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

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Anthony J. Bur, Francis W. Wang, and Ronald E. Dehl

U.S. DEPARTMENT OF COMMERCE
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Polymers Division
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Annual Report
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IN SITU FLUORESCENCE MONITORING OF THE VISCOSITIES OF PARTICLE-FILLED POLYMERS IN FLOW

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ABSTRACT

During FY87, our activity has focused on the development of measurement equipment, laboratory experiments using fluorescence monitoring, and the synthesis of a polymeric fluorescent chromophore. Laboratory equipment development has consisted of the design and construction of a capillary flow apparatus and a laboratory mixer. The capillary apparatus has been incorporated into a commercial fluorometer and is being used for the simultaneous measurement of fluorescence anisotropy and rheological parameters of concentrated polymer solutions and low molecular weight polymers. We have demonstrated the feasibility of the capillary measurement system by observing the anisotropy of a toluene solution of a polymer binder as a function of capillary head pressure from 0 to 40 psi. A mixer, which incorporates co-rotating and counter-rotating shearing elements and glass walls for viewing fluorescence, has been constructed and used to monitor the mixing of a low molecular weight polybutadiene based polymer and aluminum oxide. In other experiments, we have made observations of the dependence of the intensity of the fluorescence spectra from a doped polymer binder as a function of temperature at zero shear. In addition, we have used a cone and plate viscometer (a Weissenberg rheometer) to measure the viscosity of a polymer binder as a function of filler content (14 μm aluminum oxide particles) over a range from 0 to 75% by weight. Chemical synthesis of a polymeric chromophore is in process; it consists of reacting a bifunctional anthracene molecule with polybutadiene so that the fluorescently active anthracene is positioned at the center of the polymer chain.

Key Words: fluorescence anisotropy; fluorescence spectroscopy; polymer mixing; propellants; rheology; zero shear viscosity.

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 new endeavor which will require significant development in order to realize the full potential of the technique. From a large body of fluorescence spectra 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 zero shear viscosity, non-Newtonian viscosity, molecular orientation, intersegmental mixing at the molecular level, and the quality of mixing of specimen ingredients.

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 nondestructive 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 develop mixing equipment and equipment which can be used to measure fluorescence spectra and non-Newtonian viscosity simultaneously, (b) to carry out laboratory experiments on the fluorescence monitoring of the following: zero shear viscosity of a polymeric binder, fluorescence anisotropy of a polymer solution in capillary flow, and the mixing of two component specimens, and (c) to synthesize a polymeric chromophore which can be used to detect the molecular orientation and non-Newtonian viscosity in a flowing propellant material. We report on these efforts below.

EXPERIMENTAL PROCEDURE

MIXING EXPERIMENT

The materials for the mixing experiment consisted of the polymer binder PBAN, which we obtained from American Synthetic Rubber,[2] aluminum oxide filler particles which had a nominal grain size of 14 μm, and the chromophore coumarin 30 which was obtained from Eastman-Kodak.[2]

According to the supplier's specifications, PBAN is a ter-polymer which is 85% butadiene, 11% acrylonitrile, and 4% acrylic acid; it has a weight average molecular weight of 6000. The viscosity of PBAN at 25°C is 369 poise. The dopant chromophore which we used for the mixing experiment was coumarin 30. It was chosen because it satisfies the following criteria which we have established:

- o Fluorescence intensity must be independent of the polarity of the molecular neighborhood of the chromophore;
- o The chromophore must be chemically stable and not susceptible to photobleaching by the excitation photons;
- o Excitation and emission must occur at visible wavelengths.

The last criterion is not a necessary condition but one of convenience.

Prior to mixing PBAN with the Al_2O_3 filler, PBAN was doped with coumarin 30 to a concentration of 10^{-4} molar. To do this, a few milligrams of coumarin were dissolved in a few drops of a 50/50 ethanol/toluene mixture and then mixed with PBAN. This mixing was carried out with ease because both materials were in the liquid state.

Mixing of the doped PBAN and Al_2O_3 was carried out in a mixer which was constructed in our laboratory and is shown schematically in Figure 1. The cylindrical wall of the mixer is a glass tube which is approximately 2.54 cm in diameter by 14 cm in length. The specimen volume in the mixer is 42 cm^3. There are two sets of mixing blades which can be driven in co-rotating or counter-rotating modes of motion by the motors shown. One set of blades rotates at the outer circumference of the mixer near the glass wall.

This set is connected to the uni-directional motor and contains a flat brass piece which functions as a scraper in order to prevent material from accumulating at the wall. The other set consists of a single twisted brass piece which is connected to the bi-directional motor and rotates on the cylindrical axis of the mixer. Both motors rotate at approximately 10 rpm, i.e. with a period of revolution equal to 6 seconds.

In Figure 2, we show the experimental arrangement for collecting the fluorescence spectra during the mixing operation. A 458 nm excitation light beam from an argon ion laser was directed through a beam splitter to the glass wall of the mixer. The diameter of the light beam was approximately 1 mm, and its penetration into the sample varies with the amount of particle scattering. The beam splitter is employed in order to detect the back scattered fluorescence radiation. Fluorescence from the coumarin chromophore was isolated at one wavelength by setting the monochromator to 500 nm, and the fluorescence signal was detected by a photo tube and counter, and stored in a computer. The data sampling time was set at 0.2 seconds so that 30 data points were obtained for each revolution of the mixer motors.

ZERO SHEAR VISCOSITY EXPERIMENT

The binder which we used in the zero shear viscosity experiment was obtained from J. Manser of Aerojet General.[3] It is a copolymer of bis(azidomethyl)oxetane and nitratomethylmethyloxetane and is designated as BAMO/NMMO.[4] The molecular weight was reported to be 18,000.[3] It was doped with the chromophore, p-dimethylaminobenzylidene malononitrile (DMABMN), to a concentration of approximately 10^{-4} molar by combining chromophore and polymer in solution using methylene chloride as the common solvent. The solvent was evaporated by maintaining the temperature of the specimen above the boiling point of methylene chloride (40°C) for 24 hours.

The DMABMN chromophore was chosen for this experiment because it is known that its fluorescence intensity is dependent on the viscosity of the host material.[5]

Fluorescence spectra from 450 to 650 nm were obtained as a function of temperature from this specimen using a commercial fluorimeter which had a temperature control jacket in the specimen chamber. The excitation wavelength was 440 nm.

FLUORESCENCE ANISOTROPY

The capillary flow apparatus will be used to study the flow of concentrated polymer solutions and low molecular weight polymers by observing the fluorescence anisotropy of polymer molecules during flow as a function of shear rate. This apparatus has been incorporated into a commercial fluorometer as depicted in the schematic diagram of Figure 3. The apparatus consists of a glass reservoir vessel with capacity of 500 cm^3 which sits at the head of a vertically oriented capillary. The capillary extends through the sample chamber of the fluorometer and is connected to a collection vessel at the bottom end. It is made of pyrex glass, has a capillary diameter of 1 mm, and is 25 cm long. Conversion to other capillary diameters is easily achieved. The reservoir at the head of the capillary is surrounded by a brass pressure vessel which can be pressurized by nitrogen gas to 100 psi. Pressure is monitored by a resistance type pressure transducer. The shear rate of the liquid in flow is controlled by adjusting the pressure.

