

Isothermal enthalpy studies of poly(methyl methacrylate) stereoisomers and their blends

A. J. White and F. E. Filisko

Department of Material and Metallurgical Engineering, Macromolecular Research Center, University of Michigan, Ann Arbor, Michigan 48104

The residual enthalpies of slow cooled atactic and isotactic poly(methyl methacrylate) were measured as a function of temperature. The samples were found to contain exothermic amorphous heats which decreased linearly with temperature below their respective T_g 's. Blends of atactic and isotactic poly(methyl methacrylate) were found to be one or two phase by differential scanning calorimetry depending on the method of preparation. The residual enthalpies of the blends were lower than the pure components for the one-phase blend and a weight average of the pure components for the one-phase blend and a weight average of the pure components for the two-phase blend. Polymer-polymer heats of mixing were calculated by comparing the residual enthalpies of the blends to that of the pure components. The magnitude of the polymer-polymer heat of mixing is shown to be a measure of the extent of interaction of the blend relative to the pure components.

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INTRODUCTION

A commonly used method for establishing miscibility in a polymer blend is the determination of the glass transition(s) of the blend compared to the glass transitions of the pure components by either differential scanning calorimetry, mechanical spectroscopy, or dielectric spectroscopy. Ideally, a one-phase or miscible blend should show a single sharp glass transition between those of the pure components. A two-phase or immiscible blend should show two separate glass transitions. In the case of limited miscibility or partial miscibility, the two-glass transitions of the blend may be shifted, a blend transition may appear in addition to the glass transitions of the pure components, or a single broad transition may appear over a wide temperature range.

Most polymer blends are immiscible since the entropy of mixing of high molecular weight materials is not large enough to contribute to the free energy of mixing. Complete miscibility, as evidenced by a single sharp glass transition, has been shown in the mixtures poly(phenylene oxide)-poly(styrene),¹ nitrile rubber-poly(vinyl chloride),² poly(vinyl methyl ether)-poly(styrene),³ and poly(vinylidene fluoride)-poly(methylmethacrylate).⁴ Cases of limited miscibility are difficult to characterize by this technique since the extent of miscibility cannot be determined and the blends may phase separate in the vicinity of the glass transition.

Recently, the enthalpy as determined by isothermal microcalorimetry has been shown to be a measure of the conformational energy of a polymer.⁵⁻⁸ Similarly, the enthalpy of a polymer blend determined by the same technique should be a measure of the conformational energy of the blend. If a polymer blend is two phase, then the conformational energy will be an average of the conformational energies of the pure components and the blend enthalpy (as measured in cal/g) will be a weight average of the enthalpies of the pure components. If a blend is one phase, the enthalpy may be lowered due to an increase in the number of molecular unit contacts. The enthalpy of the one-phase blend should be lower than

the enthalpies of the pure components. This enthalpy lowering relative to the pure components should then be a measure of the extent of miscibility of the blend.

In this paper we will show that the enthalpy (as determined by isothermal microcalorimetry) of a two-phase blend of isotactic and atactic polymethyl methacrylate (PMMA) will be a weight average of the enthalpies of the pure components. In contrast, the enthalpy of a one-phase blend of isotactic and atactic PMMA will be lower than the enthalpies of the pure components.

THEORY

The integral heat of solution ΔH_s is the total heat measured calorimetrically when a polymer is dissolved in a sol-

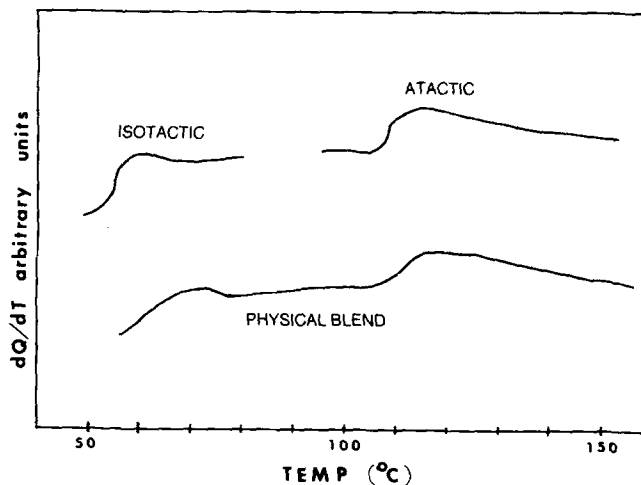


FIG. 1. DSC thermogram of two phase isotactic/atactic blend compared to the pure components.

