

SANS STUDIES OF POLYMERS*

George D. Wignall

National Center for Small-Angle Scattering Research
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Before the application of small-angle neutron scattering (SANS) to study polymer structure, chain conformation studies were limited to light and small angle x-ray scattering techniques, usually conducted in dilute solution. The unique role of neutron scattering in polymer physics arises from the difference in the coherent scattering length, b_c , between deuterium ($b_D = 0.66 \times 10^{-12}$ cm) and hydrogen ($b_H = -0.37 \times 10^{-12}$ cm) which results in a marked scattering contrast between molecules synthesized from normal (hydrogenous) and labeled (deuterated) monomer units. It was realized in the late sixties that SANS from blends of normal and labeled molecules could give for the first time direct information on chain conformation in bulk polymers. In addition, water soluble polymers may be examined in H_2O/D_2O mixtures using contrast variation methods to provide further information on polymer structure. This paper reviews some of the information which has been provided by this technique using examples of experiments performed at the National Center for Small-Angle Scattering Research (NCSASR).

The NCSASR is a national user-oriented facility dedicated to studying the structure of matter on the scale of tens to hundreds of Angstroms (10^{-8} cm). The Center, sponsored by the National Science Foundation (NSF) through an interagency agreement with the Department of Energy (DOE), was established at the Oak Ridge National Laboratory (ORNL) in 1978. NCSASR facilities include full-time use of the NSF-funded, 30-m small-angle neutron scattering (SANS) instrument (1) at the High Flux Isotope Reactor (HFIR) and a fraction of the beam time on four existing DOE-funded SAXS and SANS instruments. Beam time on the various instruments is assigned on the basis of the scientific merit of the proposed research.

The first applications of the SANS technique were made in Europe in the early seventies in the area of chain configuration in amorphous polymers. It is well known that there have been basically two theoretical approaches to the molecular conformation in these systems, based on the unperturbed Gaussian (random) coil due to Flory and co-workers on the one hand (2),(3), and the meander or bundle models (4-6), where a large fraction of the polymer molecules are envisioned in a quasiparallel arrangement. Before the development of the SANS technique there was no way of directly measuring the conformation in bulk polymers and this led to intense debate and wide disagreement on this issue in the literature. SANS experiments in a range of amorphous polymers (7-16) confirmed the general predictions of the random coil model, that the overall molecular size as measured by the radius of gyration in the bulk state is the same as in an ideal Θ -solution. Table 1 shows a summary of the results of a series of measurements made at small values of the scattering vector $Q = 4\pi\lambda^{-1} \sin\theta$ where 2θ is the angle of scatter and λ is the neutron wavelength. This type of experiment measures the (z-average) radius of gyration of the polymer chain, R_g^z , which may be converted to the weight averaged radius R_g^w if the polydispersity is known.

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Table 1. Molecular Dimensions in Bulk Amorphous Polymers

Polymer	State	$(R_g^2/M_w)^{1/2}$		Reference
		Bulk	Θ Solvent	
Polystyrene	Glass	0.275	0.275	Benoit et al. (1973)
Polystyrene	Glass	0.280	0.275	Ballard et al. (1973)
Polystyrene	Melt	0.280	0.275	Wignall et al. (1974)
Polyethylene	Melt	0.46	0.45	Schelten et al. (1976)
Polyethylene	Melt	0.45	0.45	Lieser et al. (1976)
Polyvinyl- chloride	Glass	0.40	0.37	Herschenroeder et al. (1977)
Polyiso- butylene	Glass	0.31	0.30	Hayashi et al. (1983)
Polymethyl- Methacrylate	Glass (Atactic)	0.242	0.25	Kirste et al. (1972)
Polymethyl- Methacrylate	Glass (Atactic)	0.247	0.244	O'Reilly et al. (1984)
	(Syndio)	0.289	0.244	
	(Isotactic)	0.297	0.285	
Polyethylene- Terephthalate	Glass	0.385	0.39-0.42	McAlea et al. (1984)