Although the PBAN molecule should not be fluorescently active and toluene does not display fluorescence in the wavelength range of our investigation, we observed fluorescence spectra over the range 350 to 450 nm for excitation at 325 nm. We attribute this fluorescence to an additive or an impurity in the polymer sample. The fluorescent chromophore is not necessarily chemically bound to the polymer molecule, but we have taken advantage of its fortuitous presence to test our experimental technique.

The measured quantity in this experiment is fluorescence anisotropy, r. It is defined as

$$r = \frac{I_{vv} - I_{vh}}{I_{vv} + 2I_{vh}} \tag{1}$$

where I_{vv} refers to vertically oriented excitation and emission polarizers and I_{vh} refers to a vertically oriented excitation polarizer and horizontally oriented emission polarizer. The measured intensities are appropriately corrected for differences in detection sensitivity for vertically and horizontally polarized light.

VISCOSITY MEASUREMENTS

A Weissenberg rheometer has been used to make measurements of the viscosity of PBAN filled with 14 μm grain size aluminum oxide. The measurements were carried out at room temperature for filler content over a range of 0 to 75% by weight. This instrument is being fitted with optical fibers which will be placed at the cone and plate assembly in order to obtain fluorescence anisotropy and viscosity measurements simultaneously.

SYNTHESIS OF A POLYMERIC CHROMOPHORE

For the measurement of molecular orientation and non-Newtonian viscosity, a polymeric chromophore, i.e. a molecule which is long enough to orient under the influence of processing shear stresses, will be used. We are in the process of reacting a bifunctional anthracene molecule with polybutadiene so that the fluorescently active anthracence is positioned at the center of the polymer chain. The results of these efforts will be the subject of future reports.

RESULTS AND DISCUSSION

MIXING EXPERIMENT

To prepare the specimen for mixing, aluminum oxide filler material (14 μm grain size) and PBAN were added separately to the mixer without any premixing at 58% filler by weight. Prior to turning the mixer on, the excitation light beam from the laser was directed at the chromophore-rich PBAN which produced a strong fluorescence signal, 200 kilocounts/s, as shown in Figure 4. At 150 seconds, the mixer was turn on and was operated in the counter-rotating mode. At the start of mixing, large variations in intensity were observed. The intensity variations are seen as periodic spikes in the data with a period of six seconds. These spikes occur every revolution of the mixer as the blades bring chromophore-rich and -poor regions of the specimen into the sampling volume of the mixer. In addition to the spikes, an overall decrease in fluorescence intensity occurred within the first 30 seconds of mixing. This decrease in the intensity is attributed to two causes: one, the coumarin chromophore in the sampling volume is displaced by the Al_2O_3 filler; and two, light scattering from the 14 μm filler particles occurs.

In Figure 5, we plot fluorescence intensity data taken after the mixer had been on for 60 minutes. At this time, the mixer operation is one of alternating from counter-rotating to co-rotating blade motion every 2 minutes. The alternating pattern is seen in the data and reflects the change from counter-rotation to co-rotation and vice versa every minute. It is seen that the intensity spikes which occur every 6 seconds are an order of magnitude less than that seen in Figure 4, an indication that the distribution of chromophores throughout the specimen is approaching uniformity.

At this point in the mixing experiment, the mixer was opened and more aluminum oxide was added in order to fill the mixer to maximum. This mixture contained 67% Al_2O_3 by weight. Figure 6 shows the fluorescence intensity data obtained after the additional filler was added. After nine minutes of mixing, there remains intensity spiking of approximately 1 kilocount/s, but, after 100 minutes, the intensity is constant to within the sensitivity of our measurement. Our hypothesis is that uniform mixing has been achieved when constant fluorescence intensity as a function of time is observed.

As a qualitative test of this hypothesis, we used transmission optical microscopy to examine a 100 μm thick smear of the mixture on a glass microscope slide. Figure 7 is a picture of this observation. The dark areas are filler particles in the plane of focus. The grey translucent areas contain filler particles within the thickness of the smear but not in the plane of focus. The bright regions contain PBAN only and are not overlaid by aluminum oxide particles so that light is transmitted directly through the specimen. In assessing the qualitative features of this picture, we note that 67% aluminum oxide by weight corresponds to 34% by volume.

A rigorous test of our fluorescence/mixing hypothesis will require a quantitative measure of the spatial distribution of filler particles in the polymer binder and a comparison of such observations with an accepted model or definition of a "good" mixture. This will be the subject of future work.

ZERO SHEAR VISCOSITY

Figure 8 is a plot of fluorescence spectra taken at 25, 60, and 95°C for BAMO/NMMO doped with DMABMN. The decrease in intensity with increasing temperature is attributed to the decrease in viscosity of the polymer as temperature increases.

The sensitivity of the fluorescence intensity of DMABMN to the viscosity of the host material has been studied in detail by Loutfy.[5] DMABMN belongs to a class of chromophores whose quantum yield of fluorescence is dependent on the relative magnitude of the intrinsic radiative lifetime of the excited state versus the internal rotational relaxation time, τ_r, of the chromophore in its viscous neighborhood. Loutfy found that a clear correlation exists between fluorescence intensity of DMABMN and the ratio of viscosity to temperature for the solvents ethylacetate, dimethylphthalate, and glycerol.[5] The correlation was of the form $I \alpha (\eta/T)^x$ where $x = 1.0$, 0.43 and 0.69 for the three solvents respectively over the temperature range from 0 to 90°C. The functional form of the correlation, η/T, is predicted for τ_r from the Debye-Einstein-Stokes model of a sphere or ellipsoid rotating in a viscous medium. The data of Loutfy demonstrate that viscosity is the dominant influence on the fluorescence intensity of DMABMN in each solvent, but the molecular hydrodynamics which determine the internal rotational relaxation time are different in each case.[5] Since we have not measured viscosity of BAMO/NMMO, we do not know the precise correlation between fluorescence intensity and viscosity. However, Loutfy's work supports our interpretation that the decrease in fluorescence intensity correlates with a decrease in the viscosity of BAMO/NMMO.

FLUORESCENCE ANISOTROPY MEASUREMENTS

Using the capillary flow apparatus, fluorescence anisotropy of an undoped toluene solution of PBAN was measured over a wavelength range from 350 to 450 nm as a function of the applied pressure from 0 to 40 psi. The solutions were 1/3 polymer and 2/3 toluene by volume. Under quiescent conditions, we observed that the anisotropy, r, was zero. The effect of increasing pressure or shear rate is shown in Figure 9; we note that the anisotropy is approximately zero for 10 psi. But, for 20 psi head pressure, r is 0.5 over the entire scan, indicating that there is significant orientation of the fluorescent transition dipole as the shear rate increases. At 30 and 40 psi the anisotropy was observed to decrease to zero; we attributed this to the onset of turbulence at these higher shear rates for which the flow can be characterized by Reynolds numbers greater than 2,100.

