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Anisotropic thermal conduction in polymer melts in uniaxial elongation flows

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Synopsis

Anisotropic thermal conduction was measured in two amorphous polymers that were quenched immediately after being subjected to uniaxial elongation in the molten state. The quenching is performed so that the flow-induced orientation is retained and the samples are essentially in a stress-free state. A novel optical technique based on forced Rayleigh scattering is used to measure the two independent components of the thermal diffusivity tensor as a function of strain and strain rate. The thermal diffusivity is found to increase in the direction parallel, and decrease in the direction perpendicular, to the direction of elongation. Thermal diffusivity data along with measurements of the tensile stress at the point of quenching were used to evaluate the stress-thermal rule, which is analogous to the well-known stress-optic rule. The stress-thermal rule was found to be valid for both polymers over a range of strains and strain rates. Since the quenched samples have orientation only, it appears that the primary source of anisotropy in thermal conductivity is the anisotropy of polymer chain orientation. © 2013 The Society of Rheology. [http://dx.doi.org/10.1122/1.4776237]

I. INTRODUCTION

Fiber spinning, blow molding, and injection molding are common examples of processes that involve flows of polymeric liquids. The heating and cooling of the polymer

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combined with the dissipation of large amounts of energy make polymer processing flows inherently nonisothermal. It is well known that polymer viscosity and relaxation times are strong functions of temperature. Hence, the flow of polymer liquids involves a complex interaction of mechanical and thermal transport processes. The mechanical, or rheological, behavior of polymer liquids has been an active area of research for more than 50 years. Theoretical research on thermodynamics and thermal transport in flowing polymers, while far behind rheology, has increased significantly over the past two decades [Beris and Edwards (1994); Dressler et al. (1999); Öttinger (2005); Hütter et al. (2009); Wapperom and Hulsen (1998)].

A small body of theoretical work suggests that thermal conductivity is anisotropic in deforming polymer liquids [Curtiss and Bird (1996); Öttinger and Petrillo (1996); van den Brule (1989, 1990)]. For such systems, Fourier’s law for the energy flux \( q \) is expressed as follows:

\[
q = -k \cdot \nabla T,
\]

where \( k \) is the thermal conductivity tensor. At equilibrium, the thermal conductivity tensor is isotropic: \( k = k_{eq} \delta \), where \( k_{eq} \) is the equilibrium thermal conductivity. In a more recent study [Algaer et al. (2009)], molecular dynamics simulations indicate anisotropic thermal conduction in polymers subjected to elongational deformations. Models predicting anisotropic thermal conduction in polymers are based on the simple hypothesis that energy is transported more effectively along a polymer chain than between neighboring chains. Hence, polymeric materials having an anisotropic distribution of chain orientation will display anisotropic thermal conductivity.

Using the same hypothesis, van den Brule (1989, 1990) suggested that the thermal conductivity tensor \( k \) depends on the same moments of chain conformation as does the extra stress tensor \( \tau \) in oriented polymers. As a result, he predicted the existence of the stress-thermal rule, which can be expressed as follows:

\[
k - \frac{1}{3} \text{tr} k = k_{eq} C_t \left( \tau - \frac{1}{3} \text{tr} \tau \right),
\]

where \( C_t \) is the stress-thermal coefficient, and “tr” indicates the trace of a tensor. The stress-thermal rule in (2) is analogous to the stress-optic rule, which expresses a linear relation between the refractive index and the stress tensors [Fuller (1995)].

The earliest experiments demonstrating anisotropic thermal conduction in polymers were carried out on cross-linked elastomers [Tautz (1959)]. These experiments show a significant enhancement in thermal conductivity in the direction of stretch for natural rubber subjected to uniaxial elongation. Hennig and coworkers [Hellwege et al. (1963); Hennig and Knappe (1964)] and Hansen and coworkers [Hansen and Ho (1965); Washo and Hansen (1969)] measured the thermal conductivity in the direction both parallel and perpendicular to the direction of elongation in solid thermoplastics that were quenched after deformation in the melt state. Anisotropic thermal conductivity was observed with thermal conductivity increases along the direction of elongation and decreases in the perpendicular direction for several amorphous polymers. Choy and coworkers [Choy et al. (1980); Choy et al. (1978); Choy et al. (1999); Choy and Leung (1983)] and Pietralla and coworkers [Greisinger et al. (1997); Mergenthaler et al. (1992)] have reported thermal conductivities in highly drawn polyethylene films and found the thermal conductivity in the draw direction increased by approximately a factor of 100 relative to the equilibrium value. A more recent study [Shen et al. (2010)] reports thermal conductivity increases of up to 1000 times in ultradrawn polyethylene nanofibers. The dramatic increases in
thermal conductivity reported for polyethylene are believed to be due to the presence of highly ordered crystalline domains.

