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Neutron Scattering from Polyacetylene-Polyisoprene Block Copolymers

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INTRODUCTION

The soluble block copolymers of acetylene and isoprene produced by Aldissi[1] using anionic polymerisation and Zeigler-Natta coupling catalysts show a strong dependence of electrical conductivity (after doping) on the volume fraction of polyacetylene.[2] The threshold for this conductivity occurs at about 16% (v/v) and rises very steeply at higher concentrations. Preparations up to *c* 25% are soluble in toluene or hexane and have the property of retaining residual solvent when pumped to 10^{-3} τ at 300 K in a gel state. At 30% polyacetylene, the material is a hard solid which can be slightly swollen by solvent above room temperature and which is susceptible to iodine doping from the vapour.[2]

Our interest is to relate these physical and chemical properties to the texture of the gels and solids produced by polymerisation. The problem is related to recent interest in co-polymer phase separation.[3] The properties of our materials are in contrast with other novel acetylene block copolymers[4] recently synthesised as these have, for the example of polystyrene, higher molecular weight but low conductivity.

Small angle neutron scattering[5] has been chosen to probe the polymer texture. Distance scales from *c* 10 Å to *c* 1500 Å were accessible using the small angle camera D17 at Institut Laue-Langevin, Grenoble and the small angle diffractometer (SAD) at the Intense Pulse Neutron Source (IPNS), Argonne National Laboratory. The intensity of neutrons scattered, $I(Q)$, as a function of neutron momentum transfer, Q, ($Q = 4\pi\sin\theta/\lambda$ where θ is the half-angle of scattering) may be written for our two component system as

$$I(Q) = K \sum_{j=1}^{N_p} \left\langle \left\{ \int_{V=j} (\rho(R) - \rho_s)\exp(iQ \cdot R)_d^3 R \right\}_j^2 \right\rangle \qquad (1)$$

where K is an experimental constant, $\rho(R)$ is the scattering length density at R in the jth polyacetylene particle whose volume is V_j, ρ_s is polyisoprene-solvent) and the sum is over the N_p polyacetylene particles.

To increase the contrast $(\rho_p - \rho_s)$, the polyacetylene component was completely deuterated in the synthesis and a hexane-toluene solvent mixture chosen to match the scattering length density of the isoprene for the measurements on 10% $(CD)_x$-isoprene and 20% $(CD)_x$-isoprene. The $(CD)_x$ density was taken as 1.2 gcm^{-3} and the polyisoprene density as 0.9 gcm^{-3} giving scattering length densities of 6.87×10^{10} cm^2 and 0.27×10^{10} cm^2 respectively.

To characterise the scattering patterns we have used various model scattering laws. In the lowest Q regions the radii of gyration (R_g) of the polyacetylene density distributions have been determined by least squares fitting of the Guinier[6] expression in equation (2):

$$\exp(-Q^2Rg^2/3) \tag{2}$$

Again, as a first approximation, the Guinier expression for scattering by cylinders of radius R and infinite length, in Equation 3:

$$(-Q^2Rg^2/8) \tag{3}$$

was useful for analysing the 30% $(CD)_x$ system.

Following the recent work of Schaeffer[7] and Teixeira[8] we have analysed the Porod region[6] of the scattering and tested Teixeira's fractal model over a wide range of Q, as a representation of the type of aggregation occurring from the polymerisation reaction. The scattered intensity is represented by the product of a form factor $P(Q)$ and a distribution function, $S(Q)$

$$I(Q) = n\,P(Q) \cdot S(Q) \tag{4}$$

For simplicity we have chosen, $P(Q)$, appropriate to spheres, that is we represent the scattering objects as an aggregation of monodisperse spheres of radius, R and Volume V_s.

