Development and Use of a Turbidity Analyzer for Studying the Solution Crystallization of Polyolefins

A. J. van Reenen,[1] E. G. Rohwer,[2] P. Walters,[2] M. Lutz,[1] M. Brand[1]

[1]Department of Chemistry and Polymer Science, University of Stellenbosch, P/Bag X1 Matieland 7602, South Africa
[2]Laser Physics Institute, University of Stellenbosch, P/Bag X1 Matieland 7602, South Africa

ABSTRACT: Cooling a solution of a crystalline polyolefin from 140°C to room temperature causes the dissolved polymer to crystallize. If a laser beam passes through this solution, the crystallization will cause the beam to scatter, which thereby decreases the intensity of the beam. With this principle, it is possible to follow the crystallization of polyolefins under controlled cooling. An instrument capable of doing these analyses was manufactured, and several different polyolefins were analyzed. The effect of the experimental parameters are illustrated for both cooling and reheating experiments. In addition, an interesting dependence on molecular weight was also observed for a series of metallocene polypropylenes. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3238–3243, 2008

Key words: crystallization; light scattering; metallocene catalysts; polyolefins; solution properties

INTRODUCTION

Following the article published by Shan et al.[1] on the development of a turbidity fractionation analyzer and having, at the time of the publication of that article, been in the process of designing a similar piece of equipment, we went ahead and designed and built a system similar in general design to that described by Shan et al. The use of fractionation by crystallization to study the molecular heterogeneity of polyolefins (e.g., the short-chain branching distribution) by temperature rising elution fractionation (TREF) is well known and has been covered by some excellent reviews.[2–7] Similarly, the use of Crystaf, developed by Monrabal[8] for the study of the solution crystallization of polyolefins,[6,9,10] is also well known. We have also used preparative TREF to fractionate polyolefins in several studies.[11,12] Both TREF and Crystaf are based on the assumption that the crystallization from solution of a polyolefin is dependent on the crystallizability of the dissolved polymer at a given temperature. In the case of TREF, a polymer solution is slowly cooled and allowed to precipitate onto a support. After cooling, the precipitated polymer is removed by fresh solvent as the temperature is raised. Thus, TREF gives information on the melting of the previously crystallized polymer in the presence of solvent. Crystaf, on the other hand, measures the concentration of a polymer in solution as crystallization occurs. Crystaf has an advantage over TREF in that measurements are made in a single crystallization step, whereas TREF requires both cooling and elution steps. The biggest drawback, according to Shan et al.,[1] of TREF and Crystaf is that both analytical instruments require complex instrumentation and are expensive. The use of a solution turbidity analyzer for the study of polyolefin crystallization behavior in solution seemed to be a logical step, given the reported short analysis times, the ability to crystallize the polymer from solution, and the ability to redissolve the crystallized material from solution (similar to analytical TREF) in a single experiment.[1] In our case, this would be particularly relevant, as we have built up a library of fractionation products of commercial polyolefins and those produced in-house. This article reports the initial results of experiments conducted on this instrument.

EXPERIMENTAL

Turbidity analyzer

The design of the turbidity fractionation analyzer used in our experiments to measure the turbidity of polymer solutions was based on the design published by Shan et al.[1] The schematic of the experimental setup is given in Figure 1.

The quartz sample holder fit tightly into the four-port aluminum block. The aluminum block was mounted on top of a heater/stirrer, of which the heater coil was connected to the external temperature controller. Thermal paste between the heater/stirrer top and the aluminum block ensured maxi-
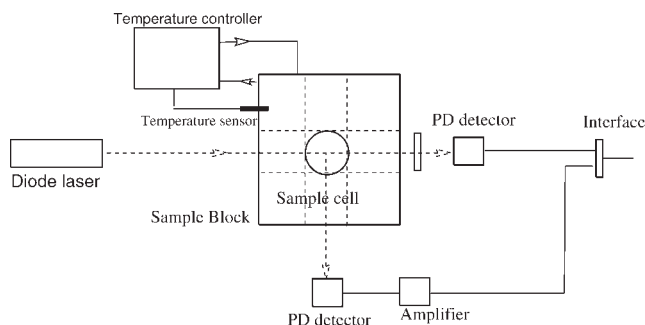
Figure 1 Schematic diagram of the turbidity fractionation analyzer, as viewed from the top.

