NISTIR 88-3892

In SITU Fluorescence Monitoring of the Viscosities of Particle-Filled Polymers in Flow

A. J. Bur, F. W. Wang, A. Lee, R. E. Lowry, S. C. Roth, and T. K. Trout

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
(Formerly National Bureau of Standards)
Polymers Division
Gaithersburg, MD 20899

November 1988

Annual Report to
The Office of Naval Research
Arlington, VA 22217
Contract No. N00014-86-F-0115
R. S. Miller, Contract Officer

Research supported by SDIO Innovative Science and Technology Office managed by the Office of Naval Research.

75 Years Stimulating America's Progress
1913-1988

NISTIR 88-3892

In SITU Fluorescence Monitoring of the Viscosities of Particle-Filled Polymers in Flow

A. J. Bur, F. W. Wang, A. Lee, R. E. Lowry, S. C. Roth, and T. K. Trout

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
(Formerly National Bureau of Standards)
Polymers Division
Gaithersburg, MD 20899

November 1988

National Bureau of Standards became the
National Institute of Standards and Technology
on August 23, 1988, when the Omnibus Trade and
Competitiveness Act was signed. NIST retains
all NBS functions. Its new programs will encourage
improved use of technology by U.S. industry.

Annual Report to
The Office of Naval Research
Arlington, VA 22217
Contract No. N00014-86-F-0115
R. S. Miller, Contract Officer

Research supported by SDIO Innovative Science and Technology Office managed by the Office of Naval Research.

U.S. DEPARTMENT OF COMMERCE
C. William Verity, Secretary
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
Ernest Ambler, Director

IN SITU FLUORESCENCE MONITORING OF THE VISCOSITIES OF PARTICLE-FILLED POLYMERS IN FLOW

A.J. Bur, F.W. Wang, A. Lee, R.E. Lowry, S.C. Roth, and T.K. Trout

U.S. Department of Commerce
National Institute of Standards and Technology
(formerly National Bureau of Standards)
Polymers Division
Gaithersburg, MD 20899

ABSTRACT

Work during FY88 has focused on three areas: the chemical synthesis of a polymeric chromophore; the design of experiments to measure fluorescence anisotropy and non-Newtonian viscosity as a function of shear rate; the design of a fiber optic velocity sensor; and, measuring the quality-of-mix of a two component material using a fluorescence microscope. Significant results from these areas of work are: (a) a polymeric chromophore, consisting of anthracene covalently bonded to polybutadiene, has been synthesized and characterized by gel permeation chromatography and infrared observations. The number average molecular weight is 12,000 which is above the entanglement molecular weight for polybutadiene; (b) experiments using the polymeric chromophore as a dopant in a Newtonian fluid, very low molecular weight polybutadiene, show that fluorescence anisotropy correlates with the viscosity, i.e. it remains constant as a function of shear rate; and, (c) using a fluorescence microscope, we have measured optical transmittance and near neighbor distances between particles in a matrix/particle mixing experiment and correlated these data with fluorescence intensity fluctuations.

INTRODUCTION

Fluorescence spectroscopy is a tool which is used in many fields of science to obtain both microscopic and macroscopic information.[1] Its application to propellant processing is a relatively new endeavor which requires significant development in order to realize the full potential of the technique. From a large body of fluorescence spectral data in the literature and from work carried out previously in this laboratory, we have conceptually established the methods by which we can use fluorescence spectrometry to measure processing parameters such as the quality of mix of ingredients, non-Newtonian viscosity, molecular orientation, velocity and velocity gradient, flow instabilities such as wall slip, and intersegmental mixing at the molecular level.

The technique involves the excitation of fluorescent chromophores and the subsequent monitoring and analysis of the fluorescence spectra. Since polymer binders are not naturally fluorescent, it is necessary to dope the processing ingredients with a low concentration of fluorescent chromophores which are added as separate entities or chemically bound to the binder. A chromophore is chosen in accordance with its sensitivity to the processing parameter of interest. To monitor several processing parameters, a separate chromophore for each parameter will be employed. Fluorescence spectra can be obtained with extremely low concentrations of chromophore in the binder (10^{-4} to 10^{-6} molar) and, therefore, their presence does not affect the materials properties of the final product.

The ultimate application is to use fluorescence spectroscopy as an on-line non-destructive probe for real-time monitoring of processing parameters. Optical fibers can be employed to transmit and receive optical energy to and from monitoring sites in the processing equipment. Optical energy which is sent to the monitoring site excites nearby chromophores which respond by radiating characteristic spectra. From an analysis of the spectra, processing conditions at the probe site can be determined.

Our research goals over the past year have been: (a) to synthesize a polymeric chromophore which can be used in the fluorescence anisotropy/non-Newtonian viscosity experiments, (b) to complete the development of fluorescence anisotropy equipment and to utilize this equipment to measure fluorescence anisotropy and non-Newtonian viscosity simultaneously, and, (c) to continue the quality-of-mix experiments using a fluorescence microscope to quantify the spatial distribution of particles in a binder/particulate specimen as a function of mixing. In the text below, the results and discussion of each of these work areas will be presented independently.

A. Synthesis of a Polymeric Chromophore

Background

In order to observe polymer materials properties, such as non-Newtonian viscosity, from fluorescence spectroscopy observations, it is necessary to use a chromophore which is covalently bonded to the polymer backbone.[2] Many fluorescent dyes are available commercially, but all are low molecular weight species and do not fit the criteria for our experimental program. The polymeric chromophore which we have designed is derived from a bifunctional anthracene which is covalently bonded to polybutadiene so that the fluorescently active anthracene resides at a central position on the polymer main chain.

Results

The chemical synthesis is shown in Figure 1. Starting with 9,10 dicarboxyl terminated anthracene, which is converted to anthracene dimethanol, we covalently bond the anthracene to a dicarboxyl terminated polybutadiene via an esterification reaction. The number average molecular weight of the starting polybutadiene was 6000. The synthesized product was characterized using gel permeation chromatography (GPC) and infrared analysis. Infrared spectra showed that: (a) the reaction to convert the dicarboxyl anthracene to anthracene dimethanol yielded the desired product; and, (b) the esterification reaction to covalently bond anthracene to the polybutadiene proceeded as planned. The conversion of the dicarboxyl terminated anthracene to dimethanol anthracene was seen in the elimination of the carboxyl absorption at 1280 cm^{-1} and the creation of the C-O stretch of the alcohol. Confirmation of the esterification reaction was obtained from the observation of the creation of the ester carboxyl line at 1734 cm^{-1}.

The GPC trace of the polymeric chromophore is shown is Figure 2 where we have plotted the GPC detector output versus the elution volume. From this plot, we show that the product, polybutadiene + anthracene, has a molecular weight which is approximately twice that of the starting material and its molecular weight distribution is somewhat broader. Analysis of the data shows that the number average molecular weight of the product is approximately 12,000 and its weight average is approximately 24,000. Referring to Figure 1, we conclude that $n \approx 1$, i.e. there is one anthracene per polymer chain and it is positioned in the center of the main chain. The polymeric chromophore is called a labelled polybutadiene and it is being used in the molecular orientation /non-Newtonian viscosity experiments.

B. Fluorescence Anisotropy and Molecular Orientation

Theoretical Background

The relationship between fluorescence anisotropy and molecular orientation has been examined in model development by several authors.[3-5] We consider a fluorescent chromophore, depicted in Figure 3, possessing a molecular axis, M, which is oriented at angles θ and ϕ with respect to the laboratory frame of reference. Here, θ is the azimuthal angle and, for our experiments, z is the direction of flow. The objective of the model calculations is to establish a relationship between average orientation moments, $\overline{\cos^2\theta}$ and $\overline{\cos^4\theta}$, and the measured fluorescence anisotropy. The usual definition of the anisotropy, r, is given as

$$r = \frac{I_{vv} - I_{vh}}{I_t} \qquad (1)$$

where I_{vv} is a measured fluorescence intensity with vertically oriented excitation polarizer and emission analyzer, I_{vh} is the intensity with vertical polarizer and horizontal analyzer, and I_t is the total light intensity. In the text below, we will use other combinations of vertically and horizontally oriented polarized light to define an alternative anisotropy, r'.

We establish a molecular coordinate system, shown in Figure 4, where the molecular axis **M** is directed along the **c** axis and **a** and **e** are the absorption and emission dipoles at angles α and ϵ with respect to **M**. In general, α and ϵ are non-zero and unequal, but for anthracene, the chromophore of interest here,

$\alpha = 0$ and $\epsilon \neq 0$. The relationship between observations in the laboratory frame of reference and the molecular frame of reference is obtained by making coordinate transformations which project **a** and/or **e** onto the laboratory frame of reference. The fluorescence light intensities are determined in accordance with the directions of the polarizer and analyzer vectors **P** and **A**.

Following the development of Chapoy and DuPre,[4] one assumes that the orientation distribution function of the chromophores, $f(\theta)$, can be expressed as a sum of Legendre polynomials which, in general, depend on θ and ϕ, but for the case of uniaxial flow along the z direction, we assume axial symmetry so that the distribution is independent of ϕ. Since $f(\theta) = f(-\theta)$, only the even polynomial terms are present. The normalized distribution function is expressed as

$$\int_{-1}^{1} f(\theta) d(\cos\theta) = 1. \qquad (2)$$

The normalized fluorescence intensity is given by

$$I_{ij} = \frac{1}{2\pi} \int_0^{2\pi} \int_0^{\pi} M_{ai}^2 M_{ej}^2 f(\theta) \sin\theta d\theta d\phi \qquad (3)$$

where I_{ij} is the emitted fluorescence intensity which results from an excitation light source polarized along the laboratory i axis and which passes through a polarization analyzer oriented in the direction of the laboratory j axis. M_{ai}^2 and M_{ej}^2 are the squares of the absorption and emission vectors which have been projected onto the laboratory axes i and j respectively via a coordinate transformation matrix, and $f(\theta)$ is the angular distribution function. We have

$$M_{a_i}^{2}{}^{2} = (a \cdot O \cdot P_i)^2 \qquad (4)$$

and

$$M_{e_j}^{2}{}^{2} = (e \cdot O \cdot A_j)^2 \qquad (5)$$

where O is the transformation matrix,

$$O = \begin{bmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \end{bmatrix} \qquad (6)$$

Equations 3 through 6 express the physical sequence of events for light absorption and fluorescence emission. The absorption vector is brought into coincidence with a component of the polarized excitation light via the transformation operation of equation (4) and the reverse occurs during emission via equation (5).