In order to calculate the polymer molecular orientation from anisotropy measurements, it will be necessary to use a labelled polymer and to have detailed knowledge of the chromophore position in the polymer chain and its fluorescence spectra. Such information is not available regarding the data of Figure 9, but these experiments have served a useful purpose in establishing the experimental approach and technique. Our future plans for this experiment and for experiments using the Weissenberg rheometer will include the use of the polymeric anthracene/polybutadiene chromophore as a dopant material.

VISCOSITY MEASUREMENTS

The viscosity measurements on PBAN filled with aluminum oxide are shown in Figure 10. These data were taken at room temperature using the Weissenberg rheometer and are reported for a shear rate of 0.55 s^{-1}. Within experimetal error, and at concentrations below 50% by weight (21% by volume), the viscosity is a linear function of Al_2O_3 weight or volume fraction. Above 50% weight fraction, a dramatic upswing in the viscosity occurs between 65% and 75% weight fraction (33% and 43% volume fraction).

In the linear regime of the viscosity vs concentration plot, concentrations below 50% by weight or 21% by volume, the behavior is viewed as being dominated by hydrodynamic interaction between the Al_2O_3 particles. At very dilute concentrations, we can apply the Einstein equation for the viscosity of a solution of hard spheres which states that viscosity is a linear function of the volume fraction of spheres.[6] For concentrated solutions of spheres, other hydrodynamic models have been developed and take into account higher order terms neglected in the Einstein treatment.[7] For these models, deviations from linearity of approximately 5% are predicted at volume concentrations of 20%, in agreement with our experimental observation. The slope of our experimental curve, however, is larger by a factor of two than that obtained from the models.[7] We note that the models do not take into account non-hydrodynamic interactions such as non-spherical particle shape, collisions, electrostatic interactions, and aggregations.

We interpret the departure from linearity in the vicinity of 50% weight fraction (21% volume fraction) to be caused by the onset of highly cooperative particle motion which involves both hydrodynamic and non-hydrodynamic effects. Below 50% weight fraction, the particles rotate or translate in the polymer matrix as single particles. Above 50%, particle motion becomes highly cooperative so that the motion of one requires the displacement of many others.

The transition from linear behavior at low concentrations to the high slope regime at high concentrations of Al_2O_3 occurs at a volume fraction for which spatial packing becomes a factor. We consider the packing of spheres at a volume fraction of 23% and assume that the spheres have a radius of 7 μm. If we place the spheres on an hexagonal lattice, then their center-to-center distance is 28 μm, i.e. the edge-to-edge distance between near neighbor spheres, 14 μm, is equal to the diameter of the spheres. Thus, 23% volume concentration is the threshold at which particle-to-particle impingement occurs during translational motion. As the volume fraction of spheres increases above 23%, the translation of a sphere in the hexagonal lattice will require an increasing amount of cooperative motion with other spheres.

SUMMARY AND CONCLUSIONS

We have described our activities regarding the use of fluorescence spectroscopy to monitor propellant processing parameters. From the mixing experiments, we have observed a constant fluorescence intensity at long mixing times which we associated with uniform mixing of PBAN binder and the aluminum oxide particulate. A zero shear viscosity experiment was carried out for which BAMO/NMMO copolymer binder was doped with a viscosity sensitive probe and its fluorescence intensity was observed as a function of temperature. The decrease in fluorescence intensity with increasing temperature was associated with the decrease in the viscosity of the BAMO/NMMO. Experiments for the measurement of fluorescence anisotropy have been developed. These include a capillary flow apparatus and a Weissenberg rheometer which is being fitted with optical fibers. While several experiments have been done with these pieces of equipment, the measurement of fluorescence anisotropies and their relationship to molecular orientation and non-Newtonian viscosity await the synthesis of a fluorescent polymer. Viscosity measurements on PBAN filled with 14 μm aluminum oxide particles were made over a concentration range from 0 to 75% by weight. The viscosity vs concentration data was linear at low concentrations, but displayed a departure from linearity at approximately 50% by weight which we attributed to the onset of particle cooperative motion involving non-hydrodynamic forces.

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2. Identification of a commercial product is made only to facilitate experimental reproducibility and does not imply endorsement by NBS.
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4. J. Manser, R. W. Fletcher and M. R. Knight, High Energy Binders Final Report, Contract no. N00014-82-C-0800, Morton Thiokol, Inc., Brigham City, Utah 84302, August, 1985.
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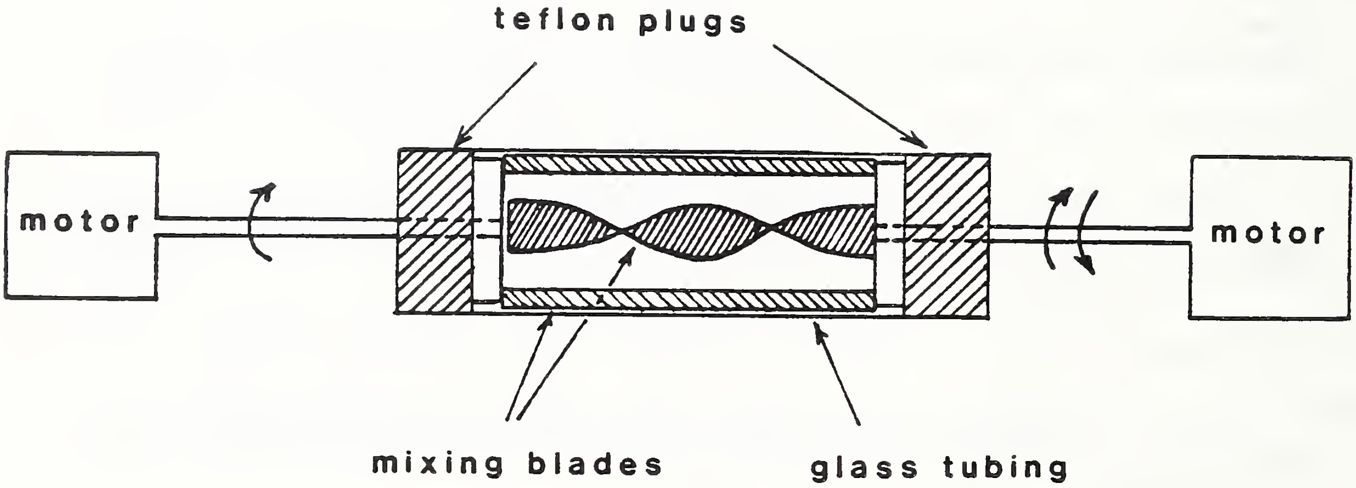


Figure 1. A diagram of the mixer is shown. The twisted blade, which rotates on the central axis of the mixer, is driven by the bi-directional motor. Three blades, driven by the uni-directional motor, are at the outer circumference of the mixer, near the glass wall; one of these is a scraper which prevents accumulation of material at the wall.