mum thermal contact. Cooling liquid flowing through the top and bottom sections of the aluminum block allowed for controlled cooling and heating. The laser beam from a 4.5-mW Thorlabs diode laser module CPS 196 (Newton, NJ) at 635 nm was focused in the center of the sample cell. For the preliminary experiments, two UDT-555D Si photodiode detectors were used to detect scattered light. Each was fitted with a preamplifier circuit to boost the signal output. The one photodiode measured the change in the intensity in the forward direction due to scattering. To protect this detector against saturation, a neutral density filter was put in the path of the laser. The second detector was mounted at 90° to the laser beam to monitor the changes in scattering caused by the crystallization of the polymer in the solution with changes in temperature. Because of the lower intensity of this signal, further amplification was required. Because the diode laser output was quite stable, a reference detector was not used in this stage of the investigation. The voltage output of each of the two photodiode detectors was connected to a Stanford Research Systems SR245 interface and a computer for data acquisition and handling. The data acquisition was triggered by a clock pulse of 1 Hz. As the setup did not allow for the amplification of the intensity at the 90° detector, only the direct beam intensity was measured in this preliminary study.

The inside surfaces of the aluminum block were painted matt black to limit scattering and reflections. Furthermore, the interference of room lighting on the detectors was eliminated by tubing between the aluminum block and the detectors.

The temperature-control system was designed in-house and offered special features. To change the temperature at a controlled rate (between 0.2 and 2°C/min) in a heating or cooling range between 30 and 100°C, we used a microprocessor temperature controller (GEFRAN 800 model, Provaglio d'lseo (BS), Italy). As input, from the heater block to the control instrument, we used a resistance thermometer probe (type PT100). Two logic outputs were used, one controlling the hotplate element through a solid-state relay and the other regulating the cooling water flow from a cold water tap through the cooling manifold using a solenoid valve switched by a solid-state relay.

Samples, preparation, and analysis parameters

Several different types of polymers were analyzed on the instrument. Typically, a solution of between 0.5 and 2 mg/mL of the polyolefin was dissolved in 1,2,4-trichlorobenzene at 130°C. The solution, in a quartz sample holder (inside diameter = 21 mm, length = 100 mm), was placed into the receptacle in the aluminum heating/cooling block, and the sample was cooled in a controlled fashion from 100°C to room temperature. Cooling rates varied between 1 and 3.5°C/min. Samples comprised two commercial polyolefins, a propylene-1–pentene copolymer prepared by a heterogeneous transition-metal catalyst and linear low-density polyethylene (LLDPE), and three polypropylenes (PPs) prepared in-house by a suitable C_2 symmetric metallocene catalyst with differing molecular weights but similar tacticities. The latter polymers were produced by the polymerization of propylene with the metallocene catalyst {dimethylesilyl bis[2-methyl-4,5-(benzo)indenyl]zirconium dichloride} and methyl alumoxane (10% solution in toluene) at 25°C and with hydrogen as a transfer agent to control the molecular weight.

Molecular weights were determined with high-temperature gel permeation chromatography. A flow rate of 1 mL/min on a PL-GPC 220 high-temperature chromatograph (Polymer Laboratories, Varian Inc., Amherst, MA) was used, and the measurements were performed at 160°C. The columns used were packed with a polystyrene/divinylbenzene copolymer (PL gel MIXED-B [9003-53-6]) from Polymer Laboratories. The sample concentration was 2 mg/mL, and the solvent used was 1,2,4-trichlorobenzene stabilized with 0.0125% 2,6-di-*tert*-butyl-4-methylphenol. 2,6-Di-*tert*-butyl-4-methylphenol was used as a flow-rate marker. Calibration of the instrument was done with monodisperse polystyrene standards (EasiCal from Polymer Laboratories). The detector used was a differential refractive-index detector. The melting temperature and crystallinity were determined on a TA Instruments Q100 differential scanning calorimetry (DSC) system calibrated with indium metal according to standard procedures. The heating and cooling rates were maintained at a standard 10°C/min. The samples of the standard fractions and original polymers were first subjected to a heating ramp up to 220°C, after which the temperature was kept isothermally at 220°C for 5 min to remove thermal history. The cooling cycle followed the isothermal stage, with the subsequent second heating scan being recorded for analysis. ^{13}C-NMR