The integrations of equation (3) yield a 3x3 matrix whose components are light intensities for various combinations of $\mathbf{P}_i$ and $\mathbf{A}_j$. Having evaluated the matrix, one can then calculate anisotropies in accordance with equation (1) where I_{vv} becomes I_{11}, I_{22} or I_{33} and I_{vh} becomes one of the off-diagonal terms. For example, when $\alpha = 0$ and $\epsilon = 0$, i.e. absorption and emission dipoles lie along the direction **M**, then vertically oriented light will be absorbed in proportion to $\cos^2\theta$. The emission, which is viewed through a vertical analyzer, is also proportional to $\cos^2\theta$. Equation (3) becomes an integral over all space of $\cos^4\theta$ weighted by the orientation function $f(\theta)$ resulting in $I_{33} = \overline{\cos^4\theta}$.

For anthracene, $\alpha = 0$, $\epsilon \neq 0$, and $\delta \neq 0$, where δ has been defined in Figure 4, Chapoy and DuPre have evaluated the following matrix:[4]

$$\mathbf{I} = \begin{pmatrix} \frac{3}{8}\cos^2\delta\,\overline{\sin^4\theta} + \frac{1}{16}\sin^2\delta\,(3\,\overline{\sin^2\theta\,\cos^2\theta} + \overline{\sin^2\theta}) & \frac{1}{8}\cos^2\delta\,\overline{\sin^4\theta} + \frac{1}{16}\sin^2\delta\,(\overline{\sin^2\theta\,\cos^2\theta} + 3\,\overline{\sin^2\theta}) & \frac{1}{2}\cos^2\delta\,\overline{\sin^2\theta\,\cos^2\theta} + \frac{1}{4}\sin^2\delta\,\overline{\sin^4\theta} \\ \frac{1}{8}\cos^2\delta\,\overline{\sin^4\theta} + \frac{1}{16}\sin^2\delta\,(\overline{\sin^2\theta\,\cos^2\theta} + 3\,\overline{\sin^2\theta}) & \frac{3}{8}\cos^2\delta\,\overline{\sin^4\theta} + \frac{1}{16}\sin^2\delta\,(3\,\overline{\sin^2\theta\,\cos^2\theta} + \overline{\sin^2\theta}) & \frac{1}{2}\cos^2\delta\,\overline{\sin^2\theta\,\cos^2\theta} + \frac{1}{4}\sin^2\delta\,\overline{\sin^4\theta} \\ \frac{1}{2}\cos^2\delta\,\overline{\sin^2\theta\,\cos^2\theta} + \frac{1}{4}\sin^2\delta\,(\overline{\cos^2\theta} + \overline{\cos^4\theta}) & \frac{1}{2}\cos^2\delta\,\overline{\sin^2\theta\,\cos^2\theta} + \frac{1}{4}\sin^2\delta\,(\overline{\cos^2\theta} + \overline{\cos^4\theta}) & \cos^2\delta\,\overline{\cos^4\theta} + \frac{1}{2}\sin^2\delta\,\overline{\sin^2\theta\,\cos^2\theta} \end{pmatrix} \tag{7}$$

We note that the matrix contains orientation moments $\cos^2\theta$ and $\cos^4\theta$ as well as the term $\cos^2\delta$ which is a molecular property and does not depend on the orientation. The value of $\cos^2\delta$ is obtained from a separate experiment; its value for anthracene is 0.733.[6] A separate measurement of $\cos^2\delta$ for the labelled polybutadiene will be carried out in the future. In general, two independent measurements of anisotropy must be made in order to calculate $\overline{\cos^2\theta}$ and $\overline{\cos^4\theta}$.

In practice we will use a single optical fiber to excite and receive the fluorescence. The design consists of an optical fiber which is inserted into the wall of a processing machine flush with the inside surface and used to probe the fluorescence in the near neighborhood. Figure 5 is a schematic representation of the physics of the situation, i.e. excitation light polarized in the z or x direction propagates in the positive y direction and emission is observed along the y direction with the analyzer oriented in the z or x directions. Anisotropies r and r′ are

$$r = \frac{I_{zz} - I_{zx}}{I_{zz} + 2I_{zx}} = \frac{I_{33} - I_{31}}{I_{33} + 2I_{31}}, \tag{8}$$

and

$$r' = \frac{I_{xx} - I_{xz}}{I_{xx} + 2I_{xz}} = \frac{I_{11} - I_{13}}{I_{11} + 2I_{13}}, \qquad (9)$$

where the denominator in the above equations is the total light intensity. By substituting the elements of the matrix of equation (7) into equations (8) and (9), we obtain

$$r = \frac{3\overline{\cos^4\theta} - \overline{\cos^2\theta}}{2\overline{\cos^2\theta}} \cdot \frac{3\cos^2\delta - 1}{2}, \qquad (10)$$

and

$$r' = \frac{6 - 20\overline{\cos^2\theta} + 14\overline{\cos^4\theta}}{(9 - 14\overline{\cos^2\theta} + 5\overline{\cos^4\theta}) - (3 - 18\overline{\cos^2\theta} + 15\overline{\cos^4\theta})\cos^2\delta} \cdot \frac{3\cos^2\delta - 1}{2} \qquad (11)$$

In deriving the above equations we have made the assumption that the chromophore rotational relaxation time, τ_r, is much longer than the fluorescence decay time, τ_d. This assumption must be checked experimentally. We note, however, that we are incorporating long rotational relaxation times into the relaxation behavior of the chromophore by covalently bonding it to the main chain of polybutadiene. Such an effect has been observed by Monerie and co-workers who found that, when anthracene was bonded to isoprene, its τ_r increased by two orders of magnitude and that $\tau_r \gg \tau_d$.[6] In general, when the rotational relaxation is taken into account, the expression for anisotropy is

$$r = F(\cos^2\theta, \cos^4\theta) \cdot G(\cos^2\delta) \cdot (\tau_d/\tau_r + 1)^{-1}, \qquad (12)$$

where F expresses the effect of orientation, G expresses the dependence on the angle δ, and the last term expresses the effect of the rotational relaxation. If $\tau_r \gg \tau_d$, then $(\tau_d/\tau_r + 1)^{-1} \simeq 1$. Based on the results of Monerie, we will neglect rotational relaxation effects, however, we intend to verify this assumption in future experiments.

Experimental Procedure

The experimental design consists of using a capillary flow apparatus and a Weissenberg rheometer to make simultaneous measurements of non-Newtonian viscosity and fluorescence anisotropy as a function of shear rate. The capillary flow apparatus, which is diagrammed schematically in Figure 6, has been incorporated into a commercial fluorimeter. It consists of a glass reservoir vessel with a capacity of 500 cm^3 which sits at the head of a vertically oriented capillary. The capillary extends through the sample chamber of the fluorimeter and is connected to a collection vessel at the bottom end. Capillary diameters of 1 or 2mm are used with a length of approximately 25 cm. Both are made of borosilicate glass which transmits excitation light with wavelengths as short as 350 nm. The reservoir at the head of the capillary is surrounded by a brass pressure vessel which can be pressurized with nitrogen gas up to 7×10^5 Pa (100 psi). The pressure is measured using a resistance type pressure transducer. The shear rate experienced by the liquid in the capillary is varied by changing the pressure. We use the classical equations of capillary flow for a Newtonian fluid:

$$\eta = \frac{\pi R^4}{8Q} \cdot \frac{\Delta P}{L} \qquad (13)$$

and

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \qquad (14)$$

where η is the viscosity, R is the radius of the capillary, ΔP is the pressure difference across the ends of the capillary, Q is the flow rate, L is the length of the capillary, and $\dot{\gamma}$ is the shear rate. Q, the flow rate of material through the capillary, is obtained by measuring the amount of material eluted from the capillary in a given time period.

A Weissenberg cone and plate rheometer is also being used in this study. This equipment has been instrumented so that fluorescence anisotropy measurements can be made simultaneously with the rheological measurements. The apparatus is depicted in Figure 7. Excitation light energy from an argon ion laser is directed to the specimen between the cone and plate. The fluorescence spectra is collected at ninety degrees by an optical fiber which sits below the optically transparent polymethylmethacrylate plate. In the experiment, the cone rotates but the plate remains stationary.

In our initial experiments, the capillary apparatus was used to measure viscosity and fluorescence anisotropy of a low molecular weight polybutadiene doped with the labelled polybutadiene at a concentration of 10^{-5} molar. The number average molecular weight of the polybutadiene is 2800 while the number average molecular weight of the labelled polybutadiene is 12,000. The low molecular weight of the specimen, 2800, is below the entanglement molecular weight, 6000, for polybutadiene so that the rheological polymeric effects should not be observed. This experiment was carried out in order to obtain a frame of reference for the behavior of a Newtonian material before proceeding with the non-Newtonian material.

The non-Newtonian polymer which we are studying is also polybutadiene but with a number average molecular weight of 24,000, i.e., well above the entanglement value. This specimen was also doped with the labelled polybutadiene at a concentration of 10^{-5} molar.

