

IX. TIME-RESOLVED SPECTROSCOPY OF CONDENSED MATTER

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1. MICROVISCOSITY IN GELS AND POLYMER SOLUTIONS

Fluorimetry has long been used as a tool to study biological molecules and much more information can be obtained when the fluorescence depolarization is studied as a function of time after a short light pulse. These tools have had much more limited applications to the study of synthetic polymers and gels. Monitoring the dichroism as a function of time induced by a mode-locked laser pulse provides as much or more information as the above techniques and permits greatly improved time resolution. Traditionally nonradiative energy transfer has been studied by measuring the fluorescence yield, but time-resolved spectroscopy can be used to measure the nonradiative lifetime directly.

We have carried out a series of experiments using the laser dye oxazine-4 as a probe of microviscosity in gels made with collagen polymers dissolved in mixtures of water and methanol. A gel is formed when the polymers become cross-linked to form a continuous network. With collagen this cross linking is due to hydrogen bonding, and thus a reversible gel-sol transition occurs around 27°C. The macroscopic viscoelastic behavior of the gel is determined by the elastic modulus of the polymer network and a frictional coefficient with the fluid medium; the latter is determined by the local viscosity of the fluid and a correlation length for polymer density fluctuations. We used the reorientation time of the dye molecules (measured by the decay of induced dichroism) as a probe of the local viscosity. Measurements of this reorientation time in solvents (without polymer) consisting of mixtures of methanol and water as a function of temperature showed the times to scale closely with the solvent viscosity calculated from the mole fractions of water and methanol and the viscosity of the pure solvents. The results of a series of experiments as a function of temperature for a series of collagen gels gave the following results. In pure water the dichroism decay at 50°C was 15% faster than one would expect from scaling the viscosity; we believe this results because the decay is a competition between reorientation and decay of the excited state of the molecules,

(IX. TIME-RESOLVED SPECTROSCOPY OF CONDENSED MATTER)

Table IX-1. Ratio of dichroism decay in gel to pure solvent.

Fraction Collagen	298° K	303° K	313° K	323° K
0	1.000	1.000	1.000	1.000
2%	1.072	1.023	1.146	1.145
4%	1.174	1.178	1.281	1.296
6%	1.256	1.240	1.349	1.401
8%	1.372	1.341	1.521	1.553

and the latter is also temperature-dependent. This effect can be normalized out by taking the ratio of decay times in the gel to those in pure solvent at each temperature. Table IX-1 gives results for four different collagen gels in pure water. In this system the gel exists below 300° K. The conclusions are that the local viscosity in the gel is to a first approximation the same as that of the pure solvent. The longer decay in gels as the polymer concentration increases shows that reorientation is hindered by interaction with the polymer chains; this hindering becomes more pronounced well above the gel transition where the interaction between polymers is less important. A quantitative measure of this effect is seen in Fig. IX-1 which shows dichroism decay for oxazine dissolved in methanol in free solution ($\tau = 97$ ps) and in the 40 Å pores of Vycor glass ($\tau = 129$ ps); the latter dichroism does not decay to zero in 500 ps because molecules bound to the Vycor cannot reorient. The curve also provides a quantitative measure of the fraction of dye molecules bound to the Vycor (37% at 20° C).

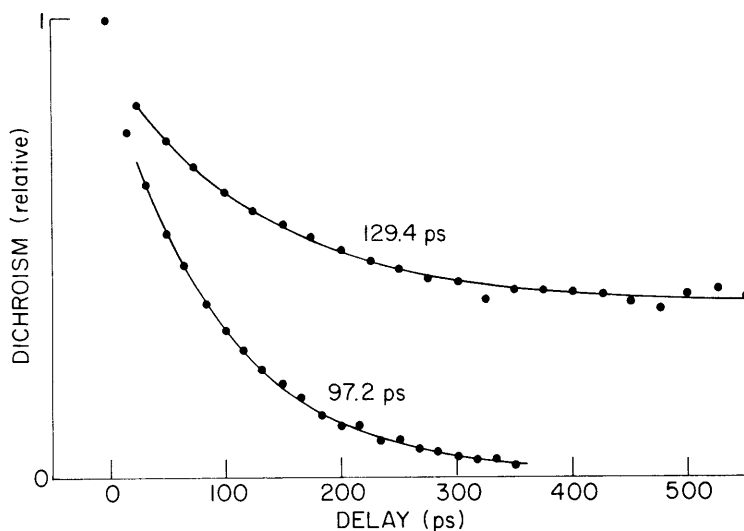


Fig. IX-1. Dichroism decay of oxazine-4 in methanol at 20° C. (Upper curve in Vycor glass.)

(IX. TIME-RESOLVED SPECTROSCOPY OF CONDENSED MATTER)

These preliminary results show that interesting information can be obtained about gels and polymers, and an article is in preparation. Other experiments in which dyes or fluorescence quenchers are bound to the polymers to reveal details of polymer chain motion will be carried out.

2. MOLECULAR MOTION IN CRITICAL MIXTURES

The motion of molecules in critical mixtures can, in principle, be studied by light scattering. In practice, strong quasi-elastic scattering can make the experiments difficult or nearly impossible. Time-domain spectroscopy should alleviate these problems. We have been able to measure the reorientation of nitrobenzene by means of the optical Kerr effect and are engaged in a study of the critical slowing down of orientational motion in nitrobenzene n-hexane mixtures.

3. EQUIPMENT CHANGES

During the past year, the stability of our mode-locked laser was improved to the point where integration times of several hours are possible. The experiment is now operated by a PDP 11/03 computer which analyzes the results on-line. A real-time pulse-width measuring device was constructed to facilitate alignment. An N_2 laser-pumped amplifier is under construction to permit Kerr-effect measurements in a wider variety of materials (e. g., liquid crystals).