In all of the experimental studies mentioned above, the state of stress in the polymer sample, either in the deformed state or just before quenching, was not measured. Hence, it was not possible to test the validity of the stress-thermal rule (2) with these data. Moreover, reported thermal conductivity data in these studies were, in most cases, obtained with experimental techniques that require relatively large temperature gradients in order to achieve reasonable accuracy, and/or rely on calibration to account for artifacts introduced by the presence of interfaces.

An accurate and noninvasive way to measure the thermal diffusivity $D = k / \rho \hat{c}_p$ (where $\rho$ is the mass density and $\hat{c}_p$ is the constant-pressure specific heat) of transparent samples is a technique called forced Rayleigh scattering (FRS) [Eichler et al. (1986)]. The first use of FRS to measure anisotropic thermal conductivity was made on liquid crystals by Urbach et al. (1978). Okuda and Nagashima (1989) applied the FRS technique to measure the thermal conductivity in polymethyl methacrylate samples that were quenched after elongation in the melt state. For the past 15 years we have developed and implemented an FRS setup that allows for measurement of time-dependent components of the thermal diffusivity tensor in polymeric materials. We have used this setup to investigate anisotropic thermal conduction in polymer melts subjected to step and constant rate shear flows [Balasubramanian et al. (2005); Schieber et al. (2004); Venerus et al. (2004); Venerus et al. (1999a, 2001)], and in cross-linked elastomers in uniaxial elongation [Broerman et al. (1999); Simavilla et al. (2012); Venerus and Kolev (2009)]. In these studies, the state of stress was also measured allowing for the first, and only, tests of the stress-thermal rule. In all cases, the stress-thermal rule (2) was found be valid. These results are consistent with the hypothesis that intrachain heat transport is more efficient than interchain, and that of van den Brule that the thermal conductivity depends on the same moments of chain conformations as the stress tensor. A somewhat surprising result from these studies is that the value of the stress-thermal coefficient $C_t$ in (2), when made dimensionless by the plateau modulus of the polymer $G_N$, is relatively insensitive to polymer chemistry and has the value $C_t G_N \sim 0.05$. This is in contrast to the stress-optic coefficient, which can vary by an order of magnitude for flexible polymer having different chain chemistries. The apparent universality of the stress-thermal coefficient raises the question of whether the anisotropy in thermal conductivity is due to chain orientation or stress or both.

In the present study, we address this question by examining anisotropic thermal conduction in polymers that have been quenched following uniaxial elongation in the molten state. The solid samples are in a (nearly) stress-free state and possess only orientation. Components of the thermal diffusivity tensor in directions parallel and perpendicular to the direction of elongation are obtained using our FRS setup. Also, from estimates of the stress at the time the samples are quenched we are able to evaluate the stress-thermal rule. Section II of this paper describes the experimental methods used to prepare oriented samples and the FRS technique. Results from this study are presented and discussed in Sec. III, and the conclusions are given in Sec. IV.

II. EXPERIMENTAL CONSIDERATIONS

Two commercial thermoplastic polymers were used as samples. One is a polystyrene (Scientific Polymers) with weight-average molar mass $M_w = 260$ kDa and polydispersity index (PDI) = 2.5 and is designated as PS260k. The other is a polymethyl methacrylate
(BASF), with $M_w = 83$ kDa and PDI = 1.8, designated as PMMA5N. The plateau modulus $G_N$ for polystyrene is 0.20 MPa, and for polymethyl methacrylate is 0.31 MPa [Fetters et al. (2007)]. Linear viscoelastic characterization of the polymers was made by performing small-strain oscillatory-shear tests over a range of frequencies and temperatures. Storage $G'$ and loss $G''$ moduli data, shifted to a temperature of 130°C using the principle of time–temperature superposition, are shown in Fig. 1. The data were fit to a discrete spectrum of relaxation times in order to obtain estimates for the mean relaxation times. At 130°C, we find for the PS260k sample a value of $\tau_{avg} \approx 3000$ s, and for the PMMA5N a value of $\tau_{avg} \approx 300$ s.