Results

Figure 8 shows a fluorescence spectrum for the anthracene labelled polybutadiene as a dopant in the low molecular weight (M_n = 2800) polybutadiene. This spectrum was obtained for an excitation wave length of 398 nm using the commercial fluorimeter. The anisotropy measurements, calculated according to equation (1), were made over a wavelength range from 420 to 470 nm and for a pressure range from 0 to 50 psi. The viscosity and shear rate were obtained using equations (13) and (14).

Figure 9 shows viscosity and fluorescence anisotropy as a function of shear rate for the doped low molecular weight (M_n = 2800) polybutadiene. We note that this material is Newtonian in its behavior over the range of shear rates from 20 to 70 s^{-1}. The anisotropy, which is also constant, correlates with the Newtonian behavior. Our interpretation of these data is that, within the limits of uncertainty of our measurements, molecular orientation is not seen in the fluorescence anisotropy for Newtonian polymer melts. Since the molecular weight of this specimen is below the entanglement value, we picture the molecule tumbling in the velocity field of the capillary, but, on the average, the molecule remains unextended.

The viscosity and fluorescence anisotropy for the higher molecular weight polybutadiene, M_n = 24,000, are being measured using the Weissenberg rheometer. These experiments, which are incomplete at this time, will be the subject of a future publication.

C. Mixing Experiments

Previous Work

In previously reported experiments on mixing, we established the feasibility of using fluorescence intensity observations to monitor the quality of mix of ingredients in a two component material.[7,8] The components used in the mixing experiments were a polybutadiene based polymer called PBAN, which was doped with a fluorophore, coumarin 30, and aluminum oxide particulate material. The mixing was carried out in a small laboratory mixer with a glass wall to facilitate light excitation and emission. We observed that the fluorescence intensity, which was monitored as a function of time at a fixed position in the mixer, became constant as mixing proceeded. These data are shown in Figure 10. Our hypothesis is that uniform mixing is achieved when fluorescence intensity is constant with time. Qualitative support for this hypothesis was obtained from micrograph observations of the well mixed material in an optical transmission microscope.[7,8]

Fluorescence Microscope Experiments

In order to establish quantitative support for the mixing hypothesis, we have continued experiments on fluorescence monitoring of mixing using an epifluorescence microscope to observe fluorescence intensity, optical transmittance, and near neighbor distances in poor and well mixed materials. The microscope, optics, and photomultiplier assemblies are products of Carl Zeiss GMBH.[9] The instrumented is fitted with a mercury arc lamp source, photomultiplier detector, grating monochromators, and a camera. The excitation wavelength was set at 366 nm (for dimethyl anthracene) and emission was observed at 429 nm. The precision in the fluorescence intensity measurement was found to be ±1.5% for these experiments.

Near Neighbor Distance Measurements

The specimen materials for these experiments were a low molecular weight polybutadiene (M_n = 2800) doped with dimethylanthracene (8×10^{-4} molar concentration)-and copper spherical particles whose average radius was 41 ± 8 μm. The copper particles were isolated from a larger batch by passing them through sieve cloth; this procedure confined their diameters to within 74 μm and 125 μm. Two specimens, one poorly mixed and the other well mixed, were prepared from copper and polybutadiene ingredients which combined to yield a mixture 83% by weight or 32% by volume copper. Both specimens were placed on microscope slides, covered with a glass slip, and pressed into a two dimensional mixture so that all of the copper particles resided in the plane between the slide and cover slip. In this configuration, the specimen thickness equals approximately the diameter of the largest copper spheres.

Eight distinct views of each specimen were obtained by randomly moving the microscope objective from one position to another. At each position, a photograph was taken and the fluorescence intensity was measured. A typical photograph of the well mixed specimen is shown in Figure 11. The central circle on the photograph, whose diameter is 281 μm, defines the region from which the fluorescence intensity was measured. Near neighbor distances were measured by isolating the central particle in the region and observing the distance to the closest six particles for comparison to a hexagonal array and to the closest four particles for comparison to a face centered square array.

The near neighbor distances and fluorescence intensity data for the mixed and unmixed specimens are presented in Tables I and II, respectively. The calculated average distances, $<d_{nn}>$, are for the nearest six particles except for two views of the unmixed specimen for which too few particles were present. The unmixed specimen is distinguished from the mixed specimen by larger fluctuations in fluorescence intensity as expressed in the standard deviations:

$$\text{Average } I_f \text{ (mixed)} = 39.7 \pm 5.7$$
$$\text{Average } I_f \text{ (unmixed)} = 39.1 \pm 17.1.$$

The overall average of near neighbor distances is:

$$<d_{nn}> \text{ (mixed)} = 86.0 \pm 16\ \mu\text{m}$$
$$<d_{nn}> \text{ (unmixed)} = 121.5 \pm 37\ \mu\text{m}.$$

These numbers demonstrate the correlation between fluctuations in I_f and uniformity in near neighbor distance and establishes quantitative support for the fluorescence/quality of mixing hypothesis. We note that $<d_{nn}>$ for the mixed specimen is nearly equal to the average diameter of the spheres, $2r = 82 \pm 16\ \mu\text{m}$, and interpret this to mean that the two dimensional specimen is more closely packed than the volume concentration would indicate (see below). The magnitude of the standard deviation for $<d_{nn}>$, $\pm 16\ \mu\text{m}$, is partially generated by the distribution in particle size, especially for the case when the particles are closely packed.

We can analyze the well mixed specimen by considering that the particles are positioned in two dimensional space in hexagonal or in face centered square arrays. For the two dimensional hexagonal array whose thickness is the diameter of the particle, the relationship between the near neighbor distance, d_h, and v_c, the volume concentration of particles, is

$$d_h = \left[\frac{4\pi r^2}{3\sqrt{3}v_c}\right]^{1/2} . \qquad (15)$$

For $r = 41$ µm and $v_c = 0.32$, we obtain $d_h = 113$ µm which is 31% larger than the overall average near neighbor distance of 86 µm. For the face centered square array, the near neighbor distance, d_{fs}, is

$$d_{fs} = \left[\frac{2\pi r^2}{3v_c}\right]^{1/2} . \qquad (16)$$

Again, using $r = 41$ µm and $v_c = 0.32$, we calculate $d_{fs} = 105$ µm which is 32% greater than the overall average of the closest four near neighbors, 79.6 µm, as calculated from the data of Table I. The discrepancy between our observations and the calculated near neighbor distance from the assumed arrays originates from the method by which the specimens were prepared. When the three dimensional specimen is squeezed into two dimensions, particle impingement and displacement must occur as the specimen is deformed into its final shape. Also, a lateral displacement of liquid, which can flow passed and around relatively stationary particles, will result in a smaller near neighbor distance in two dimensions than that which existed in three dimensions. In this case, the procedural steps of mounting the specimen on the microscope slide are viewed as part of the mixing process which yielded the well mixed specimen which we examined.

Optical Transmittance Measurements

Optical transmittance measurements were made for the purpose of establishing a correlation with the fluorescence intensity of unmixed and mixed specimens. The fluorescence microscope, described above, was also used in these experiments. The experimental procedure consisted of focusing the microscope on a section of the specimen, measuring the fluorescence intensity at 429 nm (emission for dimethylanthracene), and measuring the optical transmission intensity at 520 nm.

The materials used for these mixtures were the low molecular weight polybutadiene (M_n = 2800) and aluminum oxide particles with average grain size of 9.5 μm. The polybutadiene was doped with dimethylanthracene to a concentration of 8 x 10^{-4} molar. The samples were prepared from a combination of the two components for which the weight concentration of aluminum oxide was 42% and the volume concentration was 24%. Two specimens were examined, a non-mixed specimen and a well mixed specimen. Each was placed onto a microscope slide and covered with a glass cover slip. The diameter of the field of view was 70 μm and the thickness was held constant at 465 μm throughout the experiment. Fifteen unique views of each specimen were obtained by randomly moving the microscope objective from one position to another. At each position, the fluorescence intensity and optical transmission was measured. The data, shown in Figure 12, display the correlation which exists between the optical transmittance and the fluorescence intensity. Data from the unmixed specimen span a wide range of variation in both parameters, whereas the data from the mixed specimen occupy a confined position on the plot. Since the optical transmittance is inversely related to the number of particles in the field of view, these data demonstrate that the fifteen views of the mixed specimen contained approximately an equal number of aluminum oxide particles in this microscopic volume, the definition of a well mixed material. The concurrent uniformity of fluorescence intensity and optical transmittance for the mixed specimen provides rigorous support for the hypothesis that constant fluorescence intensity over spatial and/or temporal sampling of a material is evidence that uniform mixing has been achieved.

SUMMARY

The work described here falls into three categories of activity: the synthesis of a polymeric chromophore; the measurement of fluorescence anisotropy and molecular orientation; and, the mixing experiments to establish quantitative support for the fluorescence intensity/quality of mixing hypothesis. We have achieved significant results in each of these work areas. The polymeric chromophore has been synthesized by covalently bonding fluorescently active anthracene to polybutadiene. This new chromophore is presently being used in experiments to measure molecular orientation and to correlate these measurements with non-Newtonian viscosity. The equipment and instrumentation for the fluorescence anisotropy experiments is now in operation. The mixing experiments involved measurements of near neighbor distances and optical transmittance on two component mixtures and the correlation of these data with fluorescence intensity observations. The results of the mixing experiments give quantitative support to the hypothesis that constant fluorescence intensity with time indicates that uniform mixing has been achieved.

TABLE I

Near Neighbor Distances for the Well Mixed Specimen

Sample	d1	d2	d3	d4	d5	d6	$<d_{nn}>$[a]	S.D. d	PMT[b]
mixed#1	107	90.9	88.6	121	114	94.9	103	13.3	45.19
mixed#2	72.0	85.7	62.3	84.6	85.1	85.1	79.1	9.78	31.53
mixed#3	91.4	77.1	98.9	97.1	74.3	103	90.3	11.9	37.62
mixed#4	73.1	97.1	68.0	68.6	81.1	79.4	77.9	9.9	40.06
mixed#5	68.6	62.9	89.1	60.0	103	103	81.1	19.8	47.89
mixed#6	38.9	86.9	102	71.4	57.1	85.1	73.6	22.8	32.23
mixed#7	103	94.3	79.4	102	103	100	97.0	9.2	41.41
mixed#8	88.6	90.9	74.3	70.9	97.7	91.4	85.6	10.6	41.46

[a] Distances measured in μm.