The form of $P(Q)$ and $S(Q)$ then is

$$P(Q) = V_s^2 \left[\frac{3(\sin QR - QR\cos QR)}{Q^3R^3}\right] \tag{5}$$

$$S(Q) = 1 + \frac{1}{(QR)^D} \cdot \frac{D\Gamma(D-1)}{\left[1 + \dfrac{1}{Q^2\xi^2}\right]^{1/2(D-1)}} \times \sin[(D-1)\tan^{-1}(Q\xi)] \tag{6}$$

here ξ is the aggregate size (Å), $(\rho_p - \rho_s)$ the difference (sphere–background polymer) in scattering length densities between deuterated polymer and polyiso-

prene, D the fractal dimensionality and n the density of scattering particles (mol cm^{-3}). The sphere radius, aggregate size and fractal dimensionality are the parameters. In practice, e.g. for the 30% $(CD)_x$ sample, the cylindrical Guinier fit (Equation 3) gives a radius parameter which may be fixed in the fractal fitting process (that is, we are assuming rod-like structures made up from spheres of the same diameter). Because the small angle measurements with the different instruments used fall with different densities in Q space, the statistical significance of data varies with Q. In deciding the quality of fit this feature must be taken into account and we have attempted this by using four different error measures in the least squares process ((a) PRFMODCON, (b) PRFLOGCON, (c) PRFSQRCON and (d) PRFSTACON).

(a) modified least entropic metric $\sqrt{y}(\log y)^4 - \sqrt{\hat{y}}(\log \hat{y})^4$,
(b) the logarithmic values of the experiment and the model,
(c) the square root of the absolute difference between the experiment and the model, and
(d) the square of the difference between the experiment and the model weighted by the proportional statistical error in the experiment.

EXPERIMENTAL

Samples were contained in silica cells with a 1 mm path length. The 30% $(CD)_x$ sample was a coarse grained powder which was measured dry (at IPNS) and also when wetted with toluene. The 10% and 20% samples were measured in two ways: (a) the samples were sealed off in the cells under vacuum (10^{-3} torr) and never came into contact with air or nitrogen—these are labelled 10% $(CD)_x$ NEW and 20% $(CD)_x$ NEW respectively. They were free running solutions* and contained c 40% toluene as solvent as estimated from the stoichoimetry of the monomer solution and the acetylene uptake. In order to increase the concentration of a second set of solutions from the same initial batch, dry N_2 was blown through at 25°C in a nitrogen glove bag. These samples, called 10% $(CD)_x$ OLD and 20% $(CD)_x$ OLD, were more concentrated than the new samples but it proved impossible to dry the samples out completely at 25°C—even under vacuum.

The molecular weight of the CD blocks was about 2000 in all samples as determined by gel permeation chromatography. The corresponding figures for the polyisoprene blocks were 7500, 8500 and 10000 for the 30%, 20% and 10% samples respectively determined by the same method.

On the D17 instrument, a camera length of 3.4 m and wavelength 12 Å was used. Transmission and background measurements on cells, cells plus solvent and

*We noticed that the 10% system showed an increased viscosity over a period of a few months and after a year had phase separated. This behaviour is not seen with the corresponding fully protonated system.

a cell plus water were measured. Because statistics on the water were better than for the solvents, this was subsequently used for background subtraction—due allowance being taken for transmission. The Q-range covered was 0.004–0.06 $Å^{-1}$. At IPNS small angle diffractometer, SAD, the full range of wavelengths (c 1.0–14 Å) were used which gave a Q-range of 0.004–0.4 $Å^{-1}$. Transmissions and backgrounds were measured again. At IPNS it was found necessary to make careful corrections for the delayed neutron fraction and time-dependent detector response resulting from the characteristics of the source.

RESULTS

A. D17 measurements

The 30% $(CD)_x$ sample (after an empty cell subtraction) gave very strong scattering. In the Guinier approximation, a radius of gyration of 190 Å was extracted and reasonable fits were also observed for Q interval 0.014–0.052 $Å^{-1}$ giving a radius of 30 Å (Figure 1a). It was characteristic of this sample that the log-log plot was quite straight over nearly the whole Q-range of this instrument with a slope close to 1.0 (Figure 1b).

The 20% $(CD)_x$ (NEW) sample, after subtracting a 1 mm water background (equivalent to hexane), has a quite different scattering pattern to the 30% material both in the Guinier presentation (R_g = 232 Å) (Figure 2a) and in the log-log graph (Figure 1b) where the power law slope is approximately 2.95 at low Q. Though the scattering from 10% $(CD)_x$ NEW and OLD after subtracting a water and cell background is rather weaker than that from the 30% sample, reasonable Guinier laws were followed (Figure 2 (b), 2 (c)) as well as power law slopes near 1.0 for the OLD and NEW samples (Figure 3). The Guinier radius was 135 Å at the lowest Q and, as for the 30% sample, nearly linear regions at higher Q were observed giving R_g = 24 Å ($0.82 < QR < 1.27$) for 10% $(CD)_x$ OLD and R_g = 30 Å ($1.02 < QR < 1.57$) for 10% $(CD)_x$ NEW.