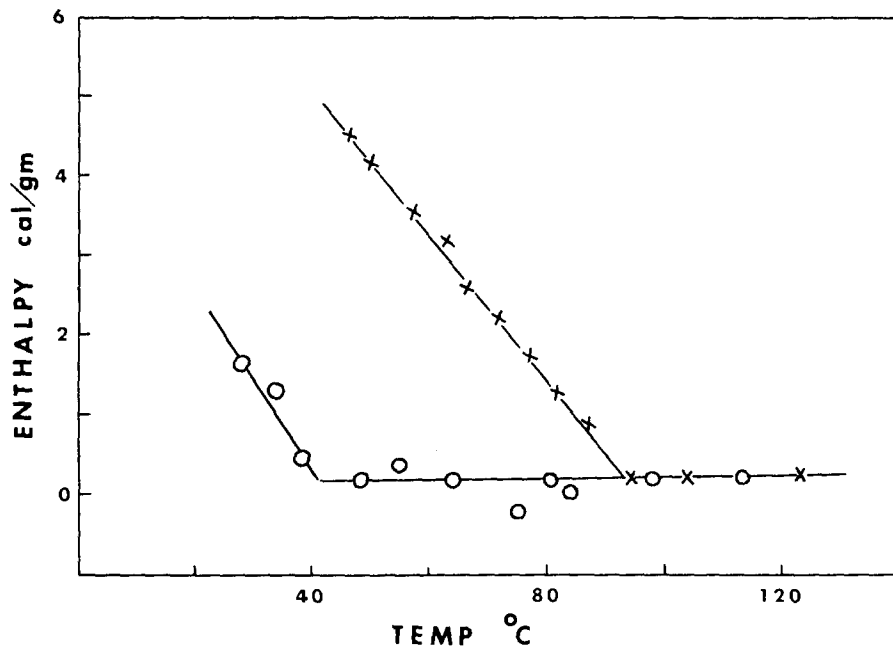
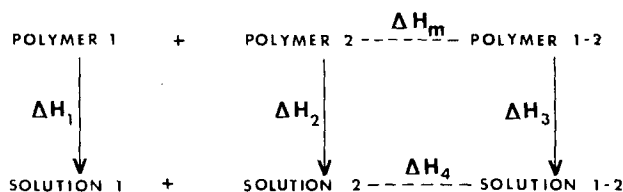


FIG. 2. Residual enthalpy as a function of temperature for pure atactic(x) and pure isotactic(o) both slow cooled from the melt.

vent. The polymer-solvent interactions can be calculated using an applicable solution theory⁹ and subtracted out of the heat of solution,¹⁰ leaving the residual enthalpy ΔH_r . ΔH_r depends on any structure in the polymer over and above that of a perfectly "amorphous liquid state." It may consist partly of an endothermic heat of fusion due to solvent induced disruption of crystallinity or order and/or an "exothermic amorphous heat" due to solvent induced disruption of non-crystalline regions if the measurement is below the T_g of the polymer.

If the heat of solution of two polymers and a blend of the two polymers is measured in a common solvent, then using a Hess's Law cycle shown below, a polymer-polymer heat of mixing can be calculated for the blend.



$$\Delta H_m = \Delta H_3 - (\Delta H_1 + \Delta H_2 + \Delta H_4) \quad (1)$$

The polymer-polymer heat of mixing ΔH_m is simply the difference between the enthalpy of the blend and the enthalpy of the pure components. ΔH_4 is considered insignificant since it involves the mixing of two dilute solutions (0.1%).