[b] PMT (Photomultiplier Tube) readings are in millivolts.

TABLE II

Near Neighbor Distances for the Non-Mixed Specimen[a]

Sample	d1	d2	d3	d4	d5	d6	$<d_{nn}>$[b]	S.D. d	PMT[c]
non-mix#1	88.6	88.6	85.7	120	127	117	104	18.8	17.22
non-mix#2	114	94.9	117	40.0	125	35.4	87.7	40.0	18.76
non-mix#3	115	135	120	103	114	106	116	11.4	39.20
non-mix#4	111	121	92.0	135	97.8	137	116	18.8	41.16
non-mix#5	154	103	90.9	131	133	169	130	29.5	26.13
non-mix#6	>234	225	202	>234	>234	>234	>234	-	58.20
non-mix#7	>234	>234	>234	>234	>234	>234	>234	-	60.36
non-mix#8	94.3	187	165	154	148	122	145	32.7	51.70

[a] Distances designated as >234 indicate that no near neighbor was within the field of view.

[b] Distances measured in μm.

[c] PMT (Photomultiplier Tube) readings are in millivolts.

References

1. Principles of Fluorescence Spectroscopy, by J. R. Lakowicz, Plenum Press, New York, 1983.

2. Polymer Photophysics, edited by D. Philips, Chapman and Hall, New York, 1985.

3. J. H. Nobbs, D. I. Bower, I. M. Ward and D. Patterson, Polymer, 15, 287 (1974).

4. L. L. Chapoy and D. B. DuPre, in Methods of Experimental Physics, Vol. 16A, Edited by R. A. Fava, Academic Press, New York, 1980.

5. J. P. Jarry and L. Monnerie, J. Poly. Sci., Poly. Phys. 16, 443 (1978).

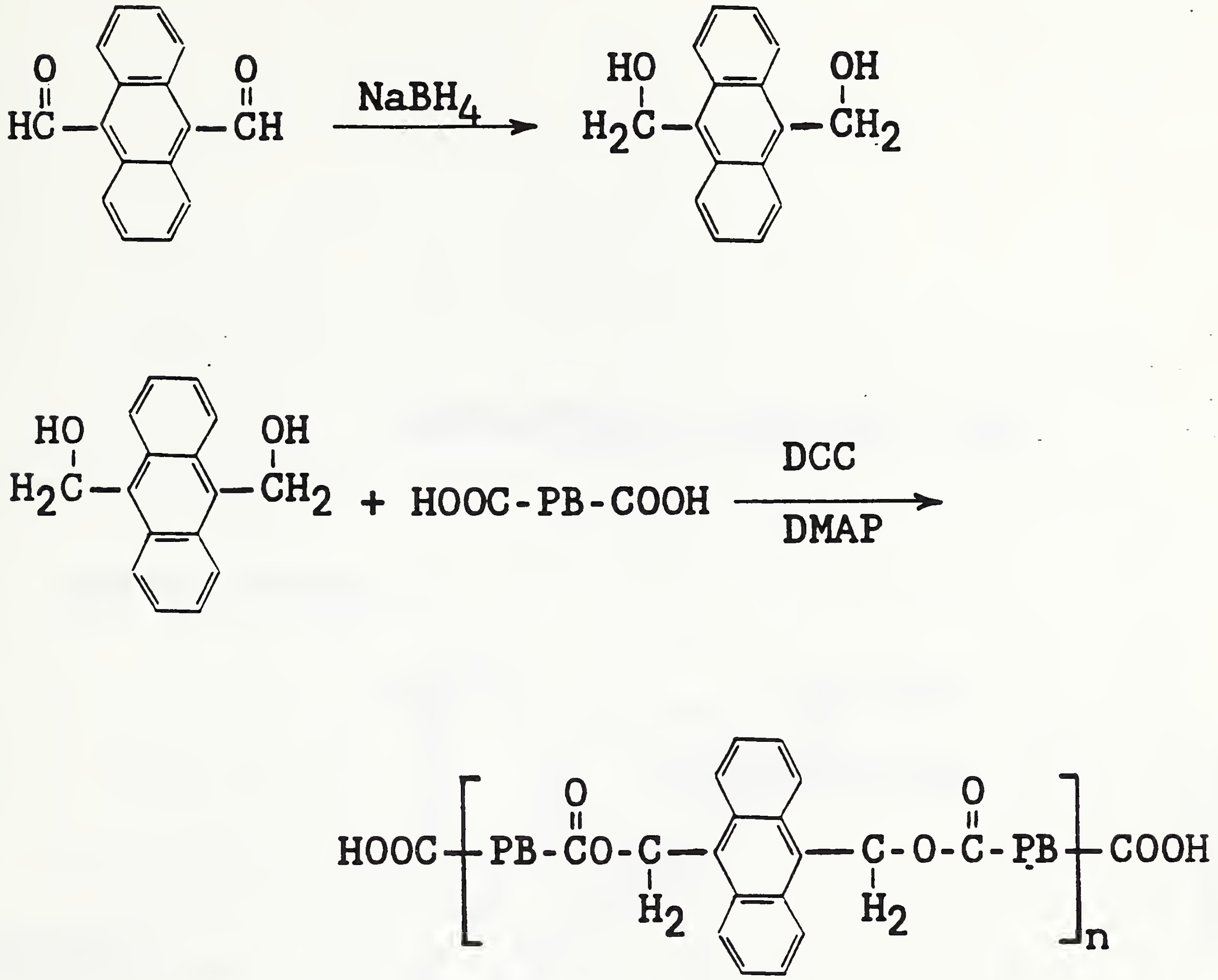
6. J. P. Jarry and L. Monnerie, Macromolecules, 12, 927 (1979).

7. A. J. Bur, F. W. Wang, and R. E. Lowry, Proc. Soc. Plastics Eng., Annual Tech. Meeting, April, 1988.

8. "In Situ Fluorescence Monitoring of the Viscosities of Particle-Filled Polymers in Flow", by A. J. Bur, F. W. Wang, and R. E. Dehl, NBS Internal Report NBSIR 88-3694, National Bureau of Standards, Gaithersburg, MD 20899.

9. Identification of a commercial product is made only to facilitate experimental reproducibility and to adequately describe experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experimental procedure.

SYNTHESIS OF POLYMERIC CHROMOPHORE



PB - Polybutadiene (M_w = 12,000)
$NaBH_4$ - sodium borohydride
DCC - dicyclohexylcarbodiimide
DMAP - dimethylaminopyridine

Figure 1. The chemical synthesis for labelling carboxyl terminated polybutadiene with anthracene is shown. It is a two step procedure: first, we convert the 9,10 dicarboxylanthracene to anthracene dimethanol, and second, covalently bond this with the polybutadiene via an esterification reaction.

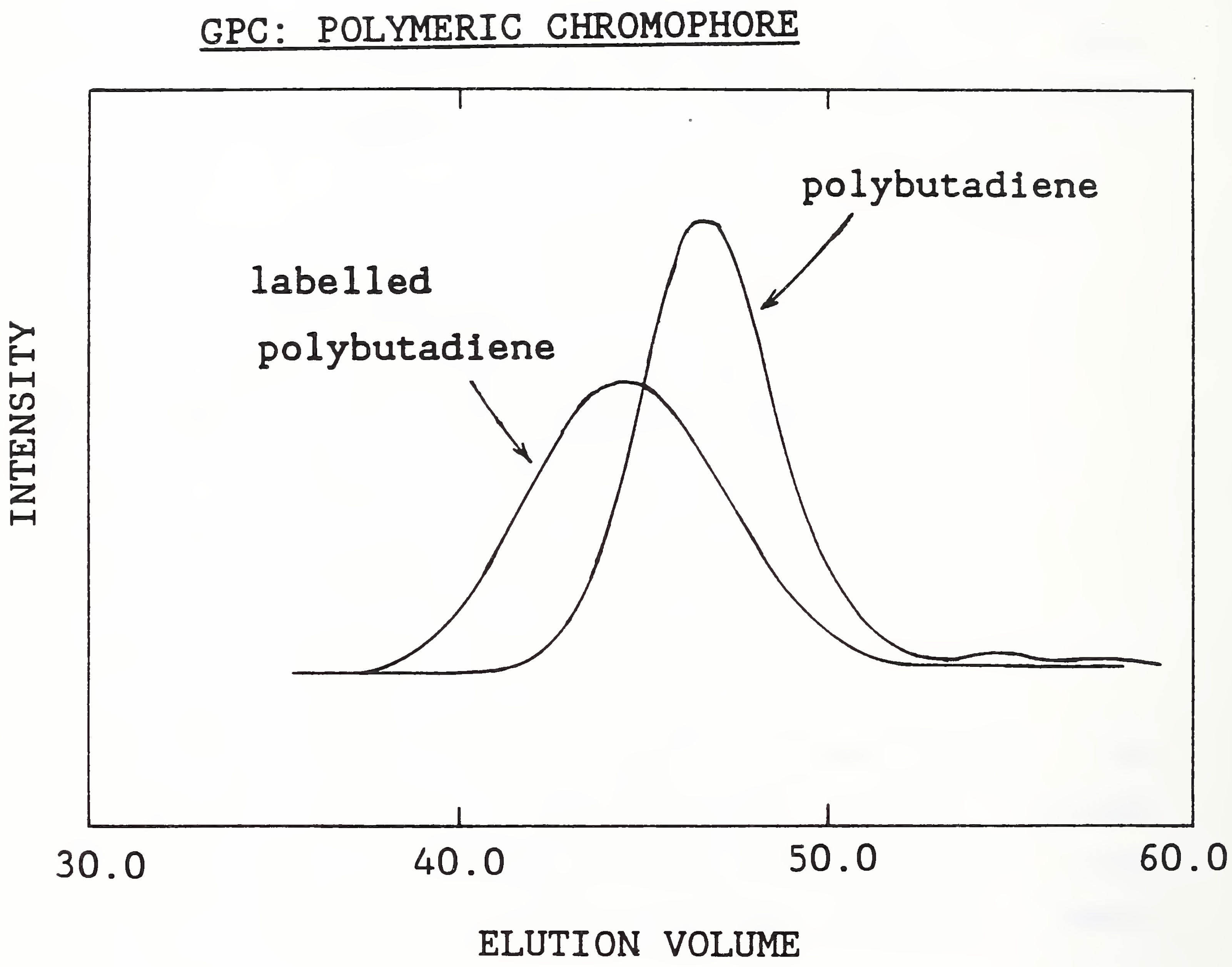


Figure 2. A gel permeation chromatograph is shown for the labelled polybutadiene and for the starting polybutadiene material. The labelled polybutadiene has a molecular weight approximately two times that of the starting material.