The FRS technique can be described as the creation (writing) of an optical grating within the sample and detecting (reading) its dynamics. Here, we give a brief description of the technique; details can be found elsewhere [Eichler et al. (1986); Venerus et al. (1998)]. The grating is written by the intersection of two beams from a coherent (Ar+) laser within a sample that contains a small amount of dye that absorbs the impinging light. The intensity of the laser within the sample is modulated spatially with period

$$\lambda \approx \frac{\lambda_{Ar}'}{\theta},$$

where $\lambda_{Ar}'' = 514.5$nm is the wavelength of the writing laser and $\theta$ is the angle at which the beams cross. If the criteria for the plane grating case [Eichler et al. (1986); Venerus et al. (1998)] are met, then the intensity is modulated only in the direction of the grating vector $\mathbf{g}$, which lies in the plane formed by the two writing beams and

![Fig. 1. Shear storage $G'(\square)$ and loss $G''(\bigcirc)$ moduli for (a) PS260k and (b) PMMA5N at 130°C. The lines are the fit of the data to a discrete spectrum of relaxation times that are used to estimate the mean relaxation time for each polymer.](image-url)
is perpendicular to their direction of propagation. By a rapid, radiationless decay of the dye to its ground state, a sinusoidal temperature field with modulation amplitude $\delta T \sim 10 \text{mK}$ is created. This temperature modulation leads to a modulation of refractive index, which is detected using a second, low-power reading (HeNe) laser that passes through the sample at the Bragg angle. The intensity of the first-order diffracted beam along with scattered light is measured by a photo-detector.

As noted above, the FRS technique requires that the sample absorb energy from the writing laser. Since the polymers used in this study are colorless, a dye (either Oil Red O or Quinizarin) was added at concentrations of less than $10^{-3}$ by weight to the as-received polymers. We have used two techniques to achieve uniform dispersion of dye within the sample: Solvent casting, and direct mixing using a small extrusion device. The latter technique has the advantage of obviating the necessity of drying the samples, which for samples of 1 mm thickness can require several months. The absorption coefficient of the dyed polymers was approximately $10 \text{cm}^{-1}$ at 514.4 nm as required for our FRS setup [Venerus et al. (1998)]. Confirmation that neither the presence of the dye, nor the processes used to prepare dyed samples, had an effect on the rheological properties of the polymers was made using dynamic modulus measurements.

Because the grating period is much smaller than the spot size of the writing laser, the dynamics of the grating temperature field can be decoupled from the bulk temperature in the sample. Following a pulse of the writing laser $\delta T$ has, for times large compared to the time scale for sound wave propagation, an exponential time dependence: $\delta T \propto \exp(-t/\tau_g)$. The grating relaxation time is given by $\tau_g = \frac{4\pi^2 \Lambda^2}{gD_g}$, where $D = k/\rho c_p$ is the thermal diffusivity tensor. A typical photo-detector output from a single writing laser pulse is shown in Fig. 2. Both the growth during the pulse and the decay following the pulse are shown; a fit to the decaying part of the signal is used to obtain a value for $\tau_g$. Note that because $\Lambda$ is on the order of tens of microns the duration of a single experiment is only a few milliseconds. Typically, an average of 100–200 experiments of the type shown in Fig. 2 was used to determine an average value of $\tau_g$. A check of the validity of assumptions used to analyze FRS experiments (i.e., plane grating, Fourier’s law, and purely diffusive transport) can be made by varying the grating period $\Lambda$, which is achieved by simply changing the intersection angle of the writing beams $\theta$. Typical

![Graph](attachment:image.png)
results from such a check are shown in Fig. 3. From this figure we see that for each of the experimental conditions shown, the expected quadratic dependence of \( s_g \) on \( K \) is observed. Values of thermal diffusivity reported in this study were obtained from the slope of data presented as shown in Fig. 3.