EXPERIMENTAL

Atactic PMMA was a free radical polymerized sample obtained from Scientific Polymer Products. The number average molecular weight was 22 380 g/mole. Isotactic PMMA was prepared by anionic polymerization in to-

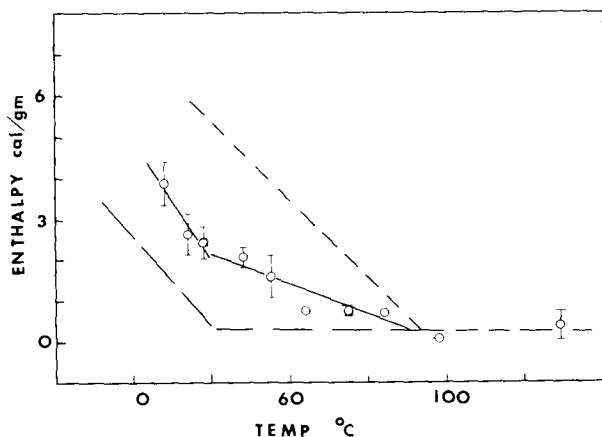


FIG. 3. Residual enthalpy of atactic/isotactic two-phase blend as a function of temperature compared to the residual enthalpies of the pure atactic (---) and the pure isotactic (- - -).

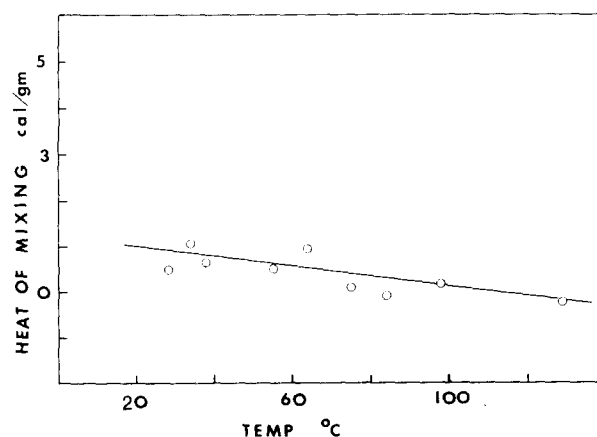


FIG. 4. Polymer-polymer heat of mixing calculated from Eq. (1) for atactic/isotactic two-phase blend.

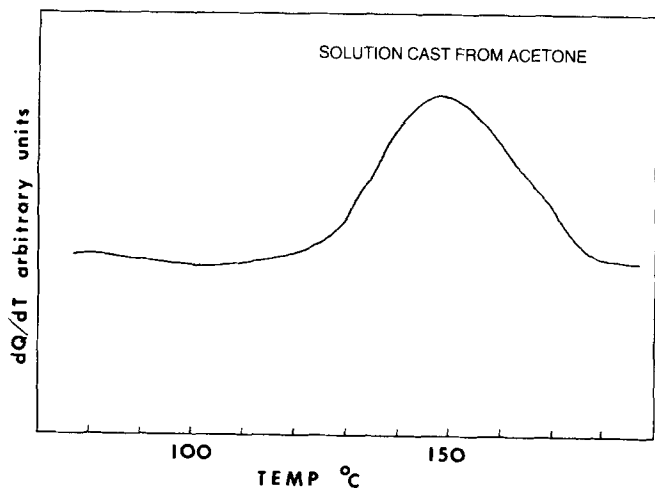


FIG. 5. DSC thermogram of 50/50 blend cast from acetone.

luene¹¹ and was shown by HR-NMR to contain 80% isotactic triads and a viscosity average molecular weight of 43 000 g/mole. ¹H NMR determined the atactic to be 55% syndiotactic.

The pure atactic and isotactic samples (referred to as the pure components) were made by pressing a few grams of the samples into films on a Hydraulic press at 200 °C and then slow cooling through the glass transition. The films were broken into 5–15 mg pieces that were approximately 6 mm wide and 0.2–0.3 mm thick. Thin films ensure quick dissolution in the calorimeter and minimize frozen in stresses.

The atactic/isotactic blends were made by two different procedures. In the first, physical blends were made by mixing dry powders of the two polymers in a 50/50 wt. % ratio. The mixture was then heated to 200 °C, pressed into a film, and allowed to slow cool in exactly the same manner as the pure components.