MIXING EXPERIMENT

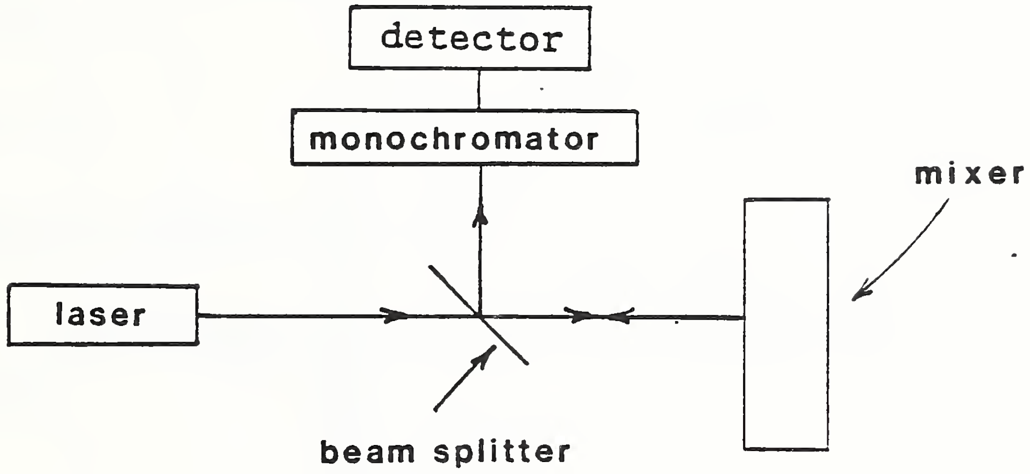
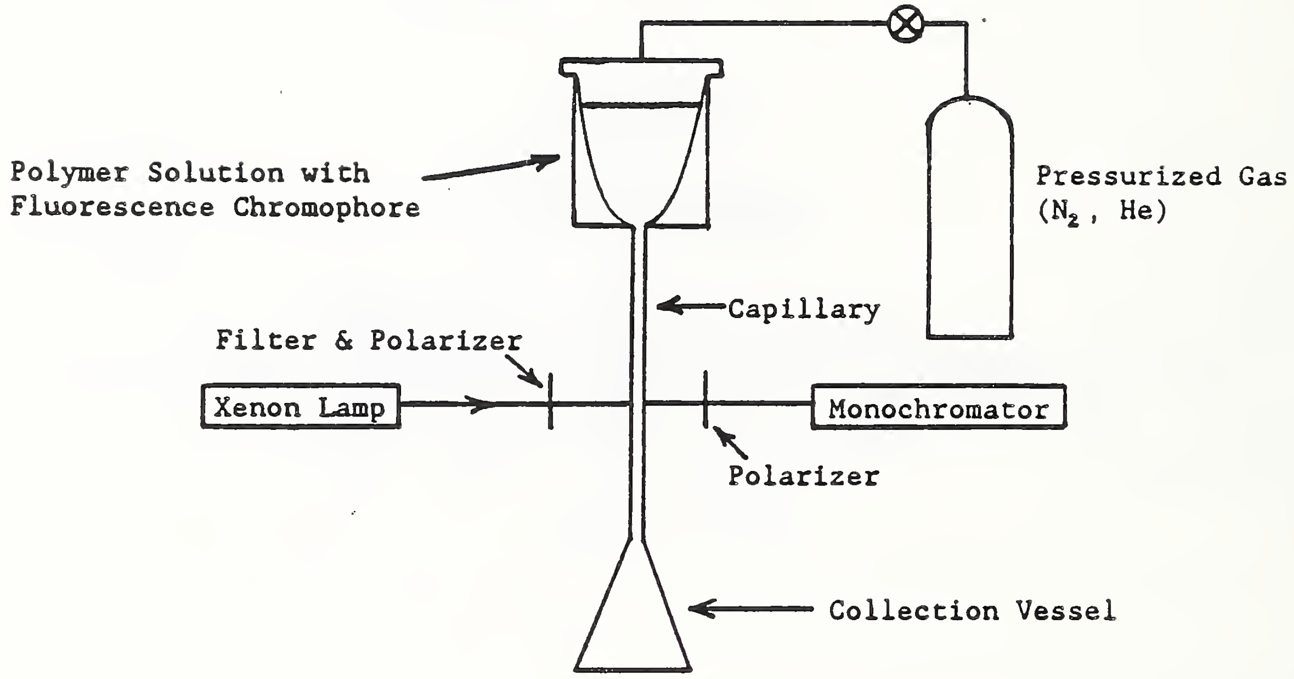


Figure 2. The optical arrangement for the fluorescence mixing experiment is shown. By using a beam splitter, the back scattered fluorescence is measured.


CAPILLARY FLOW EXPERIMENT

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

Figure 3. A diagram of the capillary flow apparatus is shown. In practice, the excitation and emission light beams are at an angle of 90° with respect to each other.

