, respectively. Furthermore, a calculation [eq. (3a)] indicated that the value of the frequency factor  $Z$  at the lower conversion range was about twice the value of  $Z$  at the higher conversion range. In the following is presented a possible explanation for such a behavior of polytetrafluoromethylene during degradation. Light and co-workers<sup>10</sup> have indicated that during the decomposition of TF in inert atmosphere, tetrafluoroethylene ( $C_2F_4$ ) is evolved predominantly, along with lesser amounts of by-products such as  $C_3F_6$  and cyclo- $C_4F_8$ . Furthermore, Madorsky<sup>7</sup> has indicated that the amount of  $C_2F_4$  decreases while the amount of  $C_3F_6$  increases as the pyrolysis temperature of TF is increased (isothermal methods). From these results, changes in mechanism would be expected during TF pyrolysis when nonisothermal techniques are em-

ployed (as in DTA). However, these changes do not appear to be appreciable based upon the values of  $E$  and  $n$  (and  $Z$ ) obtained (see Table I).

The advantages of the method employed in this paper for estimating  $E$  and  $n$  are: (1) changes in  $n$  (and  $E$ ) with conversion may be detected; (2) the precise values of RH need not be known in estimating  $E$  and  $n$  (but, of course, the value of RH should be constant during a run); (3) different initial sample weights need not be known accurately; (4) the value of  $E$  may be readily estimated from the derived data utilized in obtaining  $n$ ; (5) arbitrary units may be employed for the terms  $\log \Delta T$  and  $\log \bar{a}$  and for  $V_1$  and  $V_2$ .

Disadvantages of the method are: (1) two DTA traces are required; (2) a separate plot is required for the estimation of  $E$  (and  $Z$ ); (3) it may be difficult at times, to obtain readily two DTA traces for the same material at two different heating rates which overlap sufficiently so that the method can be employed.

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### Résumé

On présente une méthode d'estimation des paramètres cinétiques au cours de la dégradation d'un polymère au départ de deux traces d'analyse thermique différentielle. Par cette méthode, les changements de mécanisme en cours de conversion peuvent être détectés. La méthode est appliquée aux polyéthylène, polystyrène, polypropylène et au téflon. L'accord entre les valeurs observées et rapportées des paramètres cinétiques est bon. Les avantages et désavantages de cette méthode sont soumis à discussion.

### Zusammenfassung

Eine Methode zur Bestimmung der kinetischen Parameter aus DTA-Kurven während des Polymerabbaues wird angegeben. Mit dieser Methode kann eine Änderung des Mechanismus mit dem Umsatz festgestellt werden. Die Methode wird auf Polyäthylen, Polypropylen, Polystyrol und Teflon angewendet. Die Übereinstimmung zwischen den beobachteten kinetischen Parametern und Literaturwerten ist gut. Die Vor- und Nachteile der Methode werden diskutiert.

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