A rheo-light-scattering instrument for the study of the phase behavior of polymer blends under simple-shear flow

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A rheo-light-scattering instrument for investigating the influence of shear on the phase behavior of polymer blends was constructed from a commercial parallel-plate rheometer. Laser light scattering from the sample plane formed by the flow and vorticity directions was projected on a screen, and a combination of a camera lens and a charge-coupled device detector was used to record the scattering pattern. The rheometer, which can generate angular velocities of up to 100 rad/s and measure torque and normal forces up to 9.8×10⁴ N m and 9.8×10⁵ N, respectively, is suitable for studying polymer melts at stresses up to 9.1 kPa. The maximum accessible q range was from 3.72×10⁻⁵ to 7.11×10⁻³ nm⁻¹ (3°–42° scattering angle and a laser wavelength of λ=632.8 nm).

The performance of the light-scattering instrumentation and the accuracy of the correction algorithms were tested with a Ronchi ruling diffraction grating and a colloid of monodisperse polystyrene spheres. Example rheo-light-scattering measurements were made with a 50/50 blend of polystyrene and polyisobutylene oligomers and a 40/60 blend of polybutadiene and polyisoprene. All components had narrow molecular weight distributions. The first blend exhibits an upper critical solution temperature while the second blend shows a lower critical solution temperature. © 1995 American Institute of Physics.

I. INTRODUCTION

The real-time evaluation of molecular structure and morphology during flow has become a topic of considerable contemporary interest, because of its significance with regard to the development of properties during processing of a polymer melt or solution. Similarly, the influence of stress on the phase behavior of polymer solutions and blends has practical importance. In the last decade, a number of laboratories have conducted rheo-optical studies on polymer blends and both flow-induced mixing and demixing have been reported. As yet, no theory adequately explains the phenomena that have been observed, and clearly more complete experimental data are required. One obstacle to acquiring that data is the lack of suitable instrumentation for unequivocally separating dynamic and thermodynamic effects in a flowing system.

Phase separation and mixing of polymer solutions and blends have been studied by combining flow with various analytical techniques, including turbidity, fluorescence, birefringence and dichroism, and scattering. Turbidity measurement is probably the simplest and most common technique for identifying phase changes. Shear-dependent changes in turbidity may be measured by equipping a rheometer with a laser light source, optically transparent fixtures, and a photomultiplier-tube detector. The problem is that turbidity is also sensitive to the size, shape, and optical anisotropy of a dispersed phase and to the refractive index ratio of the dispersed and the matrix phases. As a result, the distinction between thermodynamic effects such as phase transitions and nonthermodynamic effects such as deformation and breakup of a dispersed phase is not always clear. Moreover, turbidity is less sensitive to phase separation when the refractive indices of the dispersed phase and the matrix are very close, such as near the critical point. By itself, turbidity reveals only the most elementary aspects of shear-induced phenomena. Thus it is necessary to use other methods to determine unambiguously the effects of flow on the phase behavior and morphology of multiphase systems. Angular-dependent light-scattering measurements can resolve the size and shape of a dispersed phase, which makes it a more appropriate technique for distinguishing between shear-induced phase transitions and droplet breakup and/or deformation.

In recent years, several rheo-optical instruments have been constructed for measuring two-dimensional (2D) light-scattering profiles from flowing polymer systems. Hashimoto et al. equipped a commercial rheometer with a quartz cone and plate or parallel-plate fixtures and a television camera or photographic film detector to obtain 2D scattering patterns during flow. Nakatani et al. improved upon the Hashimoto setup by using a charge-coupled device (CCD) detector instead of a TV camera, but their instrument was based on a custom-built rheometer so its design has limited applicability to other laboratories. CCD detectors are advantageous because of their high sensitivity and large dynamic range. The latter instrument employed an aspheric lens and elliptic mirror for focusing the scattered light on the detector. Nakatani and co-workers have also reported difficulties in the quantitative analysis of the light scattering due to stray light from diffraction off the beamstop, but apparently corrected for this problem. The limited angular range of their data (<17°), however, suggests that they may have encountered problems due to lens aberration of their focusing system. We encountered similar problems with a lens focusing system in our initial instrument design that also limited the accessible angular range. Van Egmond et al. constructed a...
also used a CCD detector to record 2D scattering patterns, but instead of focusing the light on the detector with lenses, they first focused the light-scattering pattern on a cardboard screen and the pattern was then recorded by the detector. They used a custom-built rheometer with concentric cylinder and parallel-plate fixtures; the latter could be heated to 200 °C to accommodate studies on polymer melts.