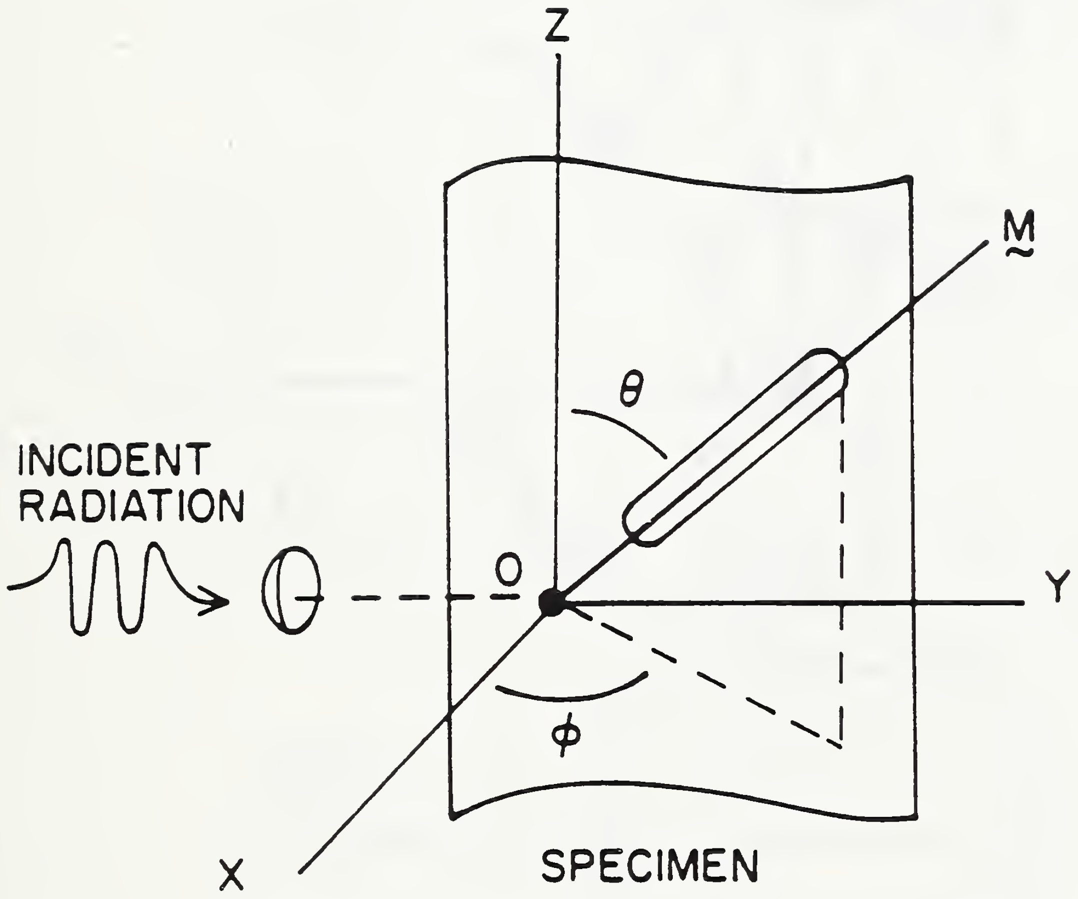


Figure 3. The laboratory coordinate system with the molecular axis of the chromophore, M, is shown.

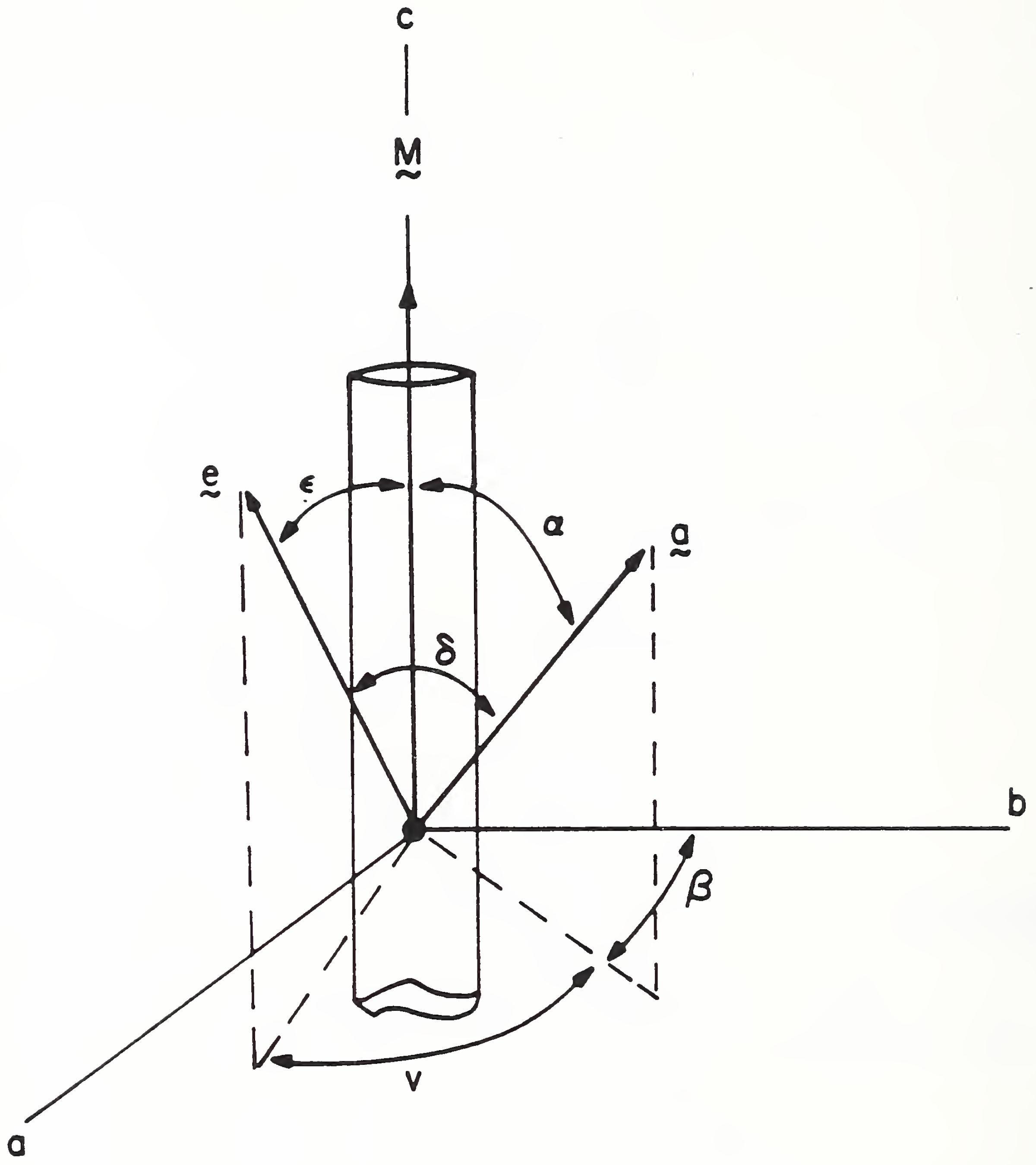
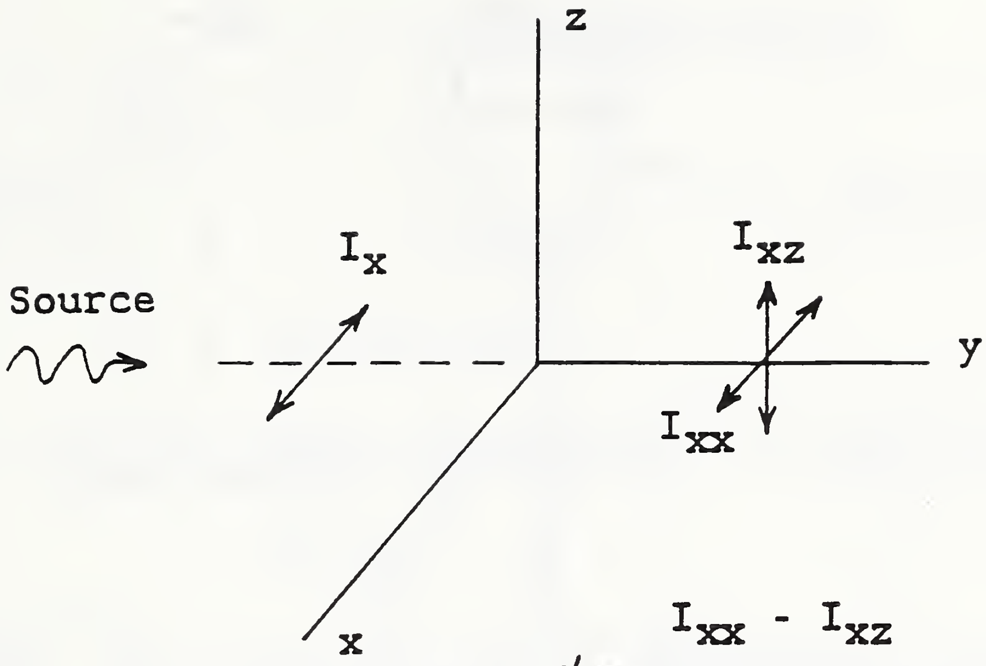
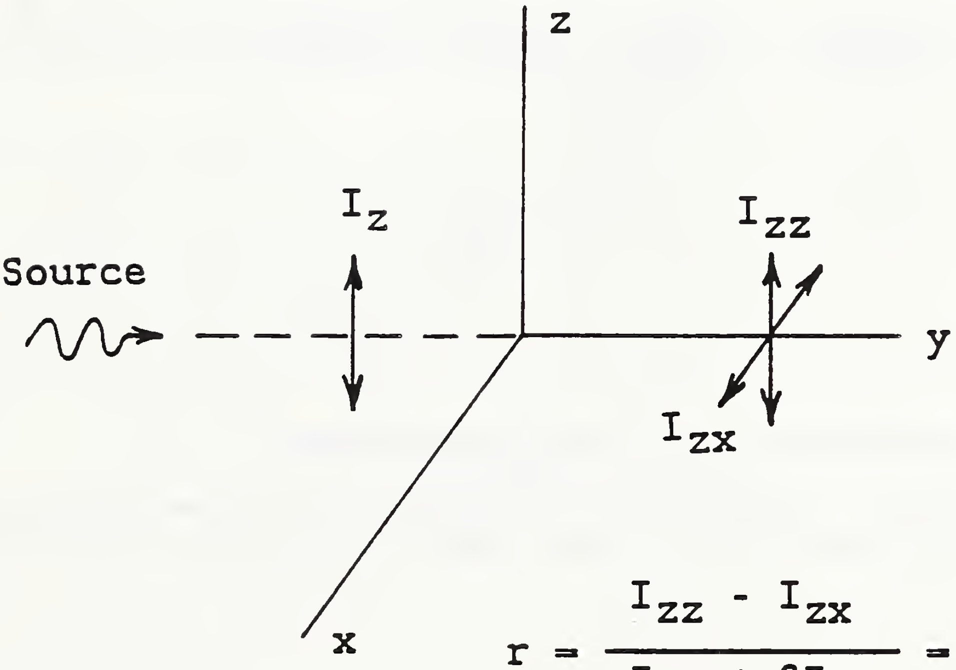