TABLE I
Characterization Data for the Polyolefins Used in this Study

Polymer	Comonomer (%)	M_w	PD	T_m (°C)	Crystallinity (DSC)	mmmm%
m-PP-1	n/a	35,962	2.7	150.9	81.0	93.8
m-PP-2	n/a	65,054	2.2	151.3	70.1	93.3
m-PP-3	n/a	141,885	3.1	149.8	55.0	93.5
PP-1–pentene	1-Pentene (1.2)	305,800	4.2	151.8	67.4	n/a
LLDPE	1-Butene (6.0)	278,050	3.8	122.9	nd	n/a

M_w, weight-average molecular weight; T_m, melting temperature; n/a, not applicable; nd, not determined.

spectra were recorded at 120°C on a Varian VXR 300 spectrometer. A pulse angle of 45° and a relatively short repetition time of 0.82 s were used. Some of the samples were also run on a 600 Varian Unity Inova NMR spectrometer equipped with an Oxford magnet (14.09 T) operating at 600 MHz, with a 5-mm inverse detection pulsed field gradient probe. Samples (60–80 mg) for ^{13}C-NMR analyses were dissolved at 110°C in a deuterated 1,1,2,2-tetrachloroethane. Analyses of the ^{13}C-NMR spectra allowed for the calculation of the comonomer content in the copolymers and the tacticity (expressed as mmmm%) of the propylene homopolymers.

RESULTS AND DISCUSSION

Chemically distinct polymers

The purpose of the first set of experiments was to see if chemically distinct polymers would give different responses on the instrument, in other words, whether the technique could distinguish between the crystallization behavior of materials that we knew to be different. To this end, the materials that were used for analyses and their molecular characteristics are listed in Table I.
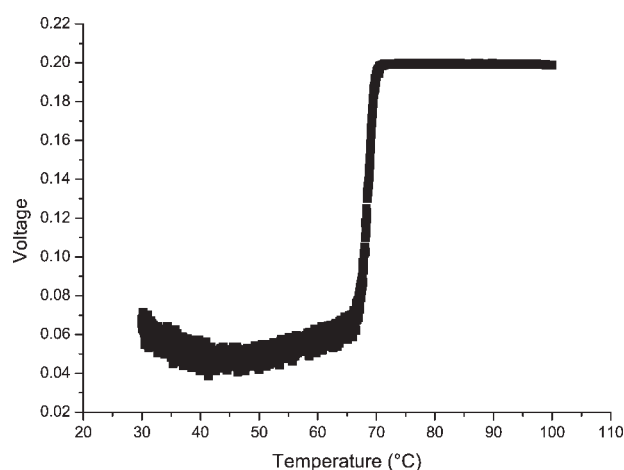
A typical response is shown in Figure 2. The sharp decrease in the signal from the diode was due to the increased scatter of the incident beam, whereas the scattered signal at the end of the run was due to the crystallites formed during the process of scattering the beam. Data were then analyzed with Origin software (OriginLab Corp., Northampton, MA). To get a peak and have the ability to analyze the peak maximum and peak width, we calculated the first derivative of the voltage data. Data were smoothed as the derivative was calculated. A typical result is shown in Figure 3.

As shown in Figure 3, extensive scatter after crystallization was evident (area marked A in the figure). In other plots presented in this article, extensive smoothing of the data in this area was done before the first derivative was taken. This was done so we could present overlays of different sets of results. The data points collected below 65°C were subject to severe scattering. A minimum voltage was observed around 45°C. Below 45°C, there appeared to be a slight increase in voltage; in other words, we saw an increase in the measured beam intensity. This was caused by the increase in crystallite size as cooling increased and crystalline particles continued to grow. This caused an increased forward scatter and
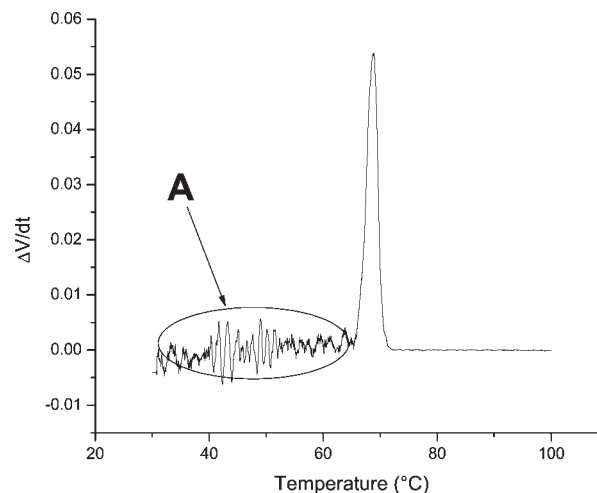
Figure 2 Raw data for the cooling scan of m-PP-3 at 2°C/min and a concentration of 2 mg/mL.