B. SAD measurements

The large Q-range covered by the SAD at Argonne allows $I(Q)$ and hence the power law of the scattering and form factor to be measured to momentum transfers of c 0.35 $Å^{-1}$.

Initial attempts to do this were frustrated by an apparent excess scattering near 0.035 $Å^{-1}$ in the 30% $(CD)_x$ data (Figures 4a, 4b). This was not due to low angle diffraction but was traced to an interesting systematic error in data from some samples due to the delayed neutron emission and detector desensitisation resulting from characteristics of the pulsed source.[9] Measurement of these instrumental quantities and suitable corrections made to the data treatment[10] gave scattering laws which were similar to those determined at Grenoble (Figures 4c, 4d).

At the lowest Q, the Guinier radius was again determined as 194 Å for 30% $(CD)_x$, (See Table I). We wished to investigate more specific models for the scat-

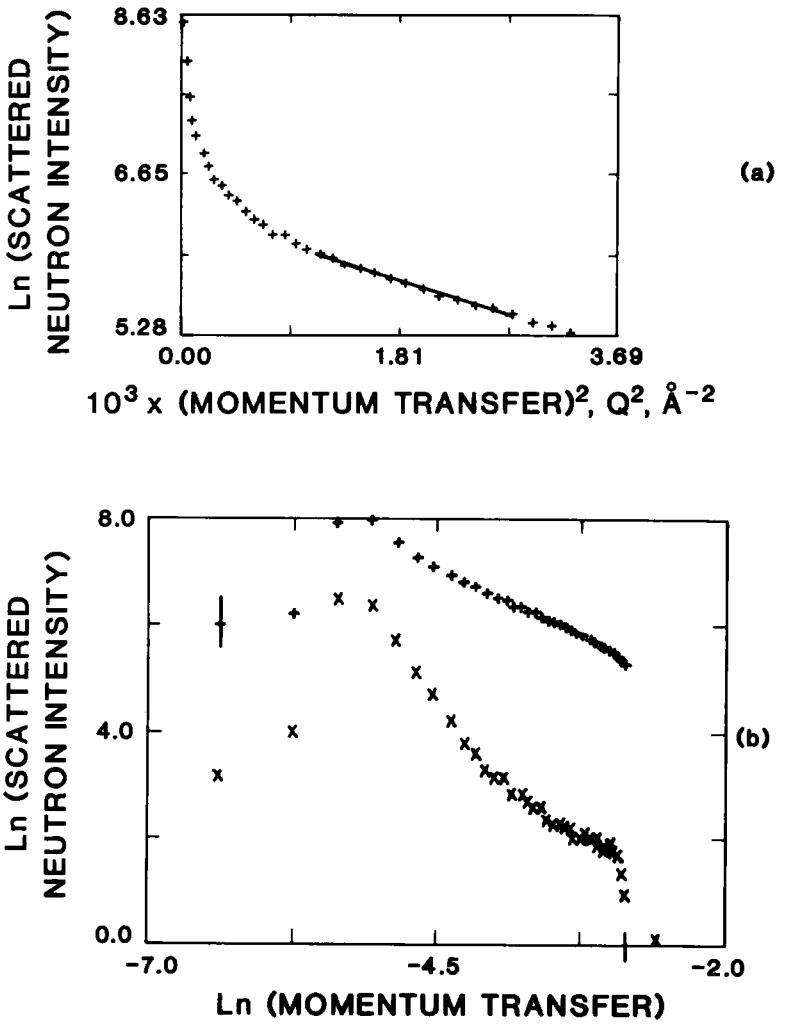

FIGURE 1

tering, so Figure 5(a) shows the data from 30% $(CD)_x$-$(isoprene)_n$ superimposed with the scattering law for isolated infinite cylinders of radius 28.6 Å using the programme PRCOSTAT.[11] This model is a fair approximation to the scattering below ln $Q = -2.0$ for this sample and was the first indication of a possible cylindrical shape for the dominant scattering species.