Figure 4. The molecular coordinate system with absorption and emission dipoles, a and e, is shown. a and e are at angles α and δ with respect to M.



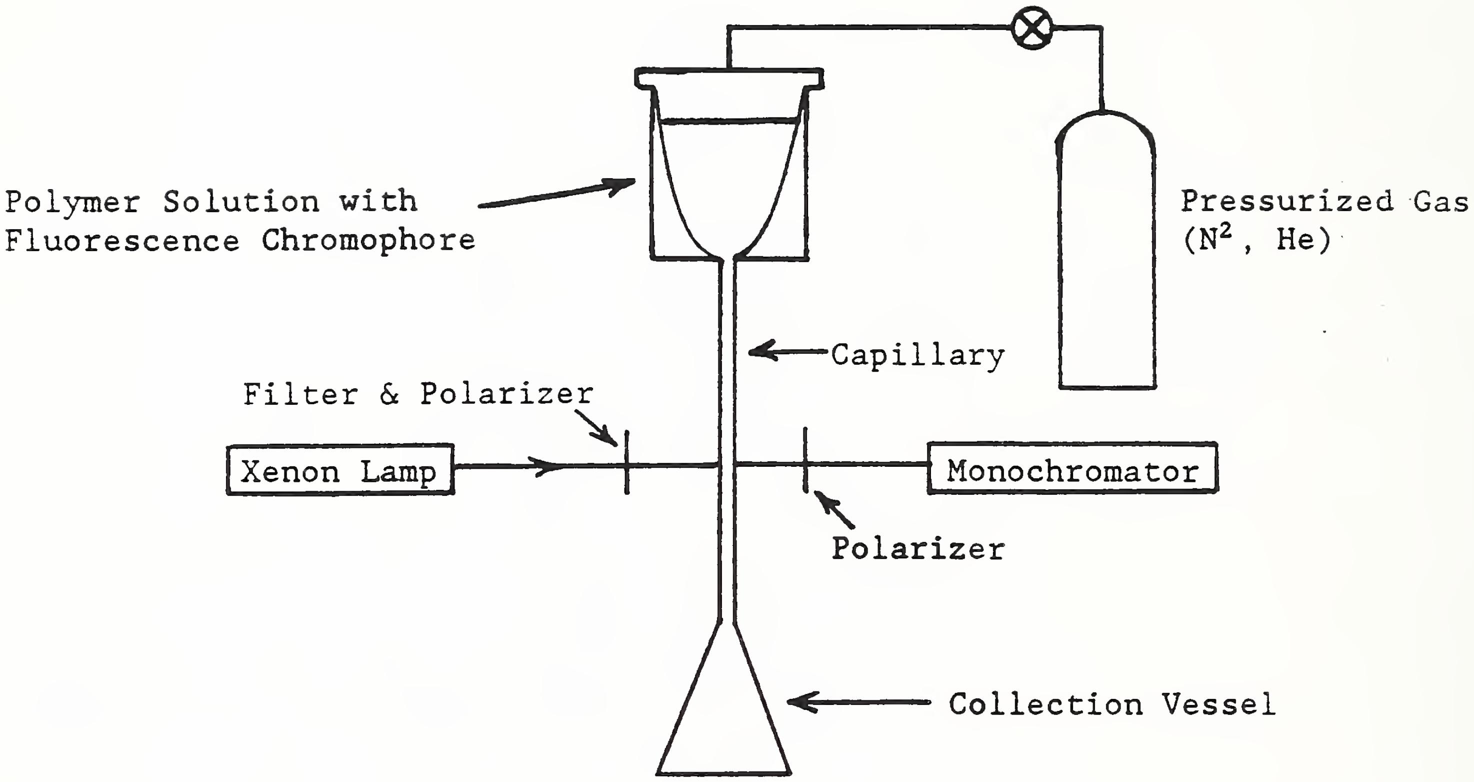
$$r' = \frac{I_{xx} - I_{xz}}{I_{xx} + I_{xz}} = \frac{I_{11} - I_{13}}{I_{11} + 2I_{13}}$$



$$r = \frac{I_{zz} - I_{zx}}{I_{zz} + 2I_{zx}} = \frac{I_{33} - I_{31}}{I_{33} + 2I_{31}}$$

Figure 5. The definitions of r and r′ are schematically portrayed. Here, I_{ij} refers to the matrix element of equation (7).

CAPILLARY FLOW EXPERIMENT



Measurement: Fluorescence Anisotropy as a Function of Shear Rate or Applied Pressure.

Figure 6. A schematic diagram of the capillary flow apparatus is shown. In practice, the excitation and emission light beams are at 90° with respect to each other.

RHEOMETER OPTICS

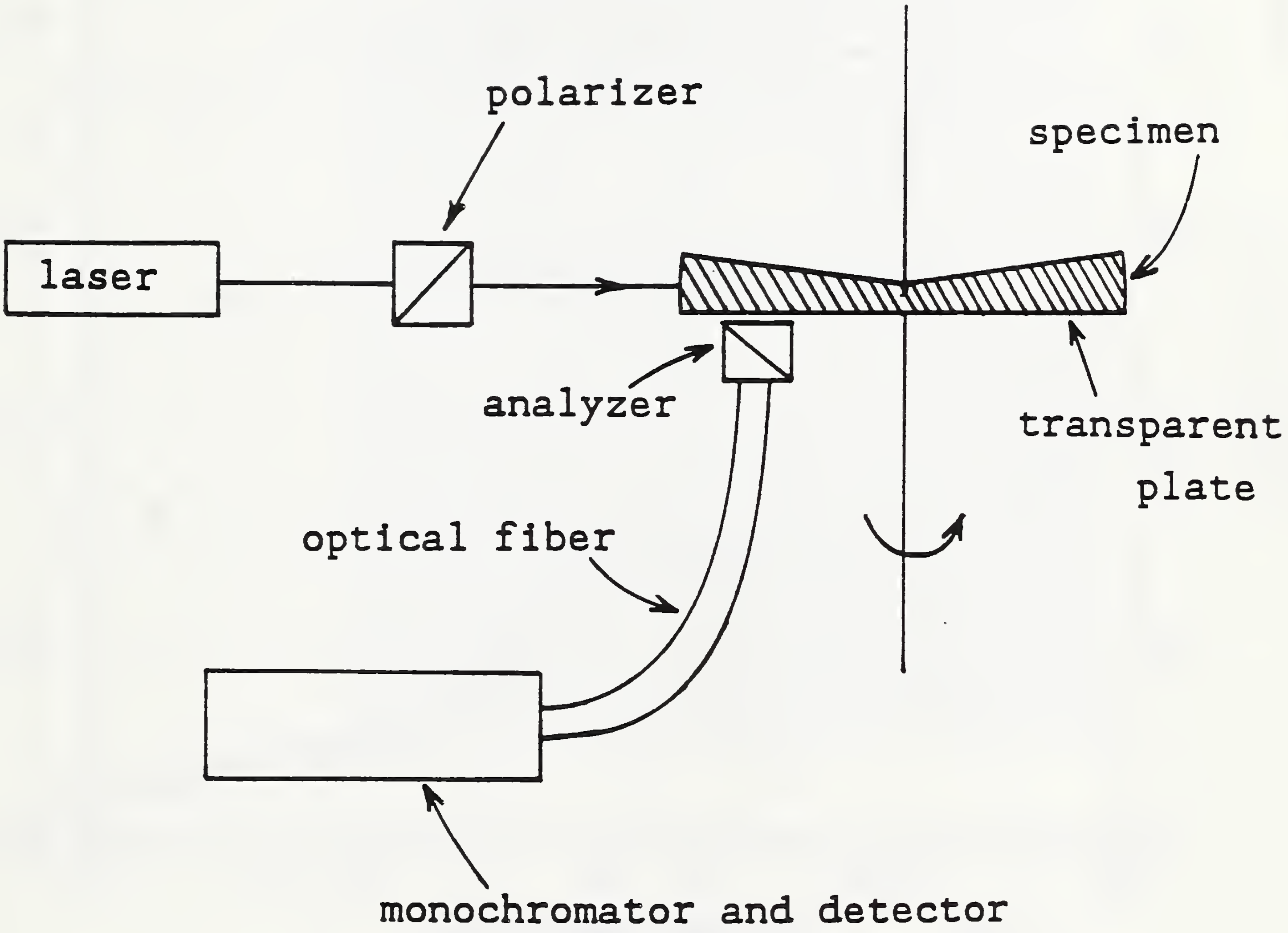


Figure 7. A schematic diagram of the optically instrumented Weissenberg rheometer is shown.