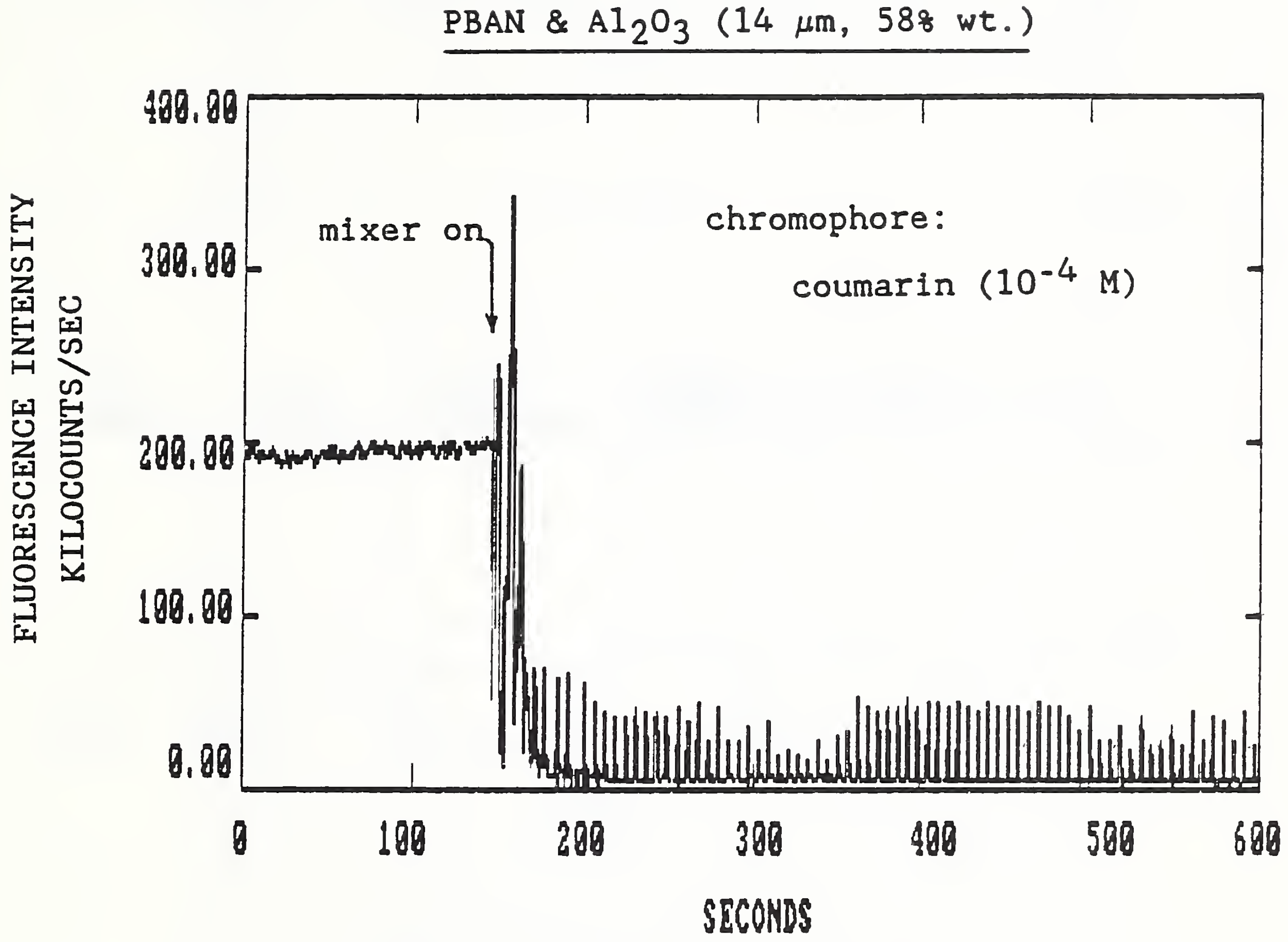


Figure 4. Fluorescence intensity versus time is plotted for mixing of coumarin 30 doped PBAN with 58% aluminum oxide by weight. Grain size of the aluminum oxide was 14 µm.

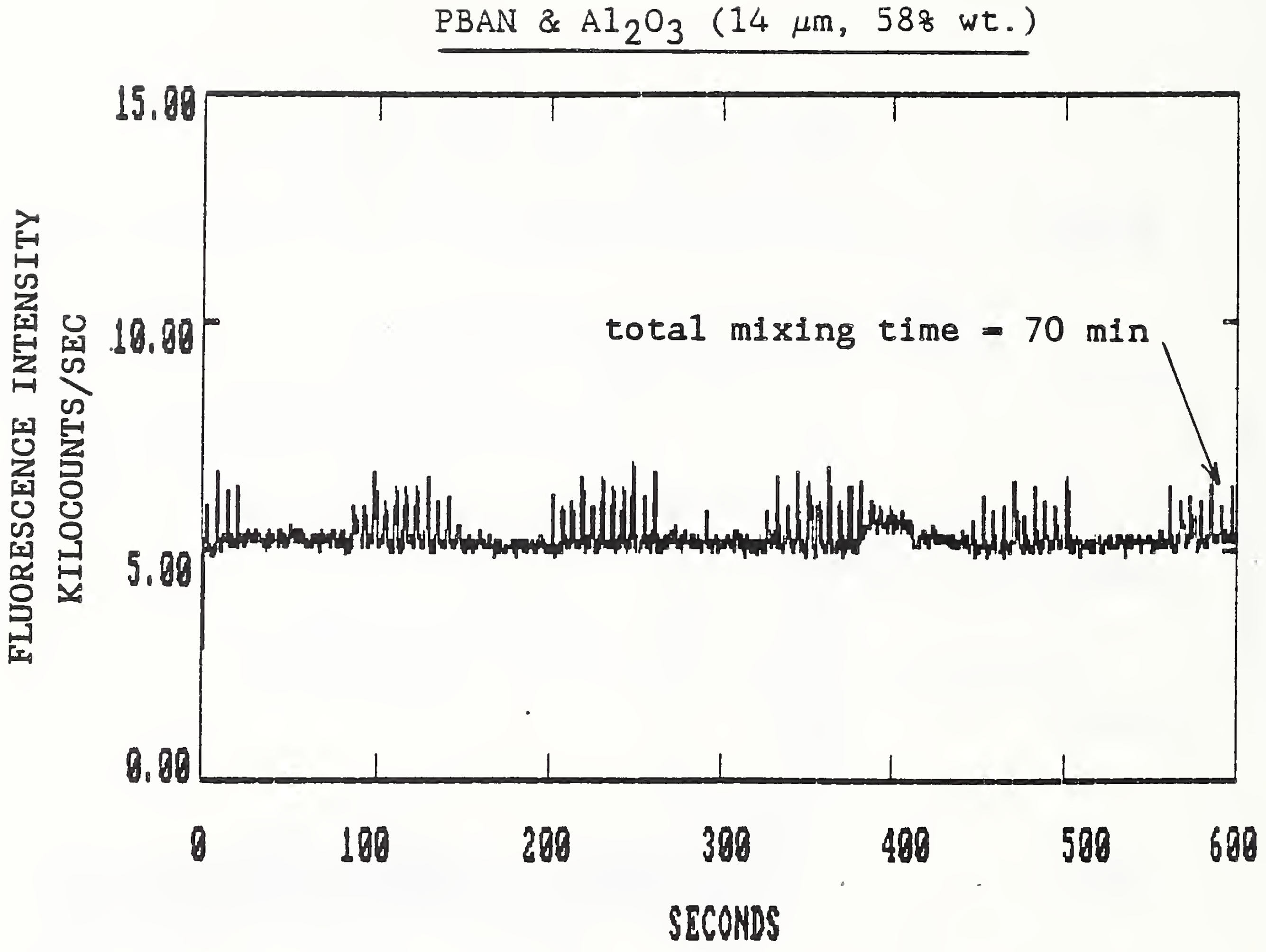


Figure 5. Fluorescence intensity versus time is plotted for mixing of coumarin 30 doped PBAN with 58% aluminum oxide by weight. This is the same specimen as was used for the data in Figure 4. The observations are for mixing times starting at 60 and ending at 70 minutes.

