In this project, we tried to study the conformation and dynamics of supramolecular solutions by developing the technique of laser light scattering and by examining the fluid behavior near the critical mixing point. We improved the technique of photon correlation spectroscopy and the method of data analysis so that we succeeded in establishing a new technique for measuring particle size distributions. By relating the tricritical point of fluid mixtures to the theta point in polymer solutions, we could now study polymer solution behavior in the semidilute and gel regions.
Report

This is the final report on the ARO project related to polymer conformation studies. When I started the project in the early nineteen sixties, laser light scattering\(^1\) was in its early stages of development. The technique of optical mixing spectroscopy using the He-Ne laser as a light source and a wave analyzer as the detection instrument was demonstrated. However, the method was sufficiently insensitive that its major contribution could only be related to studies of critical opalescence\(^2-5\) where the intensity of scattered light approaches infinity as the critical point is approached.

In a conference on Laser Scattering\(^6\) sponsored jointly by the American Chemical Society and the American Physical Society in memory of the late Professor Peter J. W. Debye, the emphasis remained on light scattering studies of fluid and fluid mixtures in the neighborhood of the critical point. Studies of macromolecular solutions even in the neighborhood of its critical mixing point deal with the intensity and the angular distribution of scattered light,\(^7\) not the spectrum of scattered light.

In the late sixties and early seventies, we concentrated on critical opalescence studies of fluids and fluid mixtures\(^8,11-17,23\) including macromolecular solutions\(^9,10\) and on instrumentation. By 1972, it became clear that preliminary measurements of critical exponents should come to an end\(^18,19\) as several well-established research groups agreed upon what the accepted values were. It then became appropriate for us to begin investigation on more complex systems. We were interested in studying the polymer dynamics of random coils and of rigid polymers. However, the instrumentation and the method of data analysis still had not yet reached maturity for a fruitful investigation of such systems. Consequently, we approached the problem by examining the liquid crystal behavior of MERA\(^20,21\) and critical fluctuations of polystyrene in cyclohexane\(^22,24,26,29\). We made some advances in understanding the polydispersity effects\(^25,27,28,31\) and realized that the polymer system could be related to the fluid system near its critical point. However, the polydispersity effect required an understanding of multicomponent fluid systems.\(^30,32,33\)

As the polydispersity effects remain unresolved, we proceeded to examine some simpler biological systems\(^34,35,41,45\), a highly monodisperse polystyrene in cyclohexane\(^36\) and the possibility of Fabry-Perot interferometry\(^37-40\) for
eventual bulk polymer studies. By the late seventies, the instrumentation finally reached maturity and we developed a histogram method of data analysis. We then used the refined technique to study the static and dynamic properties of polystyrene in transdecalin in the semidilute region, polymer diffusion in a dilute theta solution and the molecular weight distribution of poly[bis(m-chlorophenoxy)phosphazene] in chloroform. We have now developed a non-destructive technique which permits us to obtain the molecular weight distribution function of polymer solutions at extremely high molecular weights and to study polymer dynamics including coil disentanglement in the semidilute region.

The status of laser light scattering can be summarized by my book on Laser Light Scattering and more recent reviews.

References

All references of the report represent publications which were supported partially by the U.S. Army Research Office.


*Communications to the editor.
†Meeting report.