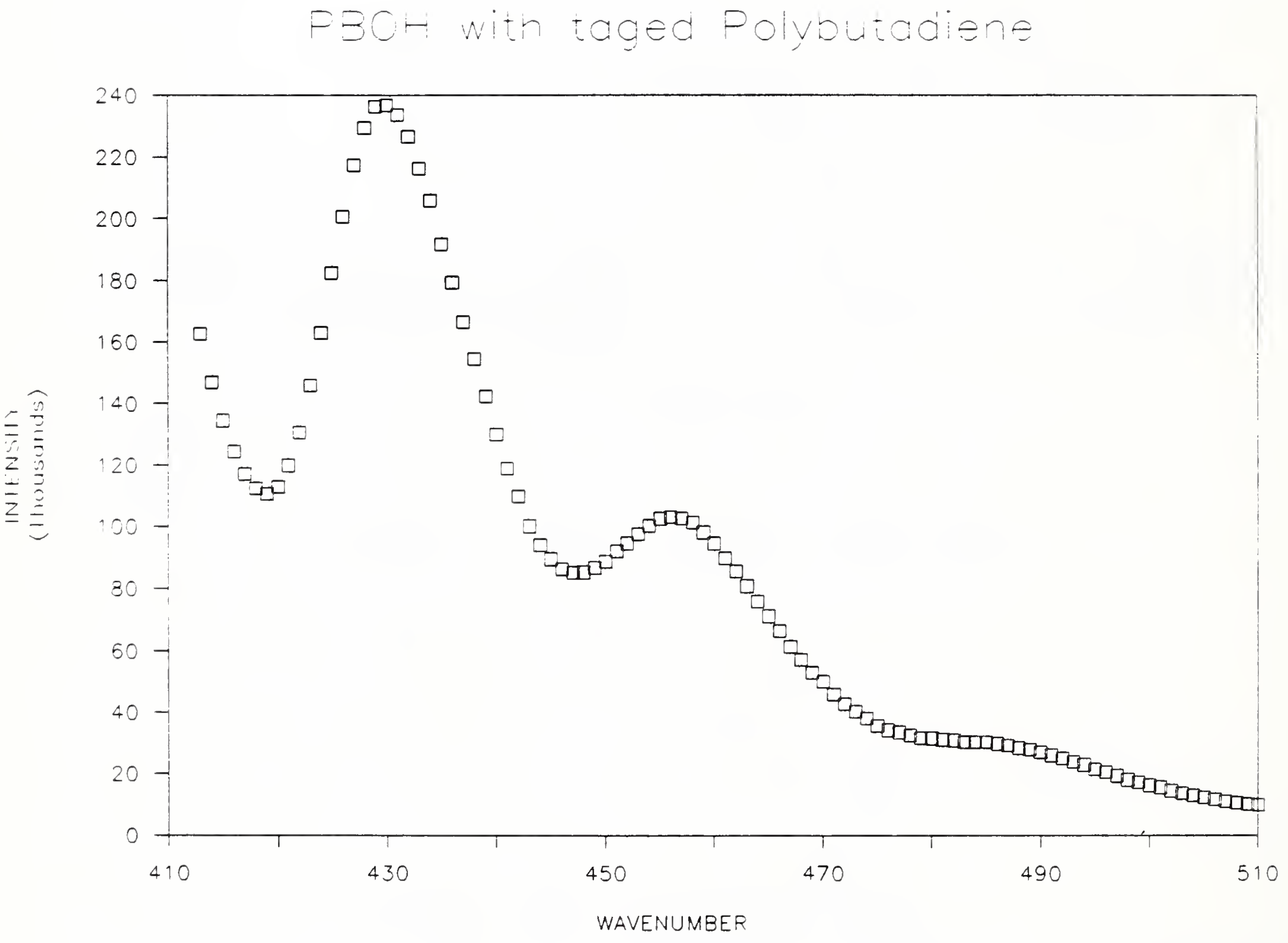


Figure 8. The fluorescence spectrum for the labelled polybutadiene doped in a low molecular weight (M_n = 2800) polybutadiene is plotted. The excitation wavelength was 398 nm.

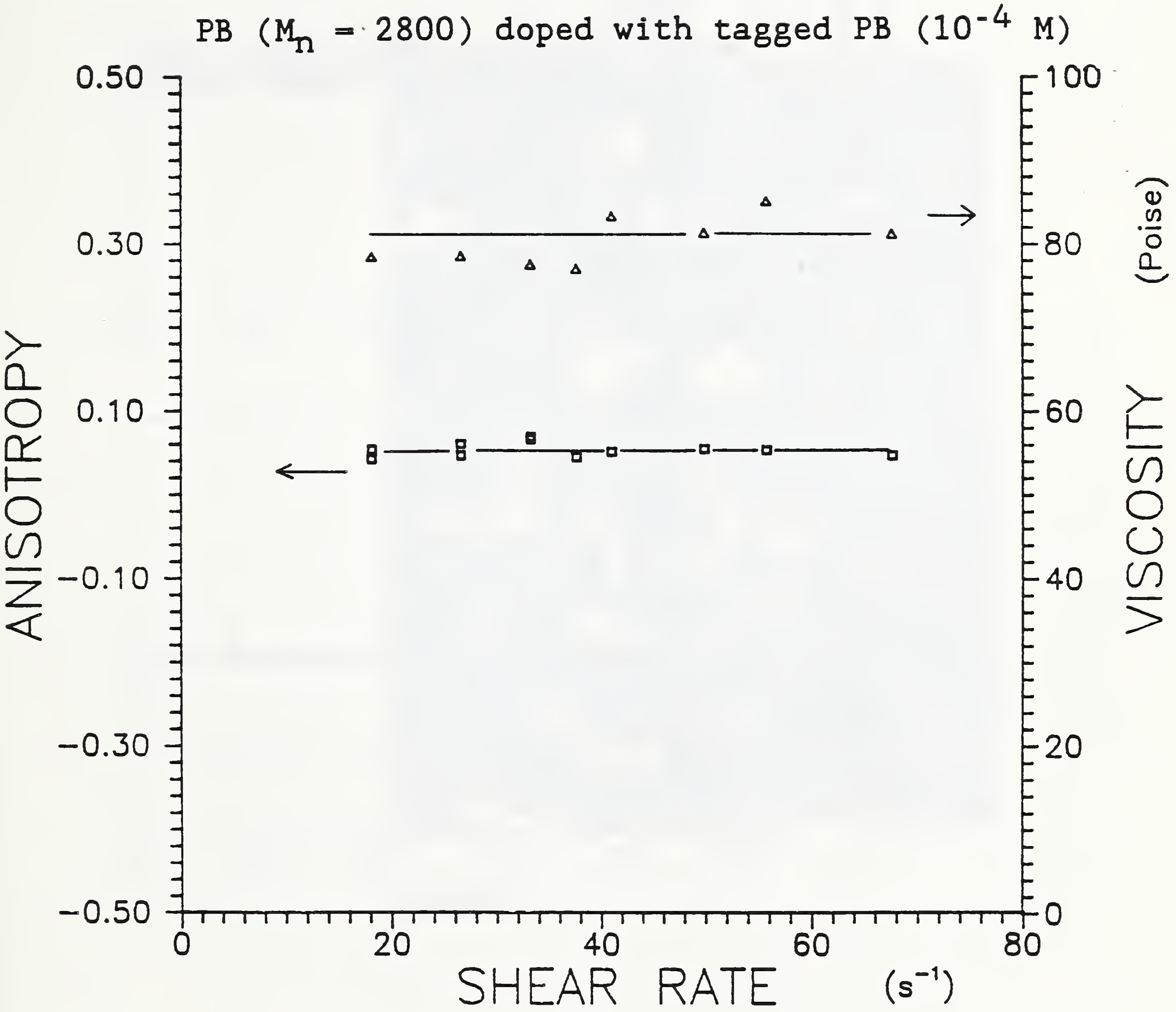


Figure 9. Fluorescence anisotropy and viscosity are plotted against shear rate for the low molecular weight (M_n = 2800) polybutadiene doped with the anthracene labelled polybutadiene.