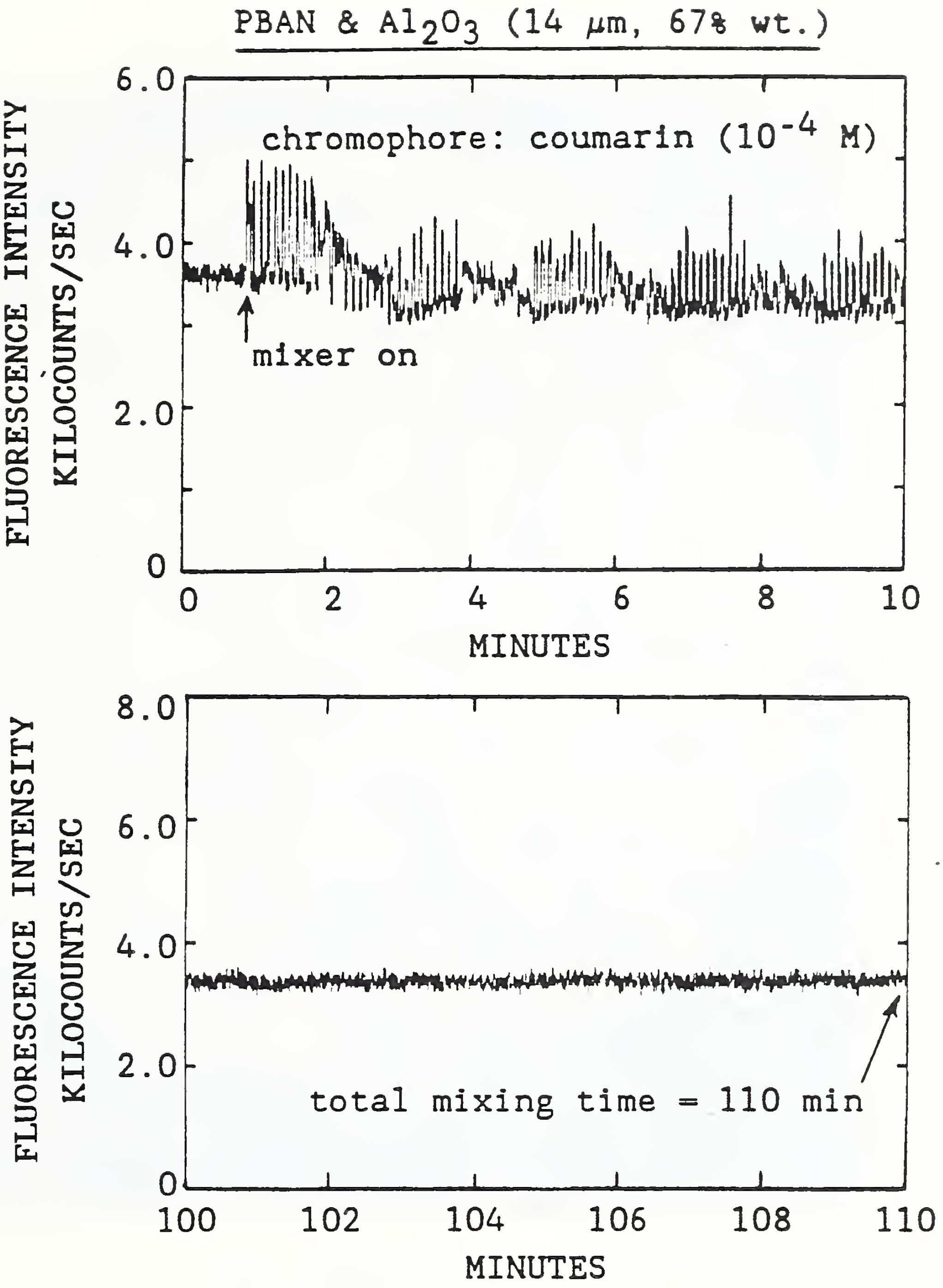


Figure 6. Fluorescence intensity versus time is plotted for mixing of PBAN with 67% aluminum oxide by weight. The starting specimen was that used for the data of Figures 4 and 5 to which more aluminum oxide was added. The plot for 0 to 10 minutes shows the intensity variations at the beginning of mixing. The plot from 100 to 110 minutes shows the intensity at the end of mixing.

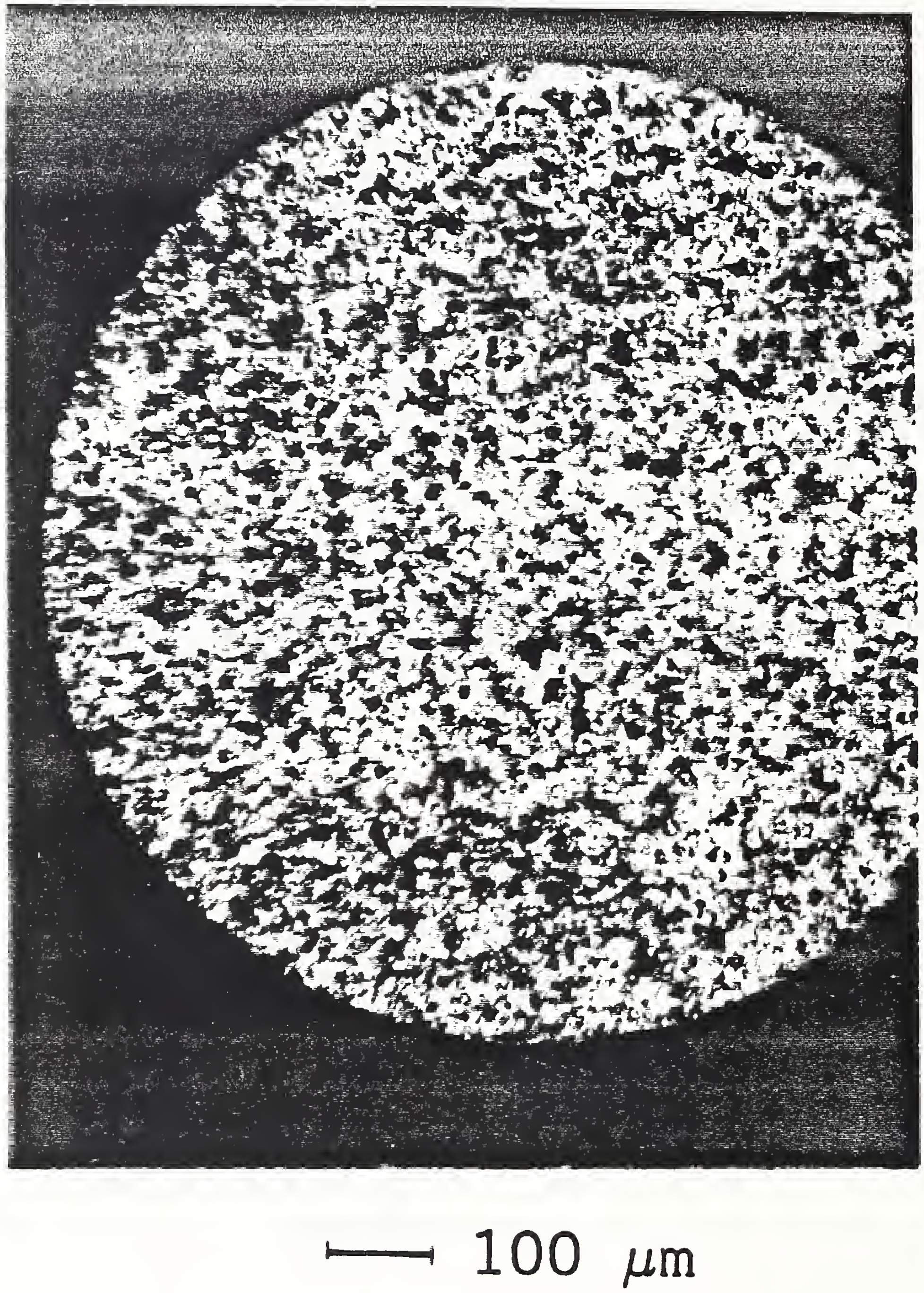


Figure 7. The specimen of Figure 6, having been mixed for 110 minutes, is shown in a micrograph of a 100 μm thick smear on a microscope slide. The picture was taken in transmission.