According to the random coil model R_g^W should be proportional to $M_w^{1/2}$, where M_w is the (weight averaged) molecular weight, with the same constant of proportionality in the bulk as in an ideal Θ -solvent. It may be seen from Table 1 that this prediction holds remarkably well for amorphous polymers. These experiments have been extended to higher values of Q to test how far the local configuration in the bulk is described by this model. This is accomplished by measuring the scattering in the intermediate Q range ($0.1 < Q < 0.6 \text{ \AA}^{-1}$) which is sensitive to the local configuration of the chain over distances $\sim 10\text{-}50 \text{ \AA}$. Measurements by H. Hayashi and P. J. Flory (14) (IBM Research Laboratories and Stanford University) on polyisobutylene (Figs. 1 and 2) show that there is virtually no difference between the chain configuration in the bulk and in a Θ -solvent over this Q range, thus confirming randomness down to distances ca. 10 \AA . The data shown in Figs. 1 and 2 are in the form of Kratky plots [$Q^2 d\Sigma/d\Omega(Q)$ vs Q] where $d\Sigma/d\Omega(Q)$ is the absolute differential scattering cross section per unit solid angle per unit volume of material. Several alternate symbols have been used by NCSASR users for the scattering vector (e.g., $Q = K = \mu$) and are shown in Figs. 1 and 2 and should be taken as equivalent in subsequent figures when the data of other groups are discussed.

Most of the early SANS experiments shown in Table 1 were performed with small relative concentrations (<5%) of labeled polymer, but measurements on the 30-m SANS instrument and elsewhere have confirmed that the same information may be obtained with concentrations of labeled molecules up to 50%. Fig. 3 shows a plot of $R_g^W/M_w^{1/2}$ as a function of the mole % of labeled polystyrene (PSD) in blends of deuterated and hydrogenated polystyrene (PSH), and shows no concentration dependence (17). This development means that experiments can be performed with much greater statistical accuracy and has been particularly

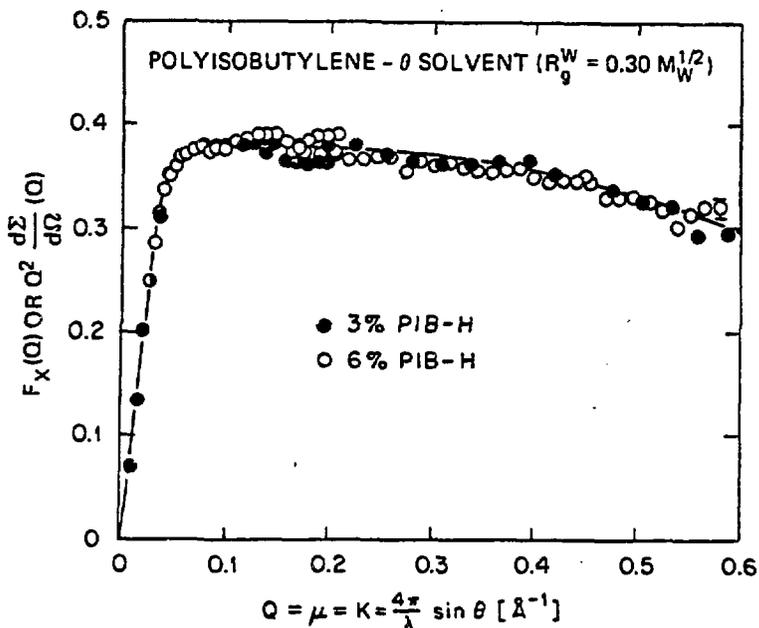


Fig. 1. Absolute Kratky functions for polyisobutylene-H in benzene-D₆. (Curve calculated from rotational isomeric theory.)

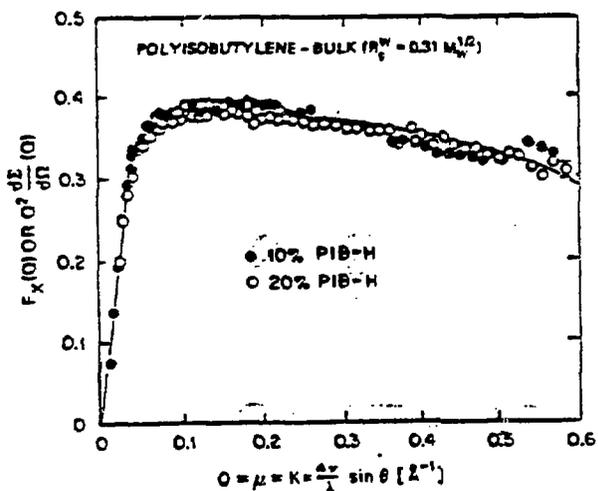


Fig. 2. Absolute Kratky functions from intermediate-angle neutron scattering (IANS) of polyisobutylene-H in polyisobutylene-D₈. The curve represents Calculations from rotational isomeric theory.