In this paper, we describe a rheo-light-scattering instrument that is constructed from a commercial rheometer and 2D light-scattering components. The design should be applicable to nearly any commercial rheometer. An accessible angular range of over twice that reported by Nakatani et al. was accomplished by focusing the scattering pattern on a screen and imaging that pattern on the CCD detector. Results for shear-induced phenomena of polystyrene/polyisobutylene blends are described. None of the previous reports of shearing of polymer blend melts with a rheo-light-scattering instrument actually showed that simultaneous stress and light-scattering measurements can be made. The ability to do this is demonstrated for a polybutadiene/polyisoprene blend.

II. RHEO-OPTICAL INSTRUMENT

A. General design considerations

Rheo-light-scattering instruments combine angular-resolved light-scattering detection and a rheometer. The latter provides a well-controlled flow field and measures the stress in the fluid. This allows simultaneous measurement of the rheological properties of the fluid and time-dependent scattering patterns. Often, when retrofitting commercial rheometers to accommodate light-scattering measurements, space restrictions in the rheometer and geometrical requirements for imaging the scattered light complicate the design of the rheo-optical device. Preferably, the design decouples the operations of the rheometer and the scattering device to simplify the alignment of the optics and reduce the transmission of vibration from the rheometer.

Two methods of conveying the scattering pattern to the detector have been commonly used. One method involves first forming a virtual image of the scattering pattern. This is the design used by Nakatani et al. This requires an objective lens with large numerical aperture and small focal length to collect scattered light and a combination of lenses (e.g., two plano-convex lenses) to focus the image onto the detector. The quality of the image depends on the characteristics and the alignment of the lenses. Usually distortion and spherical aberration become more serious for lenses with large numerical aperture and in the area away from the lens center, which especially affect the results at high scattering angles. A beamstop is usually used to block the main beam, but light diffracted by the beamstop may distort the scattering pattern at small angles. These imperfections can severely limit the experimentally accessible range of angles over which the scattering intensity data are reliable. To lessen these defects, one needs to maximize the diameters of the lenses to reduce spherical aberrations and carefully design and position the beamstop to reduce stray light.

The alternative approach for acquiring the scattering pattern is to convert the scattered light into a real image with a screen and transfer this to a detector with a high-quality camera lens or a combination of lenses. This is the approach taken by van Egmond et al. and by us. The screen requires a nonreflecting surface, and the light intensity response (brightness) of the screen must be uniform and linear over a wide dynamic range. The advantages of this approach are that the time-consuming alignment process and lens aberration problems are avoided. A larger scattering angle range can be accessed, and analytical corrections of scattering angle and light intensity are possible.

The rheometer should be able to provide a well-defined flow field and record the torque (shear stress) and the normal force. Various rheometer geometries such as parallel plates, cone and plate, and concentric cylinders may be used. Although a parallel-plate geometry has the advantage of less optical distortion, the shear rate is not uniform—it varies along the radial direction. A cone and plate geometry provides a uniform shear rate in the sample, but the nonparallel surfaces of the fixture may distort the scattered image. Temperature control should limit both temporal and spatial temperature variations, yet allow rapid changes when needed.