In the second procedure, mixtures of the atactic and isotactic polymers were dissolved in acetone and heated to 70 °C to ensure dissolution. The solutions were then cast on teflon plates and dried in a vacuum oven at 100 °C for one week. The resultant films were broken into pieces of approxi-

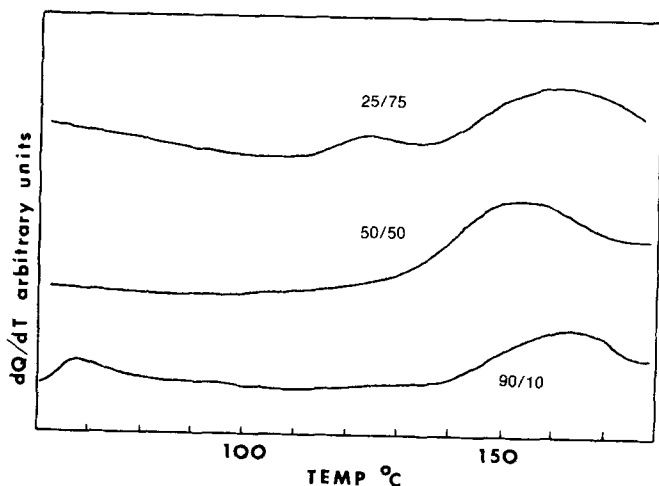


FIG. 6. DSC thermogram of isotactic/atactic blends cast from acetone. Numbers represent isotactic/atactic ratio in the blends.

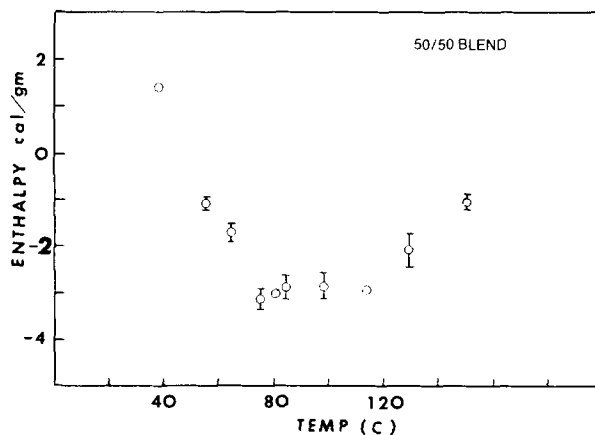


FIG. 7. Residual enthalpy of 50/50 wt. % blend case from acetone as a function of temperature. Error bars are a measure of reproducibility of the data.

mately the same size as the slow cooled samples.

The instrument used for isothermal calorimetric measurements was a microcalorimeter of the Tian–Calvet differential type. The solvent used in these measurements was orthodichlorobenzene. The magnitude of the polymer-solvent interactions was calculated using solution theory,⁹ and found to be small and endothermic (0.5 cal/g).

The scanning calorimeter used was a Perkin Elmer DSC II. All the samples were run at a scanning rate of 10 °C/min.

RESULTS

Figure 1 shows the DSC thermogram of the pure isotactic and atactic polymethylmethacrylates compared to the 50/50 wt. % physical blend. The glass transitions of the blend appear at approximately the same temperature as those of the pure components indicating that this blend is two phase.

Figure 2 shows that residual enthalpy as a function of temperature for atactic and isotactic PMMA. Since these samples were both glassy, their enthalpies are exothermic at temperatures below their respective T_g 's indicating that their conformational energy is greater than that of the "amorphous liquid state."

The residual enthalpy of atactic PMMA decreases linearly with temperature and becomes constant in the vicinity of the reported T_g (105 °C). The slope of this plot, $d\Delta H/dT$, is -0.097 cal/g °C. The residual enthalpy of the isotactic PMMA also decreases linearly with temperature with a slope of -0.112 cal/g °C and becomes constant in the vicinity of its reported T_g (50 °C).

Figure 3 shows that residual enthalpy as a function temperature of the 50/50 wt. % physical blend compared to the residual enthalpies of the pure components. It is immediately apparent that the residual enthalpy of this blend falls between the enthalpies of the pure components. The enthalpy of the blend decreases linearly with temperature from 28 to 38 °C with a slope of -0.149 cal/g °C. Between 38 and 98 °C the enthalpy decreases linearly with a slope of -0.036 cal/g °C. Above 98 °C, the enthalpy is constant with a value