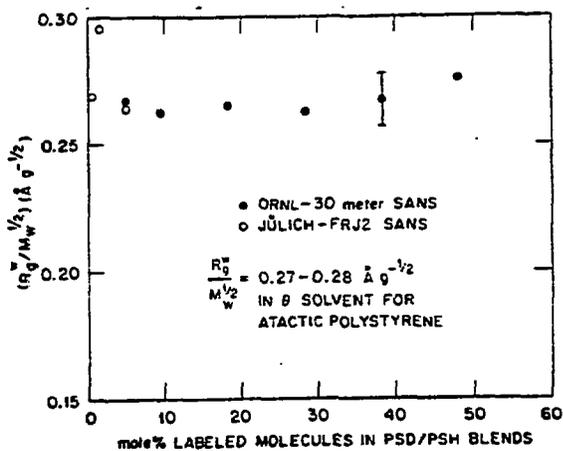


Fig. 3. $R_g^W/M_W^{1/2}$ vs mole % labeled molecules in mixtures of deuterostyrene (PSD) and normal hydrogenated polystyrene (PSH).

useful in the intermediate Q-range measurements described above, where the scattered intensities are relatively low.

The swelling of macromolecules in a good solvent arises from excluded volume interactions between pairs of monomer units on a single polymer chain. As the polymer concentration increases, the excluded volume effect is screened and diminished and in the limit of the bulk polymer the conformation of a single chain can be described as an unperturbed random coil as originally predicted by Flory (2,3) and verified by numerous SANS measurements (7-16). Since the early seventies developments in polymer solution theory involving the application of scaling methods have lead to a dramatic upsurge of interest in this area though only one systematic experimental study of chain dimensions as a function of concentration has been hitherto attempted (18). This showed that for polystyrene in CS₂ the radius of gyration varied as $c^{-0.25}$ in apparent agreement with the then current prediction of scaling laws (18). Since that time, there have been reports of many violations of scaling laws which should be valid in principle only in the asymptotic limit of infinite molecular weight. It has been a longstanding puzzle to understand why the scaling exponent (-0.25) was observed with only modest molecular weights and this had lead Professor J. S. King, W. Boyer (University of Michigan) and Dr. R. Ullman (Ford Motor Company) to attempt further measurements on polystyrene in a different solvent. Considerable effort was expended to improve the statistical accuracy of the experiment by careful attention to machine reproducibility, cross checking the consistency of the data by means of redundant data sets and also by use of high concentration deuterium labeling methods developed by G. Summerfield and Z. Akcasu (19-20) (University of Michigan). The measurements gave conclusive evidence that high concentration labeling methods give highly reproducible results and produced data with the best internal consistency of any polymer data taken at ONRL (21). Several complementary methods of analysis were employed, and each led to the conclusion that the concentration exponent (-0.163) for the molecular weight range measured (~100,000) fell substantially below that predicted by scaling theory (Fig. 4).

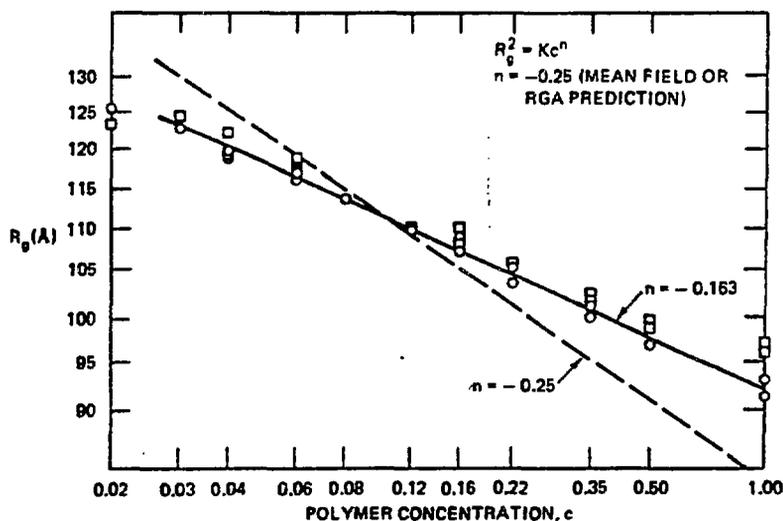


Fig. 4. Variation of R_g with c for polystyrene in toluene.