B. Instrument design

The rheo-light-scattering instrument was constructed by adding a two-dimensional light-scattering system to a Rheometrics Mechanical Spectrometer (RMS), model KMS-71C, as shown schematically in Fig. 1. The light source was a polarized 8-mW He–Ne laser (Uniphase model 1105P) with a wavelength of 632.8 nm. A series of neutral density filters (optical density range from 0.1 to 4) were used to attenuate the light intensity to avoid saturating the detector, and the beam then passed through two pinholes of diameters of 1 and 1.5 mm to eliminate stray light.

The beam was directed normal to a parallel-plate rheometer fixture, which consisted of a 75-mm-diameter top glass plate and a steel bottom plate containing a quartz window. The scattering pattern was imaged on a screen of vellum-treated tracing paper (Avlin Co.). Thin blackened brass disks ranging from 1 to 6 mm in diameter were used on separate screens as beamstops. To reduce stray light, a hole was made in the screen below the beamstop where the main beam would otherwise impinge. A screen holder facilitated rapid screen changes during the experiment when necessary, e.g., when a change in the beamstop size was required. The scat-
tering angle range covered was varied by adjusting the dis-
tance between the screen and the sample by raising or low-
ering the lens holder. The maximum accessible scattering
angle for this device was limited to about 42° by total re-
fection from the interface between the glass plate and air. The
actual scattering angle range recorded depended on the
beamstop size and the position of the screen.

The scattering pattern projected on the screen was fo-
cused by a commercial camera lens onto a two-dimensional
CCD array detector. A macrofocus lens (CANON 100-mm
Macro Lens FD) was found to minimize spherical aberra-
tions and distortions, while enabling focusing at a conven-
tient working distance. The CCD detector (Princeton Instruments
model TE/CCD-576T/UV) had a dynamic range of 16383:1
and an array of 576x384 pixels, corresponding to a rectan-
gular area of 13.2 mm×8.8 mm.

The laser, neutral density filters, mirror, screen holder,
len, and detector were mounted on an optical train placed on
a level table that could be easily moved in or out of the
rheometer. Each component on the optical train could be
adjusted separately. Once the optical path was aligned, the
beamstop size and the position of the screen holder could be
changed without disturbing the alignment of the remaining
parts of the system. The signal from the detector was taken
by a controller interface (model ST-130) and saved directly
to a microcomputer. CSMA data-acquisition software from
Princeton Instruments was used to obtain and analyze the
scattering pattern.

The RMS provided a steady shear flow to the sample,
and torque, normal force, and temperature were recorded by
a Keithley 570 data-acquisition board and an IBM PC. The
rheometer fixtures were heated by an aluminum heating
jacket containing two pencil heaters. A copper plate was
placed in contact with the bottom plate and the heating jacket
to improve the temperature uniformity. A dual-input pro-
grammable process controller (CN3003, Omega Engineer-
ing, Inc.) operated the heaters and the oven. The temperature
of the sample was measured by an independent thermo-
couple with 0.1 °C resolution.

C. Instrument calibration

The goal of a scattering experiment is to obtain accurate
relative scattering intensities over the entire accessible range
of scattering angles and at all azimuthal angles. Several fac-
tors must be considered to correct the raw scattering angle
and intensity data, including refraction and reflection by the
optical components, optical path differences, and the solid
angle covered by each pixel of the detector. The various
analytical corrections of intensity and scattering angle de-
ferred for this instrument are described in the following dis-
cussion.

1. Angular calibration

The magnification of the lens/detector system and the
positions of the respective scattering angles of the scattering
pattern as projected on the screen must be known to calculate
the scattering angle for each pixel of the CCD detector. The
magnification of the lens/detector system was calculated by
temporarily placing a scale on the screen and measuring the
number of pixels of the CCD detector that corresponded to
the image of the scale.