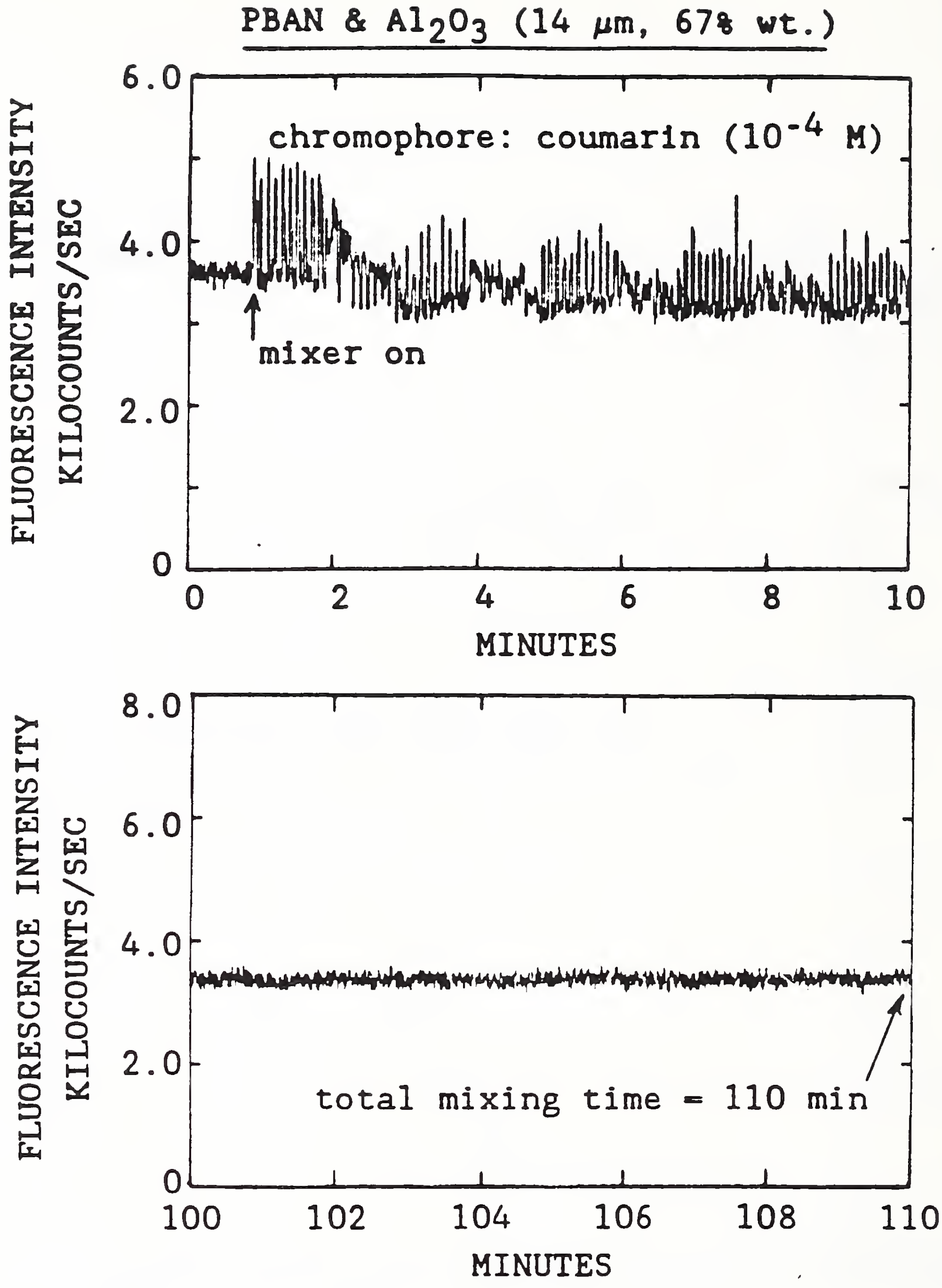


Figure 10. Fluorescence intensity vs time is plotted for a combination of PBAN and aluminum oxide particles, 67% by weight aluminum oxide. The PBAN is doped with the chromophore, coumarin 30. The uniform fluorescence intensity as a function of time indicates that uniform mixing has been achieved.

Figure 11. A photograph of the two dimensional mixture of polybutadiene and copper particles is shown. This picture is for the well mixed condition.

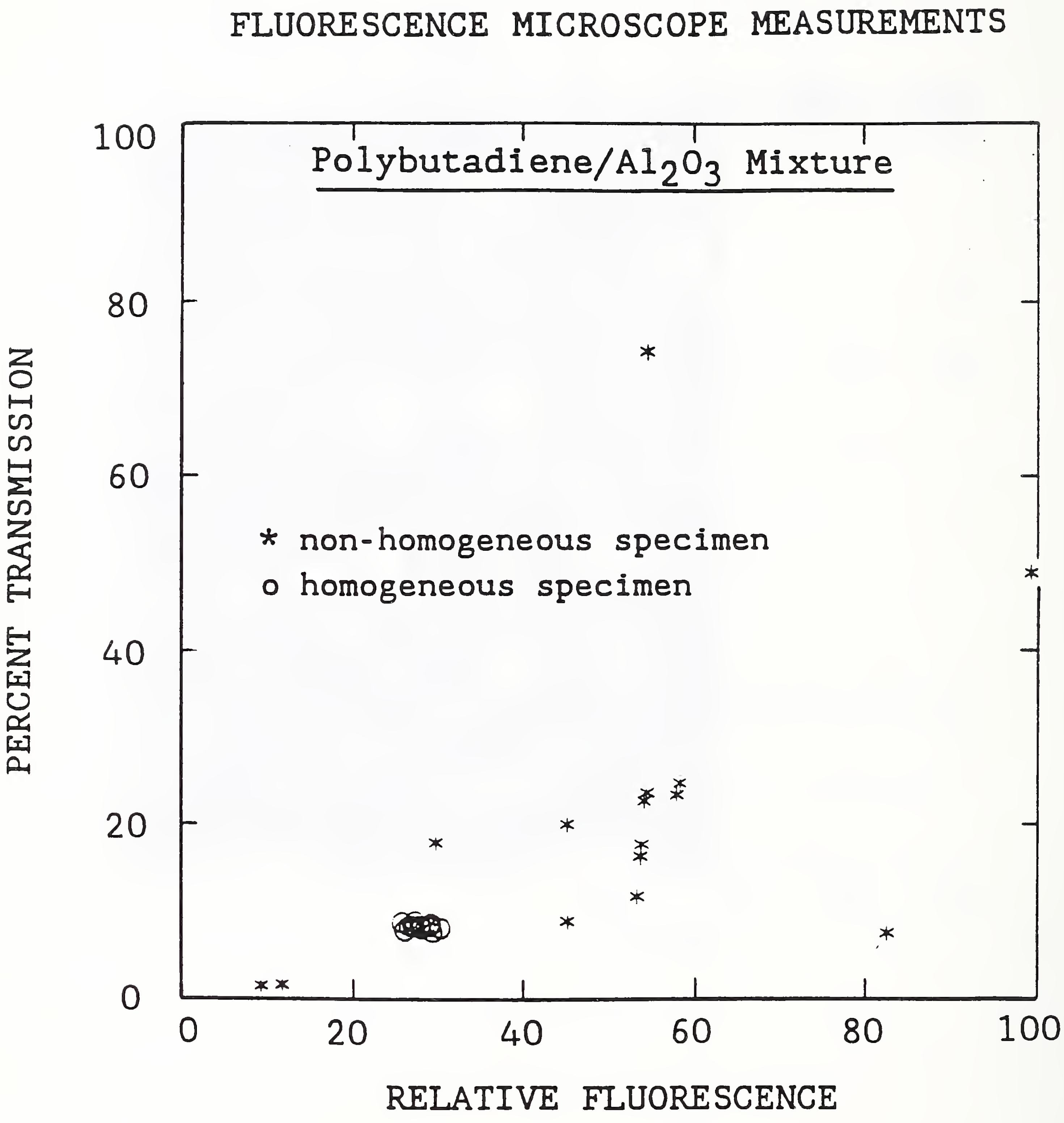


Figure 12. %Transmission is plotted vs relative fluorescence intensity for mixed (o) and unmixed (*) specimens of polybutadiene and aluminum oxide, 42% by weight aluminum oxide.

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NISTIR 88-3892	2. Performing Organ. Report No.	3. Publication Date NOVEMBER 1988

4. TITLE AND SUBTITLE

IN SITU FLUORESCENCE MONITORING OF THE VISCOSITIES OF PARTICLE-FILLED POLYMERS IN FLOW

5. AUTHOR(S)

A.J. Bur, F.W. Wang, A. Lee, R.E. Lowry, S.C. Roth, and T.K. Trout

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

N00014-86-F-0115

8. Type of Report & Period Covered

Annual Report

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

Office of Naval Research, Code 1132-P
Ballston Tower #1
800 N. Quincy Street
Arlington, VA 22217

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Work during FY 88 has focused on three areas: the chemical synthesis of a polymeric chromophore; the design of experiments to measure fluorescence anisotropy and non-Newtonian viscosity as a function of shear rate; and, measuring the quality-of-mix of a two component material using a fluorescence microscope. Significant results from these areas of work are: (a) a polymeric chromophore, consisting of anthracene covalently bonded to polybutadiene, has been synthesized and characterized by gel permeation chromatography and infrared observations. The number average molecular weight is 12,000 which is above the entanglement molecular weight for polybutadiene; (b) experiments using the polymeric chromophore as a dopant in a Newtonian fluid, very low molecular weight polybutadiene, show that fluorescence anisotropy correlates with the viscosity, i.e., it remains constant as a function of shear rate; and (c) using a fluorescence microscope, we have measured optical transmittance and near neighbor distances between particles in a matrix/particle mixing experiment and correlated these data with fluorescence intensity fluctuations.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

fluorescence anisotropy; fluorescence photobleaching; fluorescence spectroscopy; laminar flow; polymer fluorescence labelling; polymer processing; propellant mixing; propellant processing; velocity; velocity gradient; wall slip

13. AVAILABILITY

☒ Unlimited
☐ For Official Distribution. Do Not Release to NTIS
☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

36

15. Price

$11.95