One of the most important methods of synthesizing modern polymers utilizes emulsion polymerization and the product so formed is a polymer particle called a latex. In recent years much interest has focussed on the preparation of latex co-polymers with radial compositional gradients using a controlled monomer feed. Formation of the desired product requires that the locus of polymerization be at the aqueous interface of the growing particle (latex) and that the reaction be carried out under nearly monomer-starved conditions, i.e., the rates of polymerization and monomer addition must be nearly equal. The structure of the latex markedly affects the properties of the bulk polymer and while the condition of monomer starvation is achievable, identification of the locus of polymerization cannot be investigated directly and had been the subject of considerable debate. Grancio and Williams (22) postulated a polymer-rich spherical core surrounded by a monomer-rich shell which serves as the major locus of polymerization, thus giving rise to a core-shell morphology. This model, in which the first formed polymer constitutes the core and the second formed polymer makes up the shell has received much support but also significant criticism. The SANS technique has been used to investigate the structure of such polymer latexes by L. Fisher, S. M. Melpolder and J. M. O'Reilly (Eastman Kodak Company), who have studied normal (homogeneous) PMMA latexes with deuterated shells of PMMA-D or PSD polymerized on the surface. The scattering from the original PMMA-H latex is a Bessel function (23) exhibiting sharp maxima and minima for monodisperse particles, though in practice these sharp features are smeared by the finite experimental resolution (Fig. 5). Accurate desmearing procedures using indirect Fourier transform methods developed by Moore (34) and Glatter (25) have been used to remove these instrumental effects and lead to patterns showing the expected sharp minima (Fig. 5) with good agreement between the core radii determined by SANS ($R = 492 \text{ \AA}$) and independently by light scattering ($R = 485 \text{ \AA}$). Figure 6 shows the scattering pattern for a PMMA-H ($R = 495 \text{ \AA}$) core with a PMMA-D shell (thickness 30 \AA) polymerized on the surface.

Fig. 5. $I(K)$ vs K for 4.9 vol % monodisperse PMMA-H spheres (core 10111) in D_2O/H_2O mixture.

The sample was run in an H_2O/D_2O mixture which was adjusted to match the scattering length density of the core, thus leaving only the hollow shell scattering. The agreement between the desmeared experimental data and the theoretical hollow shell scattering is excellent, thus confirming a core-shell morphology for the latex (26,27). Similar experiments by

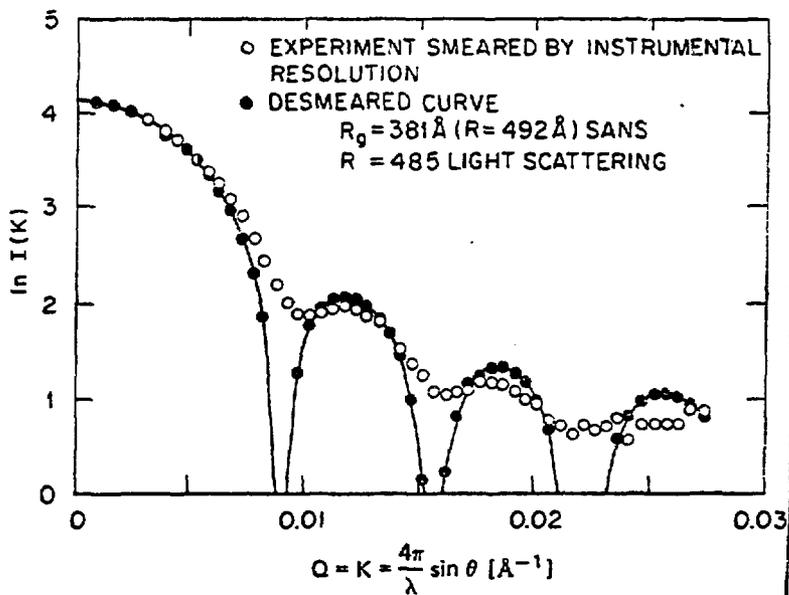
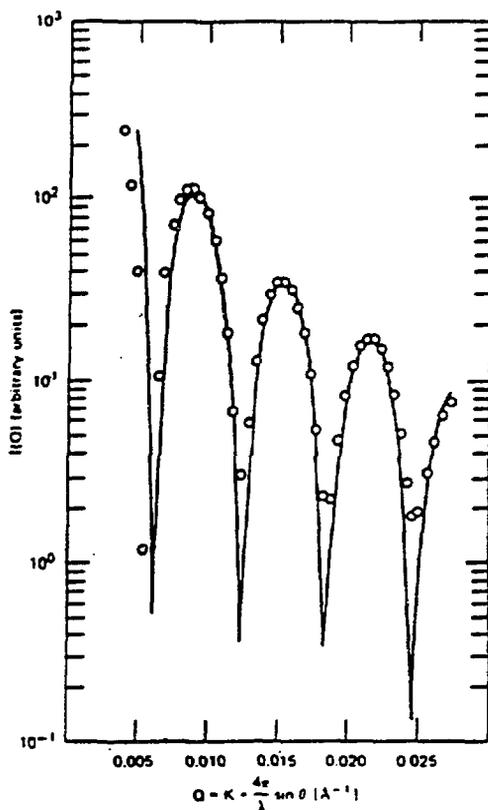