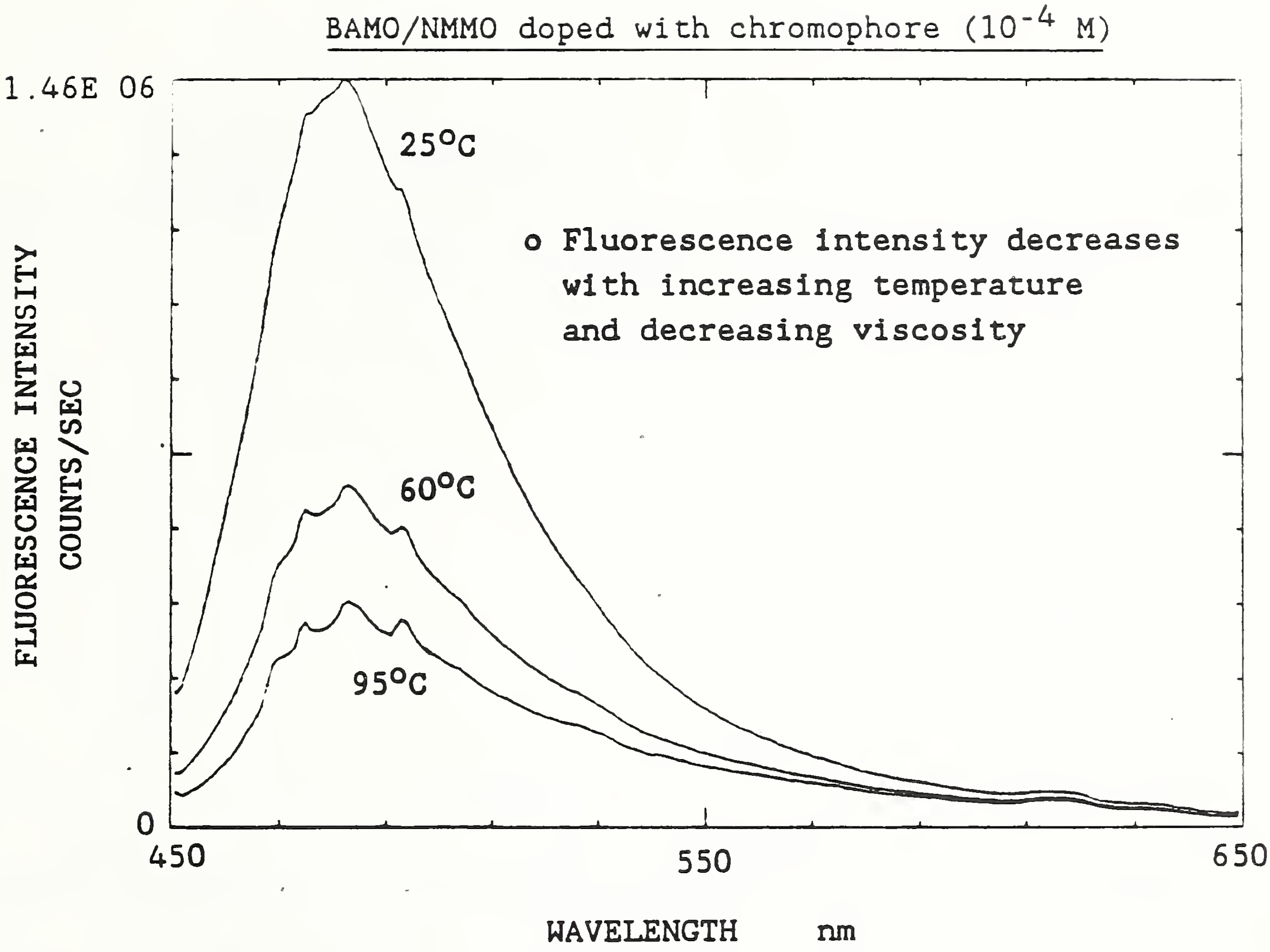


Figure 8. The fluorescence spectra of a doped polymer binder, BAMO/NMMO, are shown for 25, 60, and 95°C. The chromophore was p-dimethylaminobenzylidene malononitrile.