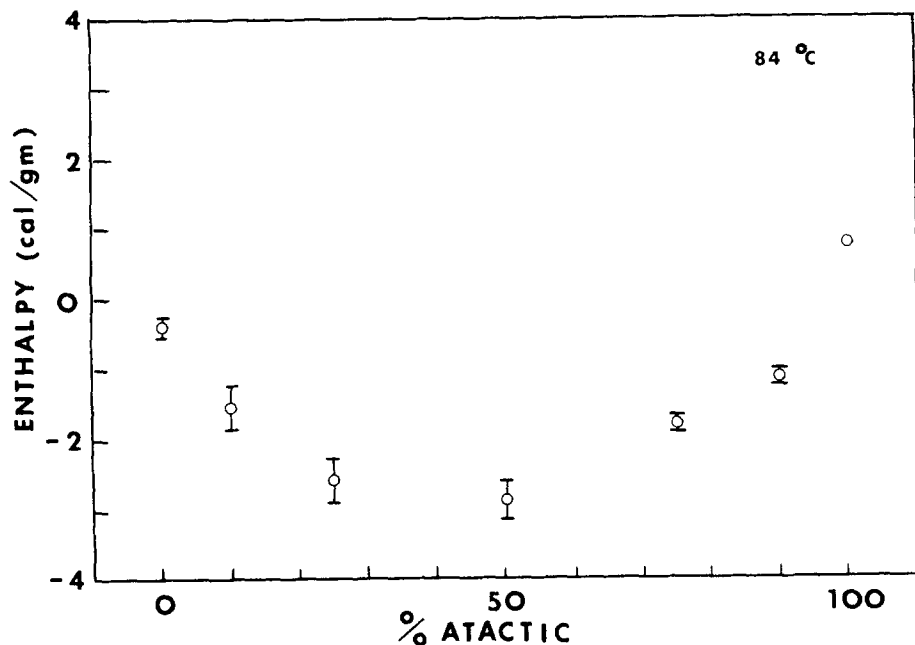


FIG. 8. Residual enthalpies at 84 °C of the isotactic/atactic blends cast from acetone as a function of composition.

approximately the same as the enthalpy of the pure components at this temperature.

Figure 4 shows the polymer-polymer heat of mixing as a function of temperature that was calculated from the residual enthalpies of the blend and the pure components. The heats of mixing range between 0.0 and 1.0 cal/g over the temperature range studied. These small heats of mixing may indicate that the blend is predominately two phase and that the enthalpies of the two phases are for the most part behaving independently of each other. In a completely phase separated blend, one would expect the ΔH_m term in Eq. (1) to be exactly zero.

Figure 5 shows the DSC thermogram of the 50/50 wt. % blend that was cast from acetone. In this case, neither of the glass transitions of the pure components are apparent but a large broad endotherm appears that peaks at approximately 150 °C. This single transition indicates that the blend is now one phase. In addition, wide angle x-ray scattering WAXS photographs of this blend exhibited discrete scattering indicating that the mixture was at least par-

tially crystalline. (WAXS patterns of the pure components cast from acetone showed no discrete scattering.)

DSC thermograms of blends cast from acetone as a function of composition are shown in Fig. 6. The broad endotherm at 150 °C appears at every composition, but at high isotactic/atactic ratios the isotactic glass transition is observed and at high atactic/isotactic ratios the atactic glass transition is observed.

Figure 7 shows the residual enthalpy of the 50/50 wt. % blend cast from acetone as a function of temperature.

All of these blend enthalpies were less than the enthalpies of the pure components indicating a lower conformational energy state. In addition, except for the point at 38 °C, the enthalpies were endothermic, indicating a conformational energy lower than that of the "amorphous liquid state." This supports the contention that the blend has conformational order or crystallinity.

The residual enthalpy of the acetone cast blend decreases linearly with temperature between 38 and 75 °C with a slope of -0.120 cal/g °C. Between 75 and 115 °C, the enthalpy is relatively constant at a value of -3.0 cal/g. This agreed well with the enthalpy obtained by integration of the endotherm at 150 °C on the DSC thermogram. Above 115 °C, the enthalpy increases linearly with a slope of 0.052 cal/g °C. This increase is attributed to partial melting of the crystalline regions as the samples equilibrated to temperature in the calorimeter.