All FRS experiments were carried out at room temperature, which was nominally 23°C. It should also be noted that we find good agreement for \( D_{eq} \) between values obtained from FRS experiments on isotropic samples with those found in the literature: \( D_{eq} = 1.14 \pm 0.01 \times 10^{-3} \text{ cm}^2/\text{s} \) for PS260k; \( D_{eq} = 1.29 \pm 0.01 \times 10^{-3} \text{ cm}^2/\text{s} \) for PMMA5N. Uncertainty was estimated by propagation of error analysis taking into account the uncertainty in the fit values of \( s_g \) and the grating period \( K \).

Samples were created by subjecting the molten polymer to uniaxial elongation followed by rapid quenching below the glass transition temperature. To prepare stress-free samples with orientation, they were quenched sufficiently rapidly to freeze in orientation, but slowly enough to avoid significant thermal stresses. This type of protocol has been used to show that the stress-optic coefficient for a quenched polymer in the solid state [Handge and Schmidheiny (2007)] is the same as that measured for the same polymer in the molten state [Luap et al. (2005); Venerus et al. (1999b)]. Samples were subjected to constant strain rate \( \dot{\varepsilon} \) uniaxial elongation by using an opposed rotating cylinder device known as the Sentmanat extensional rheometer (SER) [Sentmanat (2004); Sentmanat et al. (2005)]. As described elsewhere [Sentmanat (2004)], the tensile stress difference: \( \sigma = \sigma_{11} - \sigma_{33} \), where the sample is elongated in the 1-direction and contracts in the 2- and 3-directions, is obtained from the ratio of the tension in the sample \( F \) to its cross-sectional area \( A \). Rectangular samples with dimensions (at room temperature) of 20 \( \times \) 12.5 \( \times \) 1.65 mm\(^3\) were used in the SER device. The width and thickness of these samples are somewhat larger than recommended [Sentmanat (2004)], but were required so that the dimensions of the sample after elongation were suitable for our FRS technique. In Fig. 4, we show stress versus elongation ratio \( \lambda \) for three different strain rates for both polymers. When the sample reached the desired value of \( \lambda \), it was rapidly quenched using liquid N\(_2\). Note that in several cases samples were quenched at fixed values of stress for different elongation rates. Separate measurements of the sample temperature during quenching were made and indicate that the sample was quenched to a glassy state within
3–5 s after the deformation had ended. Residual thermal stresses can arise in such samples from temperature-dependent density, and nonuniform cooling. We confirmed that the influence of any residual stresses were effectively absent in the sample by performing experiments on fully relaxed samples that had undergone identical quenching protocol (see Fig. 3).

From measurements of the cross-sectional area \( A_{\text{avg}} \) of quenched samples, we have found that the deformations imposed on the sample using the SER device were not ideal. (This may be in part due to using samples with nonideal initial dimensions.) For all tests, the actual deformation was significantly less than the expected value, which we believe was caused by slip between the sample and the rotating cylinders. In a constant rate deformation, the elongation ratio \( k_{\text{nom}} \) increases exponentially in time: \( \lambda_{\text{nom}} = \exp(\dot{\lambda}t) \). The relation between the measured sample elongation ratio \( k_{\text{avg}} = \frac{A_0}{A_{\text{avg}}} \), where \( A_0 \) is the initial cross-sectional area, and the nominally imposed value \( \lambda_{\text{nom}} \) is shown in Fig. 5. The data fall between the ideal case and the case of complete slip on the cylinder surface, which assumes the sample slips everywhere on the cylinder except where it is clamped. The data in Fig. 5 are well described by the following expression:

\[
\lambda_{\text{avg}} = \frac{\lambda_{\text{nom}}^{1-s} - s}{1 - s},
\]

where \( s \) is an empirical parameter that ranges from 0 (no slip) to 1 (complete slip). The curve in Fig. 5 is for the value \( s = 0.33 \). The slip problem is why the data in Fig. 5 are designated as “nominal.” However, using the measured sample dimensions as shown in Fig. 5, we are able to correct for the slip effect and obtain reasonably accurate values for average stress \( \langle F/A_{\text{avg}} \rangle \) and strain \( \langle A_0/A_{\text{avg}} \rangle \).