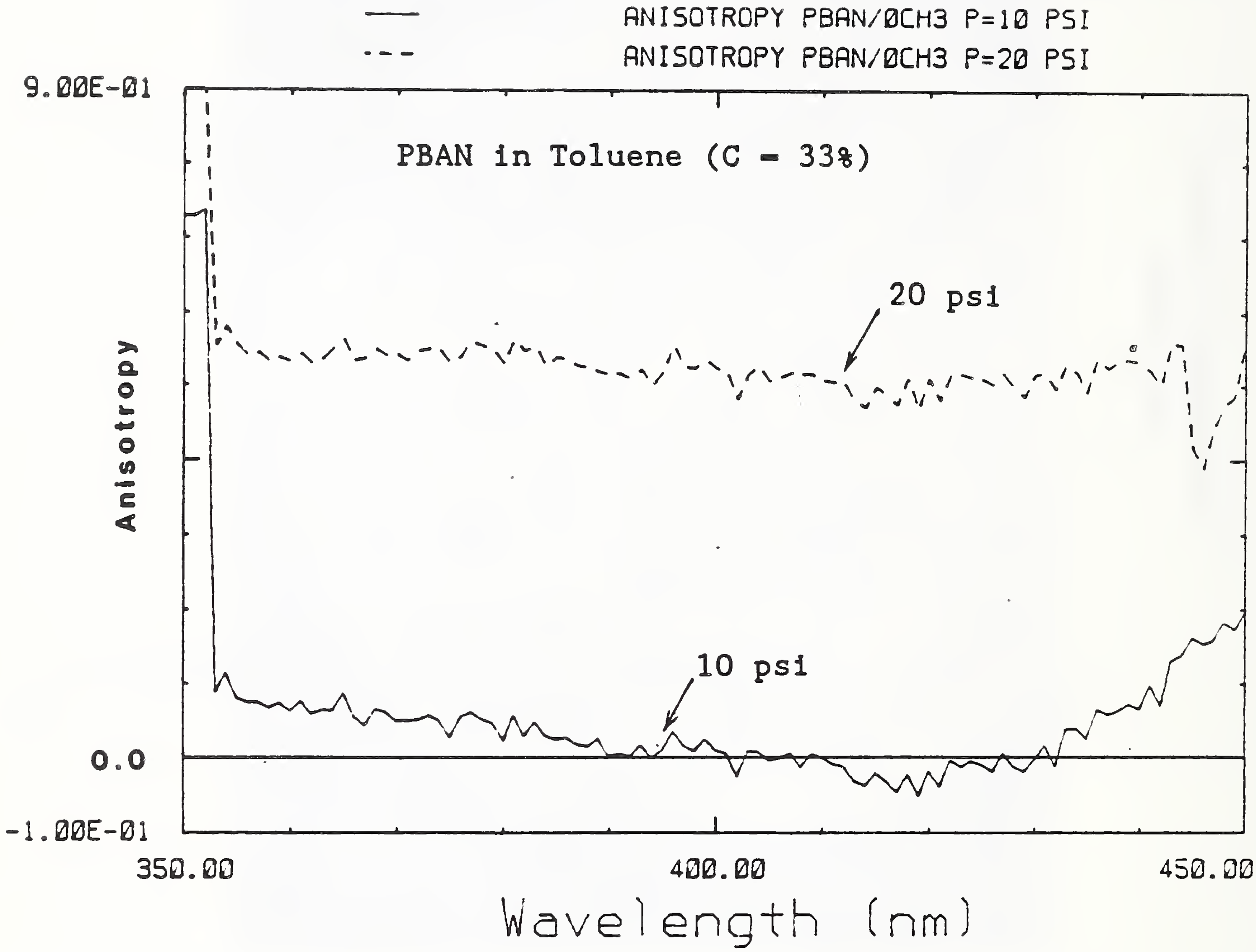


Figure 9. The fluorescence anisotropy for a concentrated solution of PBAN in toluene is shown for a wavelength scan of 350 to 450 nm for 10 and 20 psi capillary head pressures.

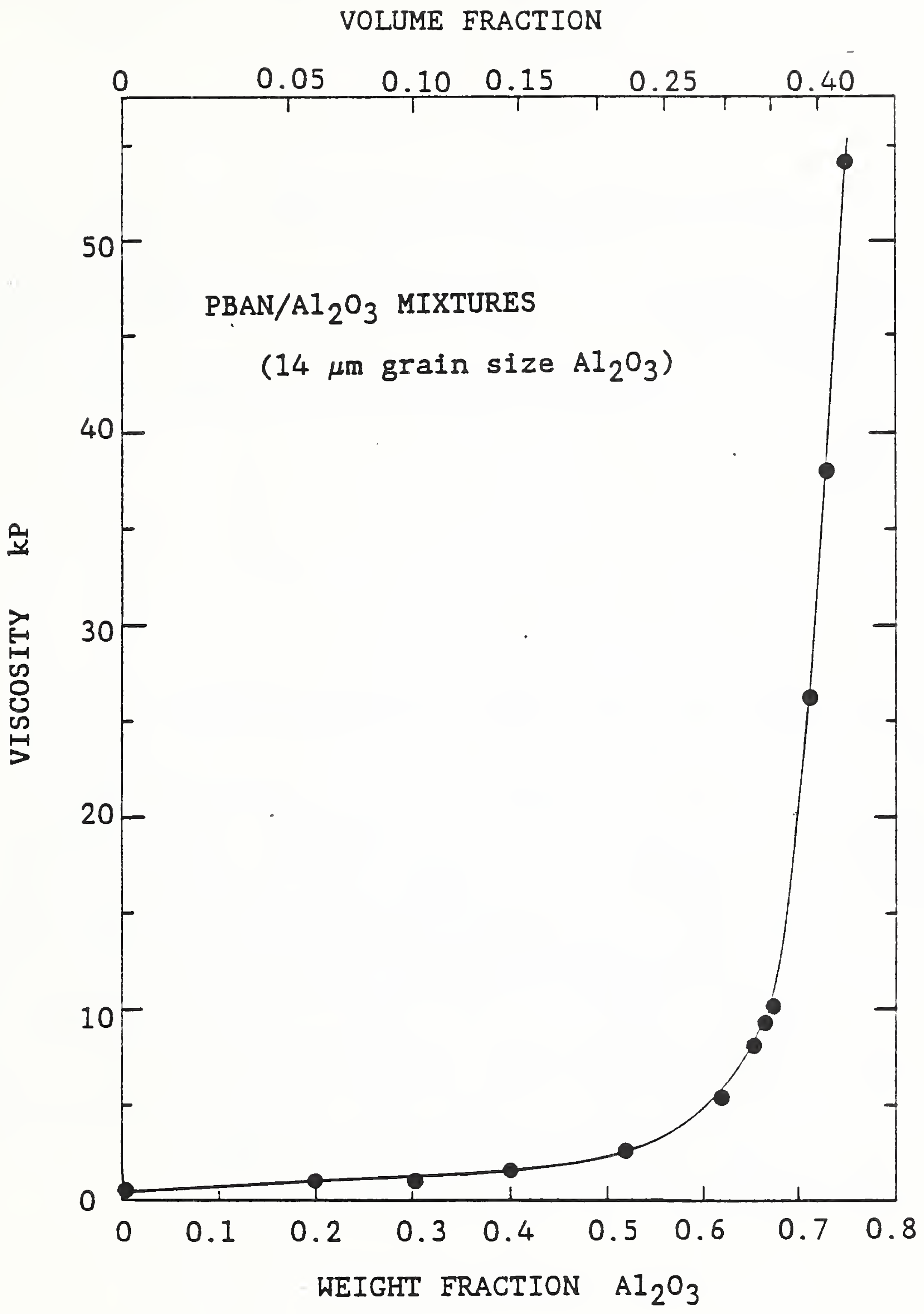


Figure 10. Viscosity vs concentration for aluminum oxide filled PBAN is shown. The measurements are reported for a shear rate of 0.55 s^{-1}.

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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)*

During FY 87, our activity has focused on the development of measurement equipment, laboratory experiments using fluorescence monitoring, and the synthesis of a polymeric fluorescent chromophore. Laboratory equipment development has consisted of the design and construction of a capillary flow apparatus and a laboratory mixer. The capillary apparatus has been incorporated into a commercial fluorometer and is being used for the simultaneous measurement of fluorescence anisotropy and rheological parameters of concentrated polymer solutions and low molecular weight polymers. A mixer, which incorporates co-rotating and counter-rotating shearing elements and glass walls for viewing fluorescence, has been constructed and used to monitor the mixing of a low molecular weight polybutadiene based polymer and aluminum oxide. In other experiments, we have made observations of the dependence of the intensity of the fluorescence spectra from a doped polymer binder as a function of temperature at zero shear, and we have used a cone and plate viscometer (a Weissenberg rheometer) to measure the viscosity of a polymer binder as a function of filler content.

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

fluorescence anisotropy; fluorescence spectroscopy; polymer mixing; propellants; rheology; zero shear viscosity

13. AVAILABILITY

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