Figure 8 shows the residual enthalpies at 84 °C of acetone cast blends of varying composition. At this temperature the enthalpies of the pure atactic and isotactic polymers are very small so the values measured are solely due to the ordered or crystalline regions. It can be seen that the enthalpies are endothermic (less than the "amorphous liquid state") throughout the entire composition range and that the enthalpy appears to maximize at a 50/50 composition. Although there is not a linear relationship between enthalpy and composition in this figure, it does show the sensitivity of this type of measurement in determining the relative amount of crys-

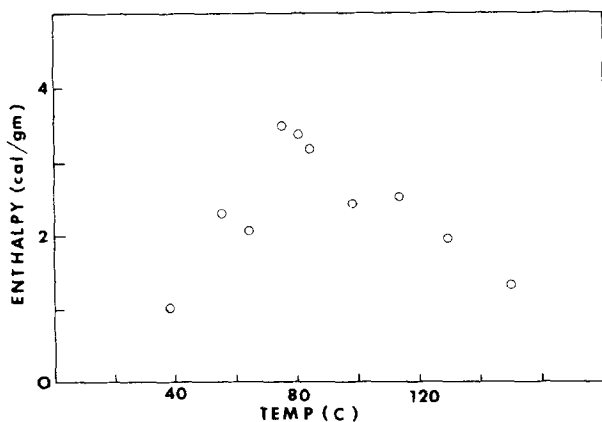


FIG. 9. Enthalpy difference between the 50/50 wt. % blend cast from acetone and the pure components.

tallinity or order in a blend. A similar plot could not be obtained by integration of DSC peak integrals.

Figure 9 shows the enthalpy difference between the 50/50 wt. % blend cast from acetone and the pure components. This enthalpy difference cannot correctly be called a polymer-polymer heat of mixing since it has been determined that the blend is partially crystalline. This difference does represent, however, the extent of interaction in the blend relative to the pure components, and at temperature above the T_g 's of the glassy polymers this enthalpy is equivalent to the heat of fusion of the crystalline regions.

DISCUSSION

Although the analysis of this data is straightforward, several basic points need to be emphasized in order to clarify the nature of this type of measurement.

First, though two stereoisomers of polymethyl methacrylate and two blends of these isomers of different morphologies were characterized in this study, the temperature dependence of the residual enthalpy $d\Delta H/dT$ was essentially the same as long as the measurements were taken below T_g . Since $d\Delta H/dT$ is equal to ΔC_p (the difference between the specific heat of the solid and the specific heat of the liquid), these studies suggest that the specific heat of all polymethyl methacrylates is the same regardless of configuration or morphology.

Wunderlich¹² has reported that the specific heat of the crystalline regions of a polymer should be the same as the glassy regions, and Filisko and Raghava have shown that for quenched and asreceived poly(phenylene oxide) the temperature dependence of the enthalpy $d\Delta H/dT$ does not change. So although the equivalence of the specific heats was not a surprising discovery, it does emphasize the very fundamental nature of this type of measurement.

Second, this method has been shown to be extremely sensitive in measuring the relative amount of conformational order in a polymer. We know of no other method that can determine the extent of interaction in a blend as a function of composition. In this study we deal with two extreme cases; an apparently immiscible blend and a blend in which the interactions between the two pure components are so strong that the blend possesses a high degree of conformational order. We feel, however, that this technique could easily be extended to characterize cases of limited and partial miscibility. From the DSC thermograms in Fig. 6, it can be seen that these blends contain both crystalline and glassy regions. We were able to obtain a profile of the amount of order as a function of composition (as shown in Fig. 8), simply by making the enthalpy measurements above the T_g of

the glassy regions.

Third, since we can find no other study that measures a blend enthalpy as a function of temperature, the polymer-polymer heat of mixing shown in Fig. 4 should be considered a first treatment of this subject. Additional measurements need to be made on other two-phase blends in order to substantiate the small exothermic heats of mixing calculated here. A certain amount of error is always incurred when one set of data is subtracted from another.

Karasz⁸ has determined the polymer-polymer heat of mixing for a polystyrene-polyphenylene oxide blend as a function of composition, but he applies a correction factor to adjust his data to the liquid standard state. Since our data is taken both above and below the T_g of the polymer such a correction factor is not necessary. It would be interesting to apply this technique to a blend that is known to phase separate at high temperature, since it has been theorized that the polymer-polymer heat of mixing goes to zero in the temperature region of phase separation.

Finally, it should be recalled that the acetone cast or single-phase blends are most probably a consequence of stereoreassociation well known for syndio- and isotactic PMMA.¹⁵⁻¹⁷

ACKNOWLEDGMENT

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