**FIG. 4.** Nominal elongational stress \( \sigma_{\text{nom}} \) versus nominal elongation \( \lambda_{\text{nom}} \) time at three different strain rates for (a) PS260k and (b) PMMA5N at 130°C.
III. RESULTS AND DISCUSSION

The elongational viscosity $\eta_E = \frac{\sigma}{\dot{\varepsilon}}$ versus time at several strain rates is plotted in Fig. 6. As noted earlier, the actual sample deformation in the SER device deviated from an ideal uniaxial elongation, and we again use the designation “nominal.” From Fig. 6 we see that the viscosity data for both polymers are self consistent at small strains, and

![Graph showing elongational viscosity vs time for PS260k and PMMA5N at 130°C.](image)

**FIG. 5.** Average elongation $\lambda_{avg}$ versus nominal elongation $\lambda_{nom}$ for PS260k and PMMA5N samples subjected to different strain rates at 130°C. Straight dashed line is for ideal deformation and curved dashed line is for perfect slip. Solid curve is fit to data using Eq. (3).

**FIG. 6.** Nominal elongational viscosity $\eta_{E_{nom}}$ versus time at three different strain rates for (a) PS260k and (b) PMMA5N at 130°C. Solid curves are the prediction for linear viscoelasticity.
display strain hardening behavior at larger strains. The latter behavior would be expected for entangled polymers at these deformation rates where $\dot{\varepsilon} \tau_{\text{avg}} \gg 1$. The data are, however, systematically shifted vertically from the linear viscoelastic prediction at small strains for all strain rates. It is not clear if this deviation is due to slip, or to a deformation that is not uniaxial, or both. Since the deviation from ideality affects both $\sigma$ (through the area) and $\dot{\varepsilon}$, we have not attempted to correct the viscosity data in Fig. 6.

The relaxation of tensile stress $\sigma$ following constant-rate elongation versus time at several strain rates is plotted in Fig. 7 for PS260k. Here we assume that the sample cross section, which is measured after quenching, remains constant during the relaxation and these data are designated as “average.” From this figure, we see that the rate of stress relaxation is larger for relaxation after larger strain rates. This may be a sign of stretched chains relaxing back to their equilibrium contour length. Similar results were obtained for the PMMA5N sample. As noted earlier, the sample was quenched to a glassy state after the deformation was stopped. To estimate the stress in the sample at the point of quenching, $\sigma_{\text{avg}}$ was determined from the average value of stress $\sigma$ over 3 s.

Thermal diffusivity measurements were made using the FRS technique (described in Sec. II) on samples quenched at different levels of stress. FRS experiments were performed for two different grating vector orientations with respect to the direction of elongation: Parallel where $g = \delta_1$ yielding $D_{11}$; perpendicular where $g = \delta_3$ yielding $D_{33}$.

In Fig. 8, we show two components of the thermal diffusivity tensor normalized by the equilibrium value as a function of elongation for PS260k. For the component measured in the direction parallel to elongation $D_{11}$ we see an increase relative to the equilibrium value $D_{\text{eq}}$ with increasing elongation, while the component measured in the direction perpendicular to elongation $D_{33}$ decreases relative to $D_{\text{eq}}$. The data in Fig. 8 show that the change in thermal diffusivity depends also on the strain rate at which the elongation is carried out. In other words, anisotropy in $D$ is not determined by strain alone. We have obtained similar results for the PMMA5N samples. The results in Fig. 8 are qualitatively similar to those found previously [Hansen and Ho (1965); Hellwege et al. (1963); Hennig and Knappe (1964); Washo and Hansen (1969)] for thermoplastics using more conventional approaches to measure thermal conductivity, and those obtained using the FRS technique for PMMA [Okuda and Nagashima (1989)] and
cross-linked elastomers [Broerman et al. (1999); Simavilla et al. (2012); Venerus and Kolev (2009)].