Fig. 6. Desmeared SANS data (O) for PMMA latex with 30 Å PMMA-D shell on surface (core contrast matched) compared with theoretical hollow shell scattering.

M. P. Wai and R. A. Gelman (Hercules Inc), on a partially deuterated PMMA shell polymerized on cores consisting of random PMMA/PS co-polymers also demonstrated a core-shell structure with excellent agreement between the overall size measured by SANS and transmission electron microscopy (28).

For economic reasons it has become increasingly difficult over the past two decades for the chemical industry to introduce new commercial polymers, and hence much interest has focussed on the possibility of producing new materials by blending existing polymers. Before the application of small-angle neutron scattering, the methods used to investigate polymer blend compatibility (microscopy, calorimetry, etc.) could indicate macroscopic segregation but could not demonstrate fine grained separation or intermixing at the level of the molecular segments. SANS from blends where a fraction of one polymer species has been deuterium-labeled is a sensitive test of compatibility at the segmental level, and also provides information on chain configuration in the blend (29). Extensive investigation of blend compatibility by SANS and other techniques have been undertaken by scientists from the University of Massachusetts, Xerox Corporation, and Exxon Chemical Company (30-32). Blends shown to be compatible at room temperature for all compositions included polystyrene/polyvinylmethyl ether, atactic/isotactic polystyrene, and Polystyrene/polyphenylene oxide. The polystyrene/polyvinylidene fluoride and polystyrene/polyortho-chlorostyrene systems have been shown to exhibit compatibility for certain ranges of composition, whereas blends of high and low density polyethylene are virtually phase separated in the solid state. The latter result is a consequence of differential crystallization effects rather than a basic incompatibility of the species (31). Recent developments in scattering theory (33,34) have shown how the Flory interaction parameter χ of binary polymer blends at high concentration may be determined from SANS data. In principle, the same information may be obtained via light scattering or SAXS, though the method is currently more suited to SANS because of the enhanced contrast which may be obtained via deuteration. This situation may change in the future as the enhanced flux of synchrotron sources permits the exploration of the χ parameters of blends with relatively low SAXS contrast.



However, the molecular radii of gyration of the different blend components may be determined only via SANS studies from 3 component blends consisting of labeled and unlabeled polymer A blended with polymer B (33). The scattering theory for phase separated blends has also been developed to the point where the R_g of molecules confined within a domain may in principle be determined from SANS (35) and several experiments along these lines have already been performed (36-38).

There is considerable current interest in the topic of the diffusion of polymer chains in the bulk polymer both from the theoretical and experimental viewpoint. Following DeGennes the diffusion on a microscopic scale is envisioned as the reptation of a chain along a tube formed by the entanglements of neighboring molecules. There had been considerable debate concerning the applicability of this concept over the distance scale ranging from a chain segment to the size of the overall radius of gyration. Over the latter range measurements had been previously performed by microdensitometry on samples of deuterated and protonated polymers which were allowed to interdiffuse at an interface which was then sectioned and examined by IR methods. Due to the limiting thickness of sections this method was effectively limited to molecular weights below 10^4 which needed time scales of the order of a month for measurements (39). Professor B. Crist, C. Bartels (Northwestern University) and Dr. W. Graessly (Exxon Research) have used SANS methods to extend the available range of diffusion coefficients which may be studied by preparing samples consisting of alternate layers of deuterated and protonated polymers. As the temperature is raised and diffusion proceeds, the spatial modulations in composition decay and the scattering grows progressively at intermediate angles, finally reaching the pattern corresponding to a uniform molecular mixture of deuterated and protonated components. Analysis of the time dependence of the scattering yields the polymer diffusion coefficient (D) and due to the small distance scale probed by the SANS method, measurements may be extended by approximately three orders of magnitude beyond the limit of IR microdensitometry (40,41). Initial measurements on monodisperse fractions of hydrogenated polybutadiene confirm the prediction that $D \sim M^{-2}$ and give activation energies in good agreement with theoretical estimates (Fig. 7).

The above experiment is an example of a study of a dynamic process via quasi-static techniques where a sample is fabricated with a nonequilibrium concentration gradient, a process is allowed to proceed for a give time and then the sample is then frozen and examined by static techniques. Another example of such a measurement using SANS is the investigation of transesterification kinetics in polyesters by K. P. McAlea and J. M. Schultz (University of Delaware) and K. H. Gardner (E. I. Dupont de Nemours Co.). Mixtures of labeled and unlabeled polyethylene terephthalate molecules were heat treated for various periods and quenched to room temperature where they were examined by SANS. Transesterification acts to alter the lengths of the deuterated and protonated sequences due to chemical reactions between the chains. The effective block length of the deuterated segments may be measured from the extrapolated $Q = 0$ cross section and Fig. 8 shows that it falls from a value corresponding to the original chain length by a factor ~ 5 in 10 mins at 270°C . To the authors' knowledge such information is not available from any other technique and is another example of the unique

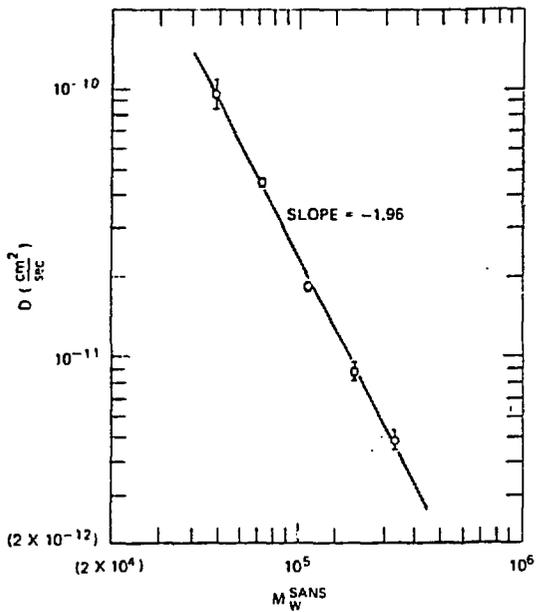


Fig. 7. Molecular weight dependence of diffusion ($T = 125^\circ\text{C}$) for hydrogenated polybutadienes.

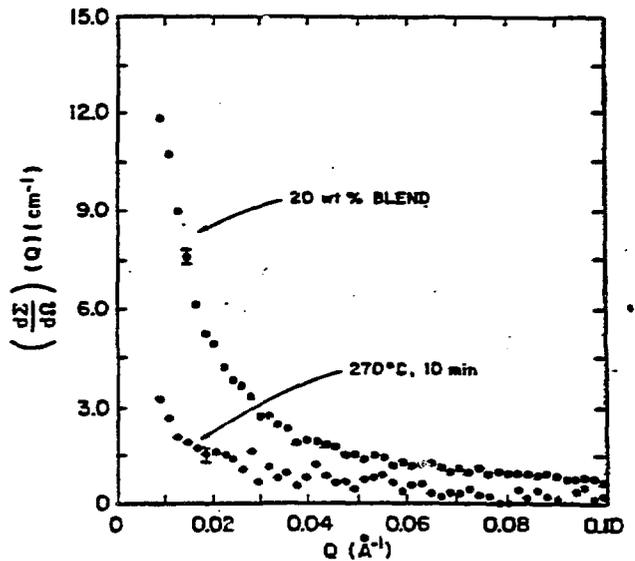


Fig. 8. $(d\Sigma/d\Omega)(Q)$ vs Q for a 20 wt % PETD sample annealed at 270°C for 10 minutes.

information which is currently being from SANS experiments on partially labeled blends. To date the majority of measurements of dynamic processes by SANS have employed such quasi-static techniques. The study of real time transient processes is just beginning and examples of this kind of work together with microscopic dynamical studies of polymer chain motion will be discussed in a paper by Dr. John B. Hayter (Oak Ridge National Laboratory) which also appears in these Proceedings.

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