Because of refraction, the scattered light transmitted
through the glass plate deviates from the actual scattering
angle \( q_1 \) to the angle \( q_3 \) shown in Fig. 2. The deviation \( d \)
of the scattered light depends on the thickness and the refractive
index of the glass plate and the distance between the glass
plate and the screen. For a specific scattering angle \( q_1 \), the
distance \( d \) measured from the center of the beam was calcu-
lated using Snell's law:

\[
d = d_1 \tan \theta_1 + d_2 \tan \theta_2 + d_3 \tan \theta_3,
\]

where

\[
\theta_2 = \sin^{-1}\left(\frac{n_1 \sin \theta_1}{n_2}\right)
\]

and

\[
\theta_3 = \sin^{-1}\left(\frac{n_2 \sin \theta_2}{n_3}\right).
\]

Here, \( n_1, n_2, \) and \( n_3 \) are the refractive indices of the sample,
glass plate, and air, respectively, and \( d_1, d_2, \) and \( d_3 \) are the
sample thickness, glass plate thickness, and the distance be-
tween the screen and the glass plate, respectively.

The relationship between the pixel numbers and the scat-
tering angle is determined from \( d \) and the magnification of
the lens/detector system. This calibration algorithm was veri-
ified by analysis of the diffraction peaks of a Ronchi ruling
and the scattering peaks of monodisperse polystyrene col-
lloids.

2. Intensity corrections

The intensity corrections for the optics of the instrument
include the refraction and the optical path of the light and the
solid angle detected by each pixel of the CCD detector. In
the rve-light-scattering instrument, the light intensity mea-
sured by the detector depends on the intensity of the scat-
tered light that exits the top glass plate. When incident light
strikes a boundary between two media, the transmitted light
intensity depends on the incident angle and the refractive

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![Diagram of light path through rheometer fixture and sample](image-url)
indices of the materials. As a result, the value of the transmitted light intensity should be corrected, especially for larger scattering angles. This correction involves solution of the Maxwell equations for the electromagnetic theory of light. The amplitude of the refracted wave is given for the following two cases (note that intensity is proportional to the square of the amplitude):

1. For the electric field $\mathbf{E}$ in the plane of incidence, the amplitude of the refracted light, $A'$, is

$$A' = \frac{2 \sin \phi' \cos \phi}{\sin(\phi + \phi') \cos(\phi - \phi')} A = f_1 A,$$

where $A$ is the amplitude of the incident wave, $\phi$ the incidence angle, $\phi'$ the refraction angle, and $f_1$ a prefactor defined in Eq. (4).

2. For the electric field $\mathbf{E}$ perpendicular to the incidence plane, $A'$ is

$$A' = \frac{2 \sin \phi' \cos \phi}{\sin(\phi + \phi')} A = f_2 A,$$

where $f_2$ is the corresponding prefactor.

In general, if the electric field $\mathbf{E}$ is oriented at an angle $\phi$ to the incidence plane, the refracted light amplitude can be resolved into components parallel and perpendicular to the plane of the incident wave. The intensity ratio of the refracted and incident light is then

$$\left( \frac{A'}{A} \right)^2 = \left[ \sin^2 \theta + \left( \frac{\cos \theta}{\cos(\phi - \phi')} \right)^2 \right] \left[ \frac{2 \sin \phi' \cos \phi}{\sin(\phi + \phi')} \right]^2.$$

Because a polarized light source was used in the rheo-light scattering instrument, the light intensity at any azimuthal angle could be corrected with Eq. (6). The circular-averaged intensity $I_r$ of an isotropic scattering pattern was corrected by integrating Eq. (6) over $\theta$ and dividing by $2\pi$:

$$I_r = \frac{2}{f_1 + f_2} I_1,$$

where $I_1$ is the incident intensity and $f_1$ and $f_2$ are defined in Eqs. (4) and (5), respectively.