The minimised function in PRCOSTAT is given in equation 7:

$$\Delta = \sum_{n=1}^{N} (I_{mod} - I_{exp})^2/(I_{err}/I_{exp}) \tag{7}$$

where I_{mod} = model intensity, I_{exp} = experimental intensity and I_{err} is the error

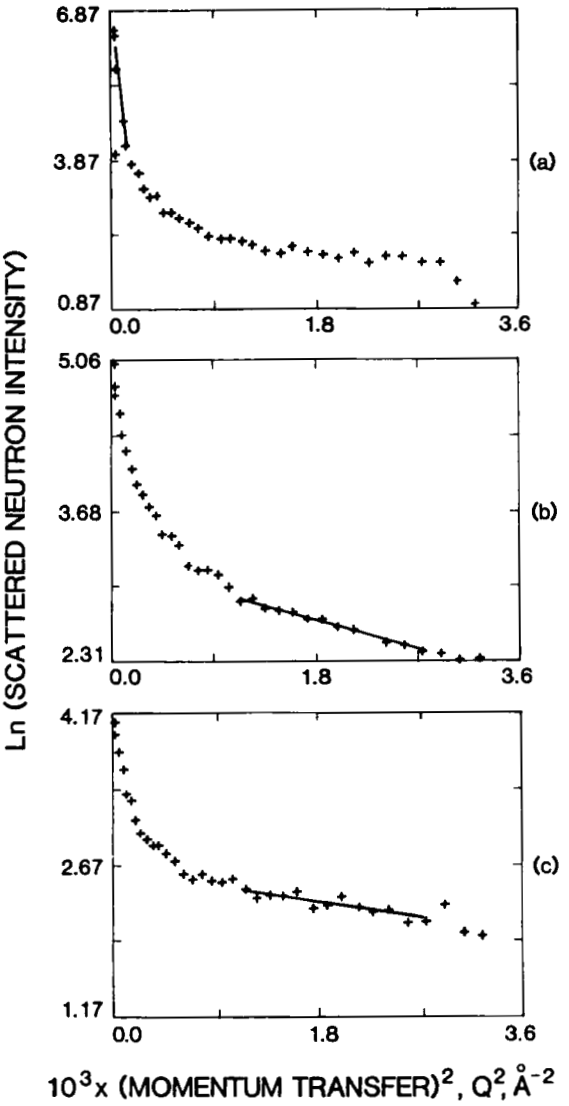

FIGURE 2

in the experimental intensity. Figure 5(b) is similar to Figure 5(a) except that the radius is constrained to a value of 25 Å. The improved fit illustrates the low-Q weighting given by use of Equation 7. It was this fact that sensitised us to the need to use different error measures in fitting data subsequently.

The infinite cylinder model is poor for both the 20% $(CD)_x$ NEW sample (Figure 6(a)) and the 10% $(CD)_x$ NEW data (Figure 6(b)). In an attempt to get a better fit of the 10% NEW solution, the infinite cylinder condition was relaxed, i.e. both