We now combine mechanical measurements with the thermal diffusivity data in Fig. 8. The results are presented in dimensionless form in Fig. 9 for both PS260k and PMMA5N. For both polymers, a linear relationship between the normalized thermal diffusivity difference and the tensile stress difference is observed; this holds independent of strain rate. If we assume that $\rho$ and $\bar{c}_p$ are independent of deformation, which one would expect to be true for amorphous polymers, then the stress-thermal rule (2) is valid. The slopes of the solid lines through the data in Fig. 9 give values for the normalized stress-thermal coefficient. For PS260k, we find $C_t G_N \approx 0.033 \pm 0.002$; and for PMMA5N, we find $C_t G_N \approx 0.054 \pm 0.003$. These values are in good agreement with values obtained for shear deformations polymer melts [Balasubramanian et al. (2005); Schieber et al. (2004); Venerus et al. (2004); Venerus et al. (1999a, 2001)] and cross-linked elastomers in uniaxial elongation [Broerman et al. (1999); Simavilla et al. (2012); Venerus and Kolev, (2009)].

**FIG. 8.** Normalized components of the thermal diffusivity tensor versus average elongation $\lambda_{avg}$ for PS260k samples subjected to constant strain rate deformations at $130°C$. The horizontal dashed line is the equilibrium case; values above this line are measurements along the direction of elongation $D_{11}/D_{eq}$, and those below are measurements perpendicular to the direction of elongation $D_{33}/D_{eq}$.

**FIG. 9.** Test of the stress-thermal rule made using the data in Figs. 7 and 8 for PS260k and PMMA5N samples. The slopes of the lines through the data give the dimensionless stress-thermal coefficient defined in Eq. (2): PS260k $C_t G_N \approx 0.033 \pm 0.002$; PMMA5N $C_t G_N \approx 0.054 \pm 0.003$. 

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The study by Washo and Hansen (1969) also included birefringence data, making it possible to use a combination of the stress-optic and stress-thermal rules to obtain an estimate of the stress-thermal coefficient. From their data we obtain a value of $C_tG_N \sim 0.04$ for PMMA, which is in reasonable agreement with the result obtained from Fig. 9. It is also worthwhile to note that for polystyrene the stress-optic rule fails at stresses that are $\sigma/G_N \sim 10$ [Luap et al. (2005); Venerus et al. (1999b)], which is a value at which the stress-thermal rule appears to be valid. In a similar study on cross-linked polyisoprene [Simavilla et al. (2012)], we have found that the stress-thermal rule is valid at elongations where the stress-optic rule fails.

IV. SUMMARY AND CONCLUSIONS

Flow-induced, anisotropic thermal conduction in two thermoplastic polymers has been investigated. Two components of the thermal conductivity (diffusivity) tensor were measured using a robust optical technique known as FRS on samples quenched after being subjected to uniaxial elongation in the molten state. Problems encountered with nonideal deformation were overcome by direct measurement of the sample dimensions after quenching. Anisotropies relative to equilibrium of up to 30% were observed with increases (decreases) in the thermal conductivity measured in the direction parallel (perpendicular) to the direction of elongation. The first evaluations of the stress-thermal rule on thermoplastic polymers have been carried out and were found to be valid for both polymers independent of the strain rate during elongation.

Values for the normalized stress-thermal coefficient $C_tG_N$ obtained in this study are consistent with those obtained in our previous work on polymers with different chemistries and in different deformation types. These results provide further evidence of universality for this material property for amorphous polymers. This is in contrast to the stress-optic coefficient, which displays a strong dependence on the chemistry of the polymer chain. It is worthwhile to note that in all previous evaluations of the stress-thermal rule, the polymer that had both stress and orientation. In this study, the samples were in a stress-free state, which suggests that polymer chain orientation is the main source of anisotropy in thermal conductivity. In a related study [Schieber et al. (2012)], we have made a similar set of experiments on the same polymers that have stress without orientation.

The results obtained in this study provide further evidence that flow-induced anisotropic thermal conduction exists in polymeric materials. These phenomena must been taken into account in the formulation of models intended for the computational design and optimization of polymer processing operations. A significant reduction in model complexity may be realized as a result of the stress-thermal rule, which appears to be valid for amorphous polymers. These results also could be used, for example, to estimate the thermal conductivity tensor in injection molded parts if the stress field at the point of solidification is known. A satisfactory understanding for the phenomena at the molecular level, however, remains to be identified. Indeed, the question of why the stress-thermal rule appears to hold at deformation levels where the stress-optic rule fails is intriguing. Further experimental and theoretical research on anisotropic thermal conduction in polymers is needed to address this situation.

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