The optical path varies with the scattering angle, as shown in Fig. 2, and, because the light intensity is inversely proportional to the square of the optical path, a correction for the optical path differences is necessary. Separate corrections for refraction and optical path differences are required for the glass plate and air, but, because the refractive index of the polymer is usually very close to that of the glass, the refraction correction for the glass/sample interface was neglected.

The solid angle of the scattered light detected by each pixel is a function of the scattering angle. The solid angle $\Omega$ corresponding to a single pixel, covering scattering angles between $\theta_{c1}$ and $\theta_{c2}$, was derived by Russell et al. for an optical multichannel analyzer (OMA):

$$\Omega(q) = 2 \tan^{-1} \left[ \frac{A_2 B}{A_2^2 + B^2 + 1} \right]^{1/2}$$

$$- \tan^{-1} \left[ \frac{A_1 B}{A_1^2 + B^2 + 1} \right]^{1/2},$$

where $A_1 = \tan \theta_{c1}$, $A_2 = \tan \theta_{c2}$, and $B$ is the ratio of the pixel width to the distance between the sample and the screen. This equation was also used for the rheo-light-scattering instrument, because of the similarity of its geometry and that of the OMA. Here, $\theta_{c1}$ and $\theta_{c2}$ are the corrected scattering angles.

For a real CCD detector, the sensitivity of each pixel may be different. The variations in pixel response can be determined by using a collimated, uniform light source, but such a source is difficult to obtain. For this instrument, the variations in pixel sensitivity were neglected. This has the effect of reducing the signal/noise ratio but has no effect on the qualitative aspects of the scattering patterns if the pixel sensitivities vary randomly over the detector.

D. Light-scattering performance

Linearity of the light intensity response of the screen, alignment of the optics, and performance of the correction algorithms for scattering angle and light intensity were inspected to evaluate the performance of the rheo-light-scattering instrument.

1. Linearity of the intensity response of the screen

The optical density (OD) of the neutral density filter is defined by

$$\text{OD} = - \log \left( \frac{I}{I_0} \right),$$

where $I$ and $I_0$ are the transmitted and incident light intensities, respectively. A semilog plot of the transmitted light intensity versus optical density should be linear. If the light intensity response of the screen is also linear, the same relationship must exist for the measured light intensity versus OD. The intensity of the main beam profile was varied by changing the OD of the neutral density filters, and the transmitted light intensities measured at scattering angles of 10° and 20° are plotted against OD in Fig. 3. Both curves were linear over a wide range of light intensity, which indicates that the light intensity on the screen measured by the detector is proportional to the true intensity.
2. Optical alignment of the light-scattering device

The alignment of the optics was assessed by measuring the scattering from a colloid of monodisperse polystyrene (PS) spheres, which should give an isotropic scattering pattern. The scattering pattern would be distorted if the optics were not adequately aligned. Figure 4 shows the scattered intensity profiles measured at various azimuthal angles for a 3.03-μm PS colloid. The superposition of the data from different azimuthal angles indicates that the optics were properly aligned.

3. Angular corrections for the scattering data

The accuracy of the algorithm for the angular correction was evaluated by comparing experimental data with theoretical predictions for the diffraction peak positions of a 118-lines/mm (3000 lines/in.) Ronchi ruling (Max Levy Autograph, Inc.) and for the scattering peaks of a 3.03-μm (standard deviation =0.043 μm) PS colloid (Polysciences Inc.). The expected diffraction-peak positions for the diffraction grating can be calculated from Bragg's law,

\[ d = \frac{n \lambda}{\sin \theta} \]

where \( d \) is the line spacing of the diffraction grating, \( \theta \) the diffraction angle, \( n \) the order of the diffraction peak, and \( \lambda \) the wavelength of the incident light. The scattering profiles of a monodisperse PS colloid are predicted by Mie theory.\(^{29,30}\)