Figure 3 First derivative of the raw data shown in Figure 2. $\Delta V/dT$ is the first derivative of the voltage data.

increased the apparent intensity. This is something we believe could be used to good effect in future experiments.

As mentioned, the initial experiments were conducted to see if we could differentiate between chemically different polymers. To illustrate this, we present the scans for two polymers, a commercial LLDPE and a commercial polypropylene-1 (PP-1)–pentene copolymer (see Table I). In each case, a cooling rate of 2°C/min and a polymer concentration of 2 mg/mL were used. An overlay of two of the scans, those of the LLDPE and the PP-1–pentene copolymer, is shown in Figure 4. Comparing this to the scan for metallocene polypropylene-2 (m-PP-2; Fig. 2), we could see that the crystallization behavior of the three polymers were different, not only with respect to the peak crystallization temperatures but also with respect to the range over which crystallization occurred. In particular, the set of conditions selected for the LLDPE led to a very broad peak, with the scattering having a severe influence on the ability to isolate and identify the crystallization peak.

Effect of the experimental parameters

Sample concentration effects

The initial experiments indicated that the crystallization behavior seemed to be dependent on the experimental parameters. This included the concentration of the polymer in solution and the cooling rates. The concentration not only affected the peak crystallization temperature (determined from the first derivative plot) but also the scatter and range of crystallization. The latter is illustrated in Figure 5, where we illustrate the effect of sample concentration on the crystallization profiles of a commercial propylene-1–
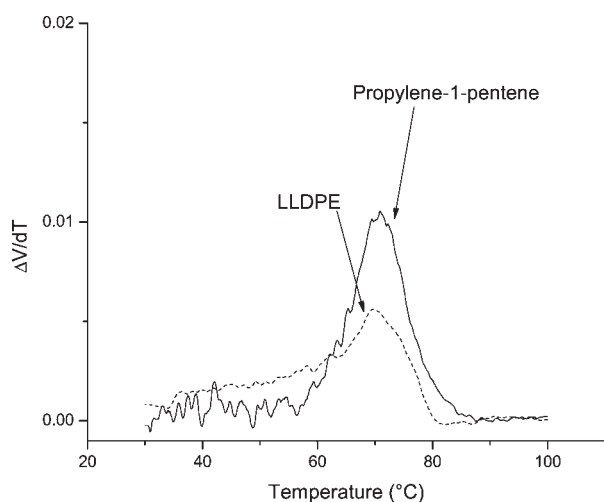

Figure 4 Comparison of a propylene-1–pentene copolymer and LLDPE analyzed under identical conditions (2 mg/mL, 2°C/min).
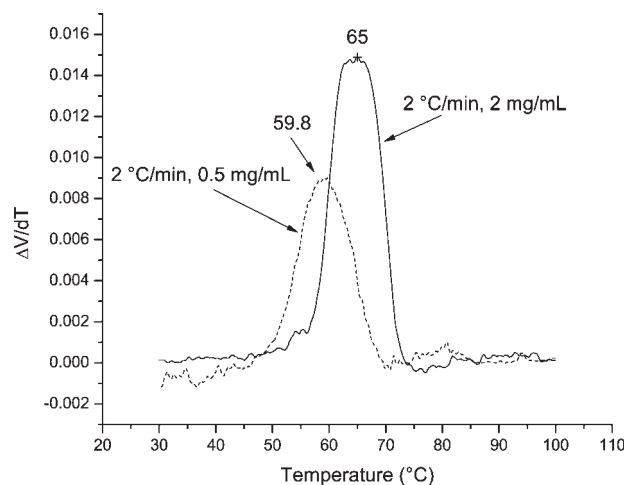

Figure 5 Concentration effects during crystallization from solution for a propylene-1–1-pentene copolymer.

pentene copolymer. Two solutions, with concentrations of 2 and 0.5 mg/mL, were compared.