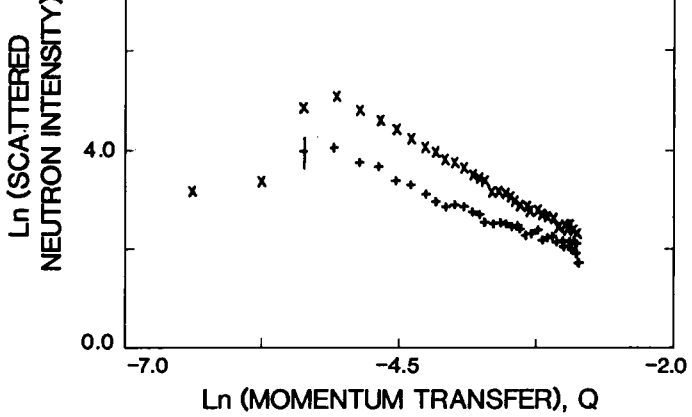

FIGURE 3

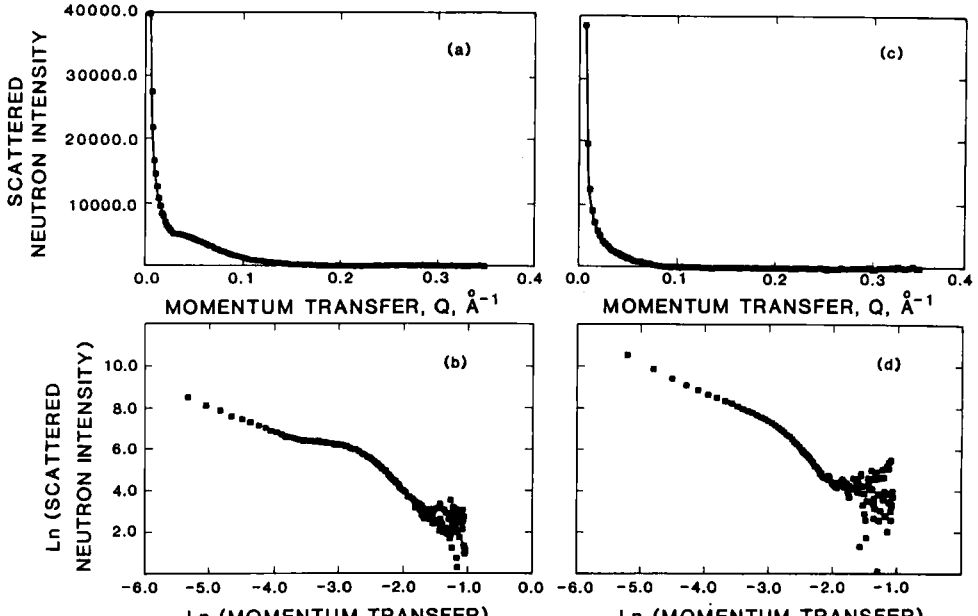

TABLE I

Sample	Run No.	abInstr.	I_o	Error	R_g	Error	Q_{min}	Q_{max}
30%	1798	SAD	600		193		0.004	0.015
	16397(2)	D17	11600	300	33	0.9	0.014	0.052
		"	13000	1200	44	7	0.014	0.026
	16397(3)	"	558	8	31	0.4	0.034	0.052
		"	3000		193		0.005	0.015
20%OLD	1813	SAD	2.2		87			
20%NEW	16401	D17	2573	230	159	7	0.006	0.014
		"	918	190	232	13	0.006	0.012
		"	11	1	27	2	0.034	0.052
10%OLD	1814	SAD	55		17			
			20		91			
	16398	D17	174	15	35	2	0.028	0.052
			263	27	56	6	0.012	0.029
10%NEW	16399		452	22	41	1	0.028	0.052
			1035	17	76	12	0.012	0.020
			25	1	30	1	0.03	0.052
			65	6	135	11	0.005	0.012

the cylinder length and radius were allowed to vary using the programme PRCSTAT.[11] The result was an even worse fit so this approach was abandoned.

The relatively large Q-range over which a power law exponent (c 1.0) fits the data for the 30% and 10% (v/v) samples suggested further modelling of the texture in these samples using a self-similar basis for the distribution function.[8] Aggregation occurs in such copolymer systems as the growing chains are released into solution by the acetylene polymerizing catalyst and this we model using a series of programs[11] based on recent developments.[7,8]

Figure 7(a) shows the 30% data up to ln $Q = -2.3$ modeled by monodisperse spheres of radius 30.4 Å in an 870 Å aggregate of fractal dimension 1.55. The precise values of these parameters are determined by the fitting process and depend on the minimisation function used. Note that the data do not fit at higher Q values—a fact which may be due to our assumption of monodispersity in the aggregate building blocks. The fits for 20% (Figure 7(b)) and 10% (Figure 7(c)) are also shown after the subtraction of a flat background. This background was that intensity required to give zero true scattering at high Q. In all of these figures we have measured deviation of the model curve from the data by a least squares procedure. We now look at the effect of different error measures.

The radii, aggregate sizes and fractal dimensionalities for various statistical ways of fitting the model to the experiment are given in Table II and the data shown in Figures 8, 9 and 10. As no turnover was observed for the 20% and 30% systems, the radius (coming from $P(Q)$) is poorly characterized—the model serves rather as mathematical construct for the scattering distribution. In only the 30% material

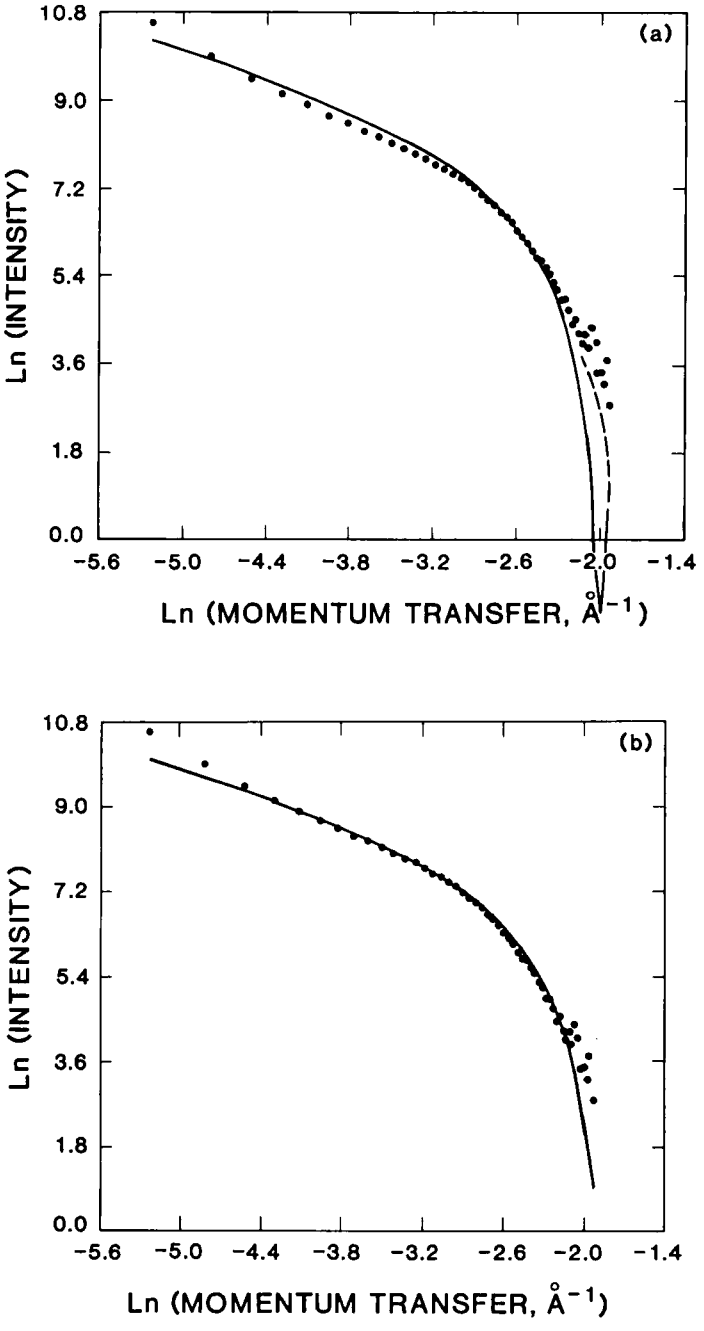

FIGURE 5

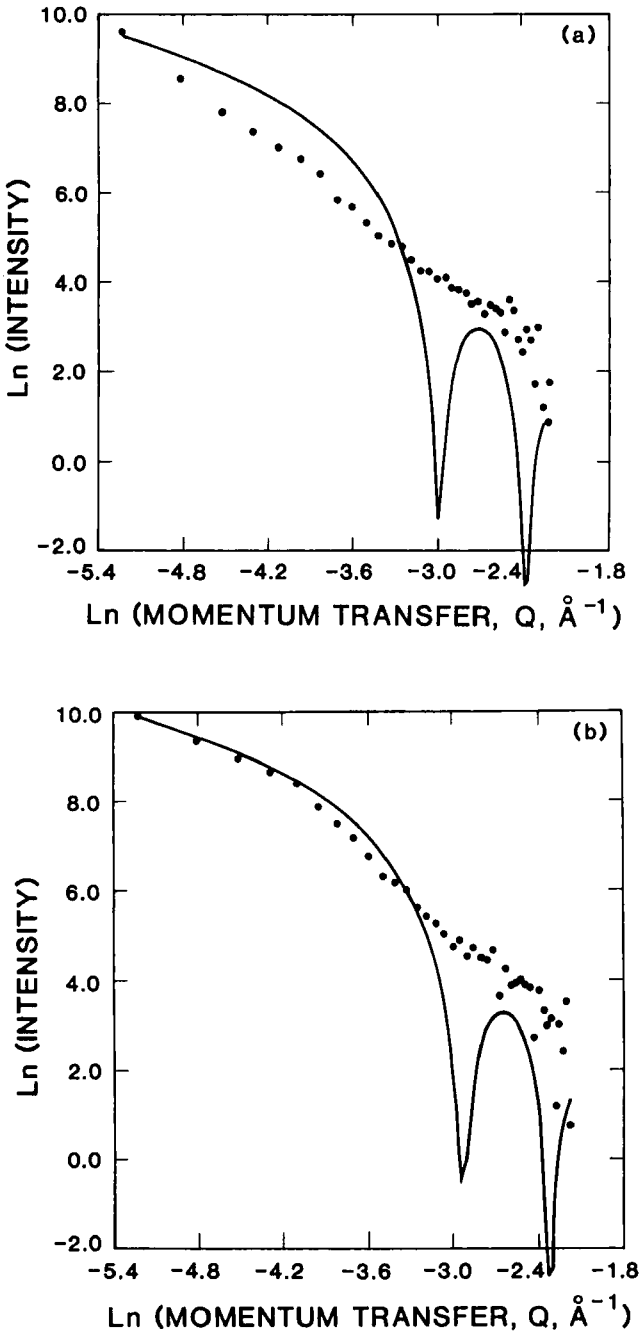

FIGURE 6

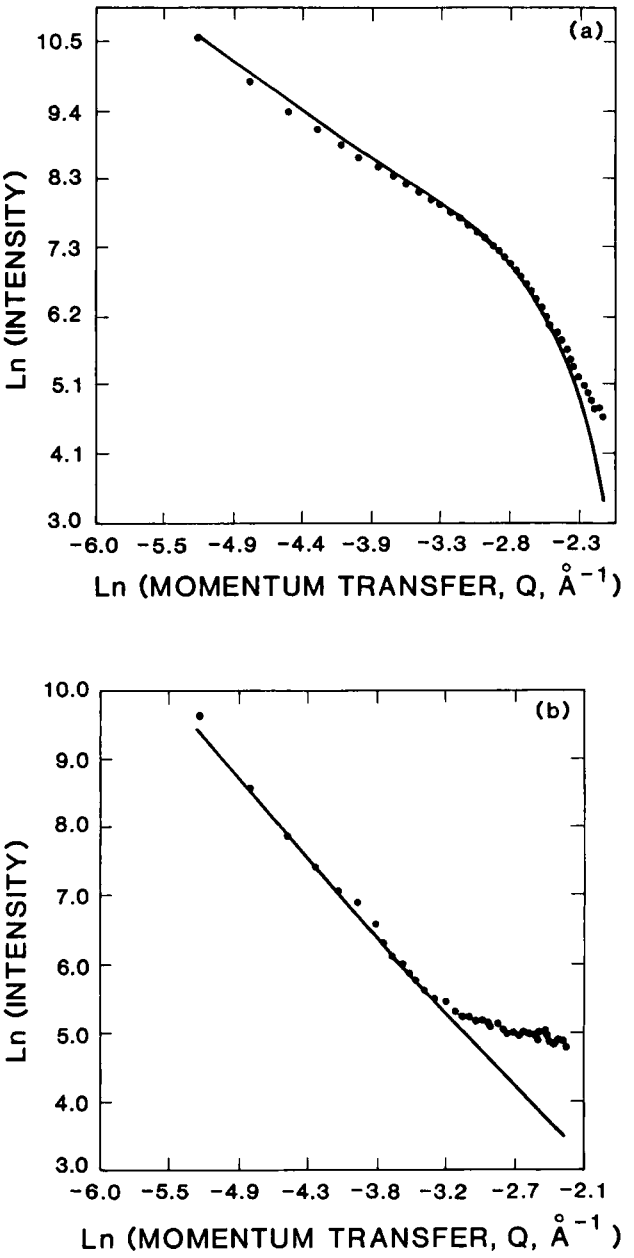

FIGURE 7