Figure 5 shows the measured light intensity as a function of diffraction angle for the Ronchi ruling along the meridian axis on both sides of the main beam. The first-order diffraction peak on the left side and part of that on the right side were masked by the beamstop. The third-, fifth-, and seventh-order diffraction peaks at 13°, 22.5°, and 32°, respectively, were very close to the theoretical values of 12.96°, 21.94°, and 31.54°. The experimental and predicted scattering profiles for the 3.03-μm PS colloid are given in Fig. 6. The refractive indices of the dispersed phase (polystyrene) and the medium (water) used in the Mie calculation were 1.59 and 1.3333, respectively. The intensities of the predicted profile were arbitrarily scaled to be comparable to the experimental intensities. Although the breadth of the peaks for the experimental and predicted profiles were different, the peak positions were similar. The small differences in the peak positions between the experimental data and the Mie predictions may be due to the uncertainty in the estimated refractive indices of the two phases. It does appear, however, that these results verify the validity of the angular corrections used.

4. Intensity corrections of the scattering data

Figure 7 shows the scattering profiles for the 3.03-μm PS colloid using the different intensity corrections described above. The peak intensities after correction were closer to the values predicted by Mie theory. The intensity tended to be overcorrected only at the higher scattering angles (>35°). This error had little effect on the experiments described in the next section, for which the data of interest was within an angular range of about 5°–25°.

III. RHEO-OPTICAL STUDIES OF POLYMER BLEND PHASE BEHAVIOR

Preliminary experiments to test the performance of the rheo-light-scattering instrument were carried out on a 50/50...
blend (PS800/PIB2300-50) of polystyrene (PS800) (Pressure Chemical Co., $M_n=800$, $M_w/M_n=1.13$) and polyisobutylene (PIB2300) ($M_n=2300$, $M_w/M_n=1.08$, provided by Professor J. P. Kennedy, University of Akron). This composition, which was close to the critical composition, had a cloud point of 67.7 °C. When the blend was cooled from the one-phase region into the two-phase region, 1.6 °C below the quiescent cloud point, the scattered intensity increased and the scattering pattern was isotropic, [Fig. 8(a)]. Upon shearing the sample at a shear rate of 46 s$^{-1}$ the isotropic scattering pattern immediately transformed into a streaklike pattern normal to the flow direction [Fig. 8(b)] and the streak pattern reached steady state within a couple of minutes [Fig. 8(b)–8(d)]. The origin of the streak pattern was most likely elongation of the dispersed phases in the flow direction. A similar shear-induced streak pattern was also observed for a solution of a polystyrene/polybutadiene blend in dioctyl phthalate.

When the PS800/PIB2300-50 blend was cooled to 0.8 °C below the cloud point, held there for 15 min and then sheared, the streak pattern appeared at lower shear rates than when the experiment was run at 1.6 °C below the cloud point. As shown in Fig. 9(a) and 9(b), the streak disappeared when the shear rate exceeded 186 s$^{-1}$ (see Fig. 9), which indicated that homogenization of the blend occurred, at least on the length scale probed by the light-scattering instrument. $>\sim 0.5 \mu m$. Two different phenomena could explain this result: (1) shear-induced mixing or (2) breakup of the dispersed phase to below 0.5 $\mu m$.
FIG. 9. Light-scattering patterns of a PS800/PIB2300-50 blend at 66.9°C after applying shear for 10 min at (a) 46 and (b) 463 s⁻¹.

A demonstration of the simultaneous measurement of stress and scattering results is provided in Fig. 10. Here the system is polyisoprene/polybutadiene (PI/PB), with a cloud point of about 60°C. The figure shows the shear stress (estimated using the Cross-Kaye rule) during the history of the shearing, along with inserts showing the evolution of the scattering patterns.

Further experiments and discussion of the effect of shear on the morphology and phase behavior of polymer blends will be presented in another communication. The brief presentation and discussion given here, however, demonstrate the capabilities and response of the rheo-light-scattering instrument and the relevance of rheo-optical experiments for dynamic studies of multiphase polymer systems.

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