As shown in Figure 5, the higher the concentration was, the higher the crystallization temperature was for a given cooling rate. Intuitively, this was to be expected, as a higher concentration of polymer would lead to more rapid crystallization. It was also noticeable that the peak width for the crystallization of the polymer with the lower concentration was wider than that of the solution with the substantially higher concentration.

Cooling rate

It was expected that the cooling rate would play a role in the data generated by these experiments. As one of the big advantages with these experiments is seen to be the fairly short scan times, we felt it necessary to see how big an effect the cooling rate had on the results. For example, in Figure 6, we illustrate the difference achieved in when cooling rates of 2, 1.4, and 1°C/min were compared.

Even with a relatively small change in the cooling rate, we saw a significant change in the peak temperature of the first derivative peaks of the cooling profiles for three solutions (1 mg/mL) of the propylene-1–pentene copolymer. The peak width of the slower cooling rate was less than that of the slightly faster cooling rate, whereas the crystallization range also appeared to be narrower when the cooling rate was decreased. Unfortunately, the data-capture package used for these experiments precluded the use of even slower cooling rates.

Heating rates

It was obvious that the reverse of the cooling experiments could be done. The suspension of crystallized
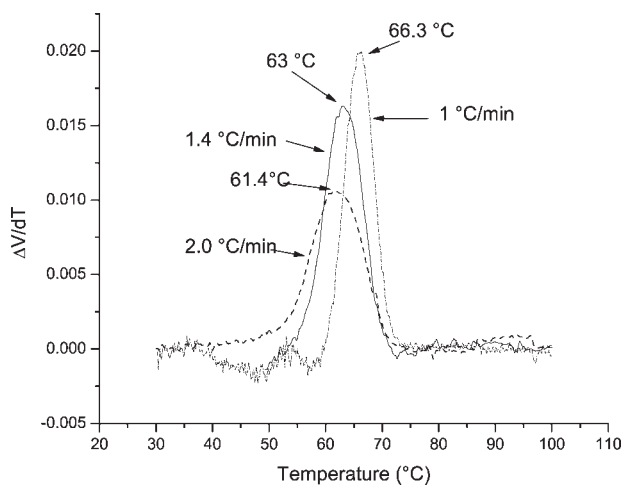
Figure 6 Effect of the cooling rate on the crystallization of PP-1–pentene. Cooling rates of 1, 1.4, and 2°C/min were used. The solution concentration was 1 mg/mL.

material was heated, the disappearance of scattering was recorded, and upon derivation and smoothing, a heating curve was obtained. In Figure 7, the results of the heating experiments of similar solutions of a propylene-1–pentene copolymer are shown.

In Figure 7, the dashed line represents the first derivative of the heating curve of a solution of 1-mg/mL propylene-1–pentene copolymer heated at 1°C/min, whereas the solid line represents the 2°C/min experiment. The peak with an apparent shoulder of the crystallized material heated at 2°C/min was clearly resolved into two maxima when the material was heated at 1°C/min. It is possible that some more peaks might have been present at lower temperatures, but the amount of scatter makes it impossible to make statements in this regard. Similar
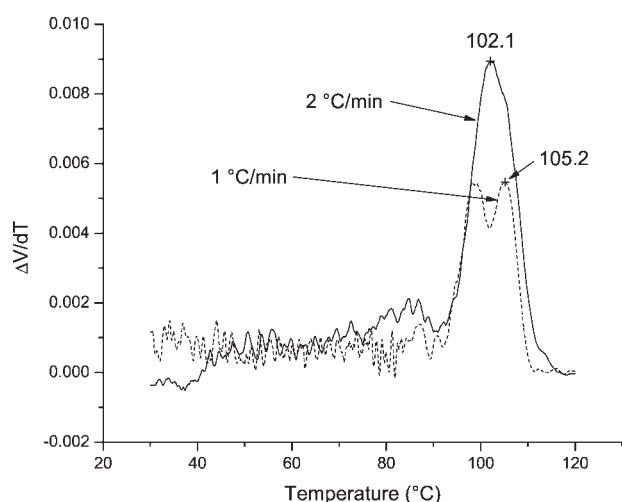
experiments conducted at 3.5°C/min yielded a very broad peak with a severe tailing toward higher temperatures. There also appeared to be a slight increase in the 2°C/min scan around 40°C, but as this area was severely affected by scattering (crystallites reflecting light), no real conclusion could be drawn about any of the data in this area.

Molecular weight effects

As an additional experiment, we synthesized three metallocene copolymers with the same metallocene catalyst, keeping the catalyst/cocatalyst/monomer ratio constant for all three reactions and while varying the amount of hydrogen introduced into the reaction. The tacticities are given in Table I. In this experiment, we compared two materials with noticeably different molecular weights. The overlay of the crystallization experiment is shown in Figure 8. In this case, it was clear that a molecular weight effect appeared to be present during the solution crystallization of the polymers. This was significant, as molecular weight effects are generally ignored during fractionation crystallization experiments. The effect of the molecular weight on the fractionation was considered by Wild et al.[13] The data obtained by Wild et al.[13] indicated that if the polymer chain ends were considered to be the equivalent of a branch point, the molecular weight dependence on the fractionation mostly disappeared. They also showed that the molecular weight dependence fell away as soon as the molecular weight reached approximately 10^4 g/mol. In our experiment, we concluded that molecular weight did, in fact, play a significant role when two polymers of similar tacticity crystallized from solution.
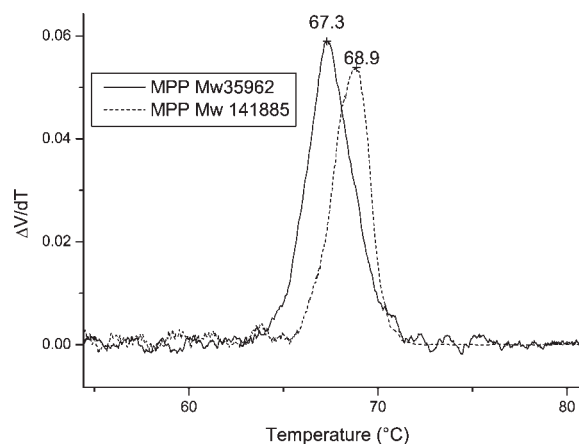

Figure 7 Heating profiles of 1-mg/mL solutions of a PP-1–pentene copolymer. Heating rates of 1 and 2°C/min are shown.

Figure 8 Crystallization profiles of two PPs prepared by a metallocene catalyst. The dashed line represents the polymer with a molecular weight of 141,885, and the solid line represents the polymer with a molecular weight of 35,962. The sample concentration was 2 mg/mL, and the cooling rate was 2°C/min. MPP is metallocene polypropylene.

CONCLUSIONS

It was possible to draw some conclusions regarding the structure/property relationships of the polymers and the results obtained from the initial experiments with the turbidity analyzer. There were, however, some aspects that made us reluctant to make definitive statements in this regard. One aspect that we feel needs further investigation is that of the effect of the forward scatter. In the study presented here, we measured the intensity of the incident beam and attributed the decrease in the detector voltage to the phenomenon of crystallization. However, as soon as the crystallites became large enough, they scattered light very effectively and, as such, should have contributed to the measured light intensity.

Although we are as yet not in a position to make definitive statements about the reasons for the variations that we saw in the crystallization behavior of the polymers that we investigated, we can conclude that we are able, by means of the turbidity analyzer, to differentiate between polymers of different chemical and morphological composition. The first results indicate that the experimental parameters played a big role in this setup. This makes it difficult to compare chemically dissimilar polymers, but with chemically similar polymers, it does appear possible to compare materials. In this regard, we showed an apparent dependence of molecular weight during the solution crystallization of m-PP samples. Both cooling (crystallization from solution) and heating (melting and dissolution) experiments were successfully demonstrated, and it was shown that both cooling and heating rates, as well as polymer concentration, affected the molecular weight.

Shan et al.[1] concluded that there is tremendous potential for the use of a turbidity analyzer for the study of polyolefin crystallization, and we must concur. The method is easy to use, rapid, and allows for both cooling and heating experiments to be conducted in a short space of time. We feel that some work still needs to be done on the data collection aspect, to ensure that what is measured is due to crystallization and not some experimental artifact.

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