High-speed synthesis of thermo-responsive polymers by boosted polymerization of *N*,*N*-diethyl acrylamide in high-temperature water

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Abstract

The transition toward a circular plastic economy and sustainable chemical industries requires the development and implementation of green methods of free-radical polymerization. In this study, the high-speed radical polymerization of *N*,*N*-diethyl acrylamide (DEAA) was achieved in high-temperature water (150 °C, 0.5 MPa) without using potentially contaminating organic solvents. Precipitation polymerization was completed within 2 min. The molecular weight of the resulting polymer (27.7×10^3; dispersity of 1.78) was comparable to that of polymers obtained by typical polymerization at 70 °C and significantly exceeding those of polymers obtained by polymerization in high-temperature organic solvents. This implies that the main factor governing the polymerization rate is a kinetic effect due to hydrogen bonding between the carbonyl groups and water molecules; under these conditions, disproportionation termination was suppressed. The polymerization process developed herein using high-temperature water is offers the benefits of a short reaction time and low environmental impact, thus holding great promise for industrial applications.

Keywords: Environment-friendly polymerization, Radical polymerization, High production rate, Molecular weight, Dispersity, Solvent-free, Recombination.

INTRODUCTION

The increasing awareness regarding global warming and related environmental issues is changing our view on production processes in terms of, not only cost and efficiency, but also environmental impact in view of achieving a sustainable society.[1,2] The polymeric materials widely exploited as plastic, fibers, rubbers, and adhesives are invaluable to society. Since the discovery of chloroprene polymerization,[3] the radical polymerization of vinyl monomers, such as styrene, (meth)acrylates, vinyl acetate, and acrylamides, has significantly contributed to industrial polymer production. In radical polymerization, processing temperature substantially affects polymer formation kinetics, final molecular weight (MW), and MW dispersity.[4] Therefore, temperature control is crucial for obtaining the desired products. Given that bulk polymerization is exothermic and therefore suffers from excessive heat release, industrial-scale radical polymerization typically involves the suspension polymerization of hydrophobic vinyl monomers in water and solution-phase polymerization in homogeneous systems. To avoid the unfavorable use of organic solvents, supercritical fluids[5,6] and high-temperature water (*i.e.*, water at 100–374 °C and 0.1–22.1 MPa with controllable dielectric constant and ionic product[7–10]) are used in solution polymerization. For example, Kinoshita *et al.*[11] conducted the radical polymerization of acrylic acid in high-temperature water using a flow-type apparatus. Typically, radical polymerization is performed around the 10-h half-life temperature (T_{10}) of the initiator to avoid frequent termination and MW decrease. Nevertheless, the radical polymerization of acrylic acid in high-temperature water generates high-MW polymers within several minutes.[11]

Although radical polymerization in high-temperature water may contribute to improved polymer production and thus promote the establishment of a sustainable society, the use of flow-type reactors in radical polymerization limits the range of applicable monomers,[12] because both the monomers and resulting polymers must be soluble in water to keep the reaction system homogeneous. In particular, *N*,*N*-diethyl acrylamide (DEAA) is soluble in water, whereas the corresponding polymer is insoluble above the lower critical separation temperature (LCST) of 32 °C.[13] Therefore, DEAA is not a suitable monomer for flow-type reactors. In this study, the radical polymerization of DEAA was performed in high-temperature water and other solvent in a batch-type reactor under tunable reaction (e.g. reaction time and temperature). The behavior and mechanism of the polymerization process in high-temperature water were investigated.

MATERIALS AND METHODS

DEAA was kindly donated by KJ Chemicals Co. The initiator [4,4'-azobis(4-cyanovaleric acid), V-501], ethanol (EtOH), and *N*,*N*-dimethylacetamide (DMAc) were purchased from FUJIFILM Wako Pure Chemical Corporation. D_2O (100.0 at% D) was supplied from Acros Organics. 1,4-Dioxane (DO) was purchased from Kishida Chemical Co., and *N*,*N*-dimethylformamide (DMF) was purchased from Yoneyama Yakuhin Kogyo Co., Ltd.

Gas chromatography (GC) was performed using a Shimadzu GC-2014 gas chromatograph equipped with a flame ionization detector (FID) and an SH-Rtx-5 capillary column (30 m × 0.32 mm, 0.25 μm; Restek) with He as the carrier gas (linear velocity = 30 cm s^{-1}) and make-up gas. The vaporization chamber was maintained at the starting temperature of 50 °C for 2 min and subsequently heated to 300 °C at a rate of 20 °C min^{-1}.

MWs and their distributions were determined using size-exclusion chromatography (SEC), which was performed using a JASCO EXTREMA chromatograph equipped with two SEC columns (Shodex HK-404L) and ultraviolet (UV-4070, JASCO, 235 nm) and refractive index (RI-4035, JASCO) detectors. Tetrahydrofuran (Wako Pure Chemical Industries, HPLC grade, flow rate = 0.4 mL min^{-1}) was used as the eluent at 40 °C. MWs were calibrated using standard polystyrene samples (TSK-gel oligomer kit, Tosoh, MW = 1.03×10^6, 3.89×10^5, 1.82×10^5, 3.68×10^4, 1.36×10^4, 5.32×10^3, 3.03×10^3, and 8.73×10^2).

A 6-mL stainless-steel tube was charged with a solution of DEAA (0.200 g, 1.57 mmol) and V-501 (5 mg, 17.8 μmol) in H_2O (3.0 g), immersed into an oil bath held at 150 °C for a predetermined time (2−180 min), and rapidly cooled to 20−25 °C in a cold-water bath. The temperature inside the tube was directly measured using a thermocouple. An analogous procedure was adopted for polymerization at 70 °C, and in other solvents, and in the bulk.

Monomer conversion was determined from the GC-FID peak areas of DEAA before and after polymerization as

$$\text{Monomer conversion (\%)} = \left(1 - \frac{\text{DEAA peak area after polymerization}}{\text{DEAA peak area before polymerization}}\right) \times 100. \qquad (1)$$

RESULTS AND DISCUSSION

The heating process affecting radical polymerization[4] was investigated in a batch-type stainless-steel reaction tube. Figure 1 (a) shows the internal temperature profiles of the batch reactor immersed into oil baths heated to different temperature. Given that the reaction started when the reactor was submerged into the oil bath, the reaction time included the initial heating period. After a given reaction time, the reactor was removed from the oil bath and was rapidly quenched in a cold-water bath to cool it to 20–25 °C. The reaction was also performed without any solvents (bulk polymerization).

At 70 °C, the heating period (2 min) was much shorter than the reaction time (180 min), thus exerting a modest influence. Conversely, at 150 °C (reaction time 2 min), polymerization occurred within the heating period, which critically affected the obtained products. Owing to the high heat capacity of the stainless-steel reactor, the heating processes at 70 and 150 °C were similar, although the molar heat capacities of water[14] and DMF[15] at a constant pressure were different, 75.3 and 146 J K^{-1} mol^{-1}, respectively. For bulk polymerization, no solvent was available to dissipate the heat of polymerization, and the temperature rapidly exceeded the set value (150 °C) because of the autoacceleration of exothermic propagation.[16] Afterwards, the temperature gradually decreased because of the deceleration of the polymerization reaction due to an increase in viscosity.[17] Therefore, the outcomes of bulk polymerization tests were not influenced by the set temperature, with polymerizations at 70 and 150 °C resulting in similar MW distributions (Figure 2 (a) and Table S1).

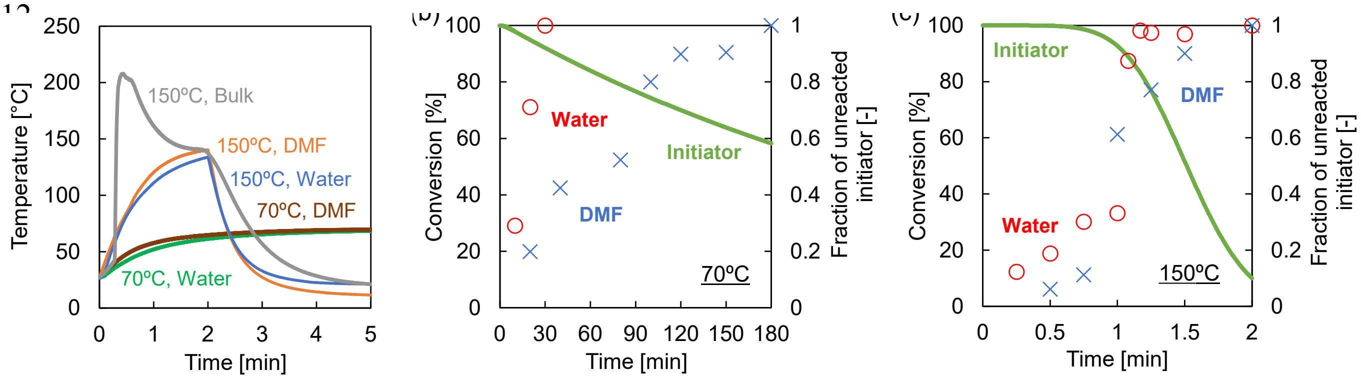
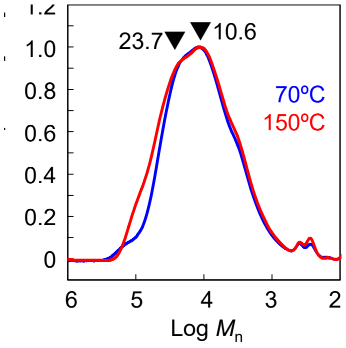


Figure 1. (a) Internal temperature profiles of the reactor over time. (b, c) Correlation between DEAA conversion and reaction time in water and DMF at (b) 70 °C and (c) 150 °C; and calculated degree of the thermal homolytic cleavage of the initiator.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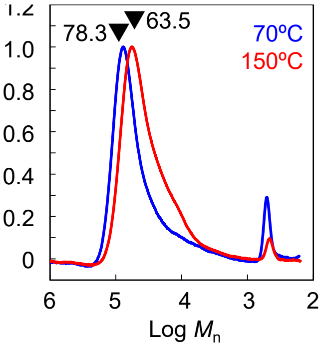
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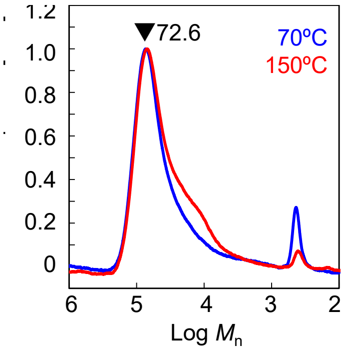
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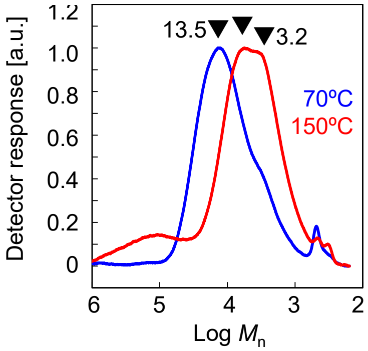
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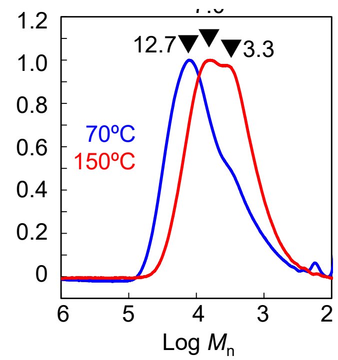
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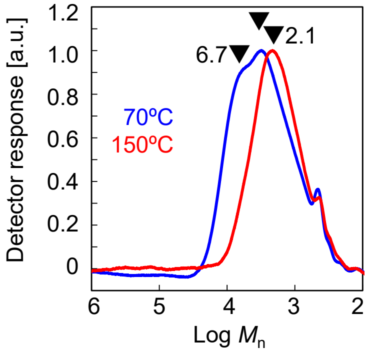
Log M_n


Detector response [a.u.]
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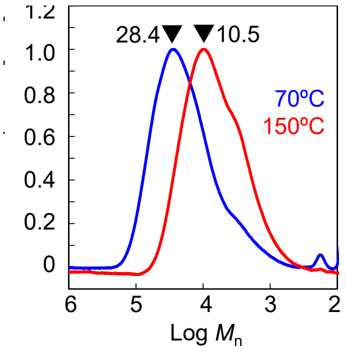
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Log M_n

Figure 2. Molecular weight distributions of polymers obtained in (a) bulk, (b) water, (c) deuterated water, (d) *N,N*-dimethylformamide, (e) *N,N*-dimethylacetamide, (f) ethanol, and (g) 1,4-dioxane at 70 and 150 °C.

Figures 1 (b) and (c) show the reaction-time-dependent conversions of DEAA in water (red circles) and DMF (blue crosses) at the set temperatures of 70 °C and 150 °C, respectively. At 70 °C, the monomer conversion reached 100% after 30 min in water and after 180 min in DMF. In contrast, complete monomer consumption at 150 °C in water and DMF were achieved after 1.1 and 1.5 min, respectively. The average MWs and their dispersity in water and DMF at 150 °C were almost constant regardless of monomer conversion (Table 1), which indicated that the steady-state approximation was also valid under boosted polymerization conditions. Therefore, the accelerated polymerization at 150 °C essentially followed the same mechanism as the general radical polymerization at 70 °C. Nevertheless, when polymerization at 150 °C performed in a transparent glass tube, we observed the precipitation of the resulting polymer, poly(DEAA), in line with its insolubility in water above 32 °C (Movie S1). Therefore, for lab-scale poly(DEAA) synthesis, batch-type reactors are preferred to flow reactors. However, flow reactors would be promising for poly(DEAA) production at an industrial scale.

Table 1. Monomer conversions and molecular weights obtained at different reaction times in radical polymerization at 150 °C.

Solvent	Reaction time (min)	Monomer conversion (%)	M_n (×10^{-3})	M_w (×10^{-3})	*Đ*
Water	0.75	30.1	21.4	28.9	1.35
Water	1	33.2	26.8	49.8	1.86
Water	1.08	87.4	21.0	30.9	1.47
Water	2	100	27.7	49.1	1.78
DMF	1.25	77.1	4.6	9.0	1.95
DMF	2	100	3.5	6.6	1.86

The green curves shown in Figures 1 (b) and (c) indicate the thermal cleavage degree of the V-501 initiator at 70 and 150 °C, respectively, estimated by Equation (2):

$$k_\mathrm{d}\ (\mathrm{s}^{-1}) = 6.21 \times 10^{15} \exp\left(\frac{-1.33\times10^{5}}{RT}\right), \tag{2}$$

where k_d is the rate constant of thermal hemolytic cleavage, R is the universal gas constant, and T is the absolute temperature. The activation energy and pre-exponential coefficient in Equation (2) were measured in the temperature range of 40–80 °C[18] and were assumed to be independent of temperature, solvent type, and the monomer presence. At 70 °C, more than half of the initiator was present even after 180 min. Conversely, at 150 °C, V-501 was almost completely converted into radicals within 2 min. Therefore, the fast consumption of DEAA at 150 °C was ascribed to the combined effects of fast propagation and sufficient radical supply. Concurrently, high radical concentrations typically afford low-MW products because they result in fast termination reactions and decreased monomer-to-radical ratios. When organic solvents (DMF, DMAc, EtOH, and DO) were used, the MWs of products generated at 150 °C were lower than those of products obtained at 70 °C (Figures 2 (d)–(g)). In contrast, in water (H_2O and D_2O; Figures 2 (b) and (c), respectively), polymers with higher MWs were obtained even at 150 °C, although the values were slightly lower than those for polymerization at 70 °C. Therefore, in water, the high propagation rate was the main contributor to the increased termination rate at high temperatures. The fact that polymers obtained at 70 °C in water had higher MWs than those produced in organic solvents indicated specific fast propagation. Water molecules formed hydrogen bonds with carbonyl groups, resulting in fast DEAA polymerization, as previously reported for the polymerization of acryl monomers.[19–22] The difference between the MWs of products obtained at 70 and 150 °C was smaller in D_2O than for water, which was ascribed to the higher strength and temperature stability of deuterium bonds compared to hydrogen bonds.[23]

Termination reactions in radical polymerization proceed via disproportionation and recombination, with the latter mechanism affording products with double the MWs than those achieved by the former. The unimodal MW distributions of products obtained at 70 °C (Figure 2, blue lines) featured a main peak with a shoulder in the low-MW region, except for polymerization in the bulk and in EtOH (Figures 2 (a) and (f), respectively). The main and shoulder peaks resulted from recombination and disproportionation, respectively. Therefore, recombination was the main termination pathway at 70 °C. Furthermore, the curves related to polymerization in DMF, DMAc, and DO (red lines in Figures 2 (d), (e), and (g), respectively) indicated that a bimodal distribution was obtained at 150 °C. The MW corresponding to the first peak was twice that corresponding to the second peak, which indicated that the first and second peaks corresponded to termination by recombination and disproportionation, respectively. Conversely, the MW of the product formed in EtOH at 70 and 150 °C had a bi- and unimodal distribution, respectively, and was lower than those of polymers formed in other solvents, which suggested that EtOH exerts a unique solvent effect. In contrast to polymerization in organic solvents, the differences between the products formed at 70 and 150 °C in water were negligible, and recombination was dominant at both temperatures. These results highlight the solvent effect exerted via hydrogen bonding, which promoted the propagation reaction, even at 150 °C. Thus, the specificity of water was crucial for enhancing the polymerization reaction.

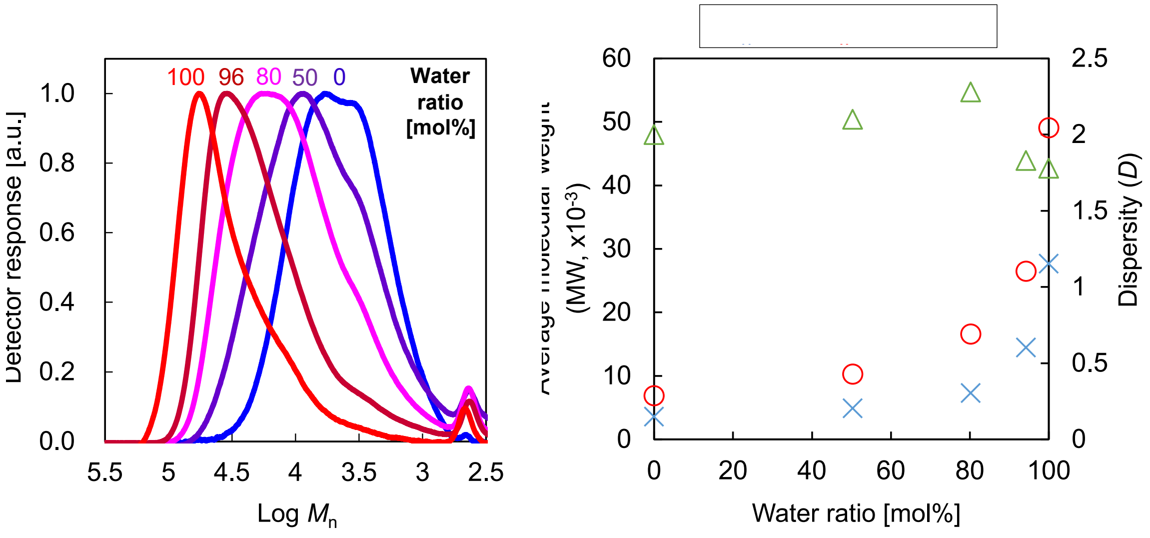

Figure 3. Effect of the water/DMF ratio on the (a) molecular weight distribution and (b) average molecular weights and their dispersity (*D*) at 150 °C.

To assess the water volume required to promote high-speed polymerization, we conducted polymerization experiments in water–DMF mixtures of different compositions and examined the effects of solvent composition on MW distribution, average MW, and MW dispersity at 150 °C (Figure 3). The shape of the MW distribution changed from unimodal to bimodal with increasing DMF content (Figure 3 (a)), in accordance with the change of the termination mechanism discussed above. These results also suggest that in water, hydrogen bonding leads to high-speed polymerization at high temperatures, affording high-MW products and suppressing disproportionation termination. The MW of the polymer obtained at a DMF content of 4 mol% was substantially lower than that obtained in pure water (Figure 3 (b)). Therefore, a small amount of DMF was sufficient to affect polymerization behavior.

The polymerization solvent may also affect the mechanism of chain transfer to the polymer. In water, when the monomer is soluble and the polymer is insoluble, precipitation polymerization would occur. On the other hand, in organic solvents, the polymer may dissolve without precipitating. Thus, chain transfer to the polymer in water could have been suppressed by precipitation. If such chain transfer occurred in organic solvents, a branched polymer with a multimodal and broad MW distribution should be formed. However, bimodal and not multimodal MW distributions were obtained in organic solvents. Therefore, we believe that chain transfer to the polymer did not occur in either water or organic solvents.

Considering non-isothermal polymerization (Fig. 1), the reactor temperature profile obtained in water was almost identical to that obtained in DMF. If the bimodal MW distributions in DMF were due to non-isothermal polymerization, the bimodal peaks should have also been obtained in water. Therefore, non-isothermal polymerization was not the main cause of the solvent effect on MW distributions.

A previous study of the radical polymerization of acrylamides at around the T_{10} of the initiator[24] showed that each polymerization stage (initiation, propagation, and termination) was affected by solvent type, which was attributed to various reasons, including chain transfer to the solvent and differences in solvent polarity and dielectric constant. In addition, the radical polymerization of acrylamides in water was significantly faster than that in other organic solvents, and a higher polymerization rate and MW were observed when water was added to dimethyl sulfoxide. Herein, we found that the effect of the solvent type at a high temperature of 150 °C was similar to that at 70 °C. The higher polymerization rate and MW observed for high-temperature water compared to those observed for organic solvents were attributed to differences in propagation rate and termination mode, which are influenced by the solvent polarity and dielectric constant.

CONCLUSIONS

High-temperature water (150 °C, 0.5 MPa) enabled the high-speed radical polymerization of DEAA, resulting in complete conversion into high-MW products within a short time (2 min). Although the polymers obtained in water precipitated because of their low LCST, pure water was more favorable than organic solvents, which induced disproportionation and frequent termination reactions, even when added in small amounts as cosolvents. Further work is required to elucidate the effect of polymer precipitation in various solvents at high temperatures. A batch-type reactor was effective for application in such precipitation polymerization reactions in water. However, given that a short reaction time (within 2 min) was sufficient in high-temperature water, flow reactors may potentially be used in industrial settings. High-speed radical polymerization offers the advantage of low environmental impact and is completed in a short time without the use of any organic solvents. Moreover, the examined process is promising for application in the polymer industry for reducing its environmental impact and operating costs by considerably increasing the production rate.

ASSOCIATED CONTENT

Supporting Information. Details of the experimental conditions, monomer conversion, and molecular weights and their distributions obtained at different temperatures (Table S1); video showing the polymerization of DEAA in high-temperature water at 150 °C in a transparent glass tube (Movie S1).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

DEAA, *N*,*N*-diethylacrylamide; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DO, 1,4-dioxane; EtOH, ethanol; FID, flame ionization detector; GC, gas chromatography; LCST, lower critical separation temperature; MW, molecular weight.

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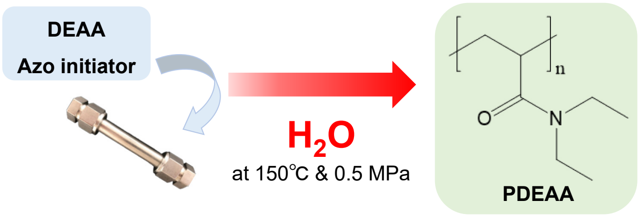
Graphical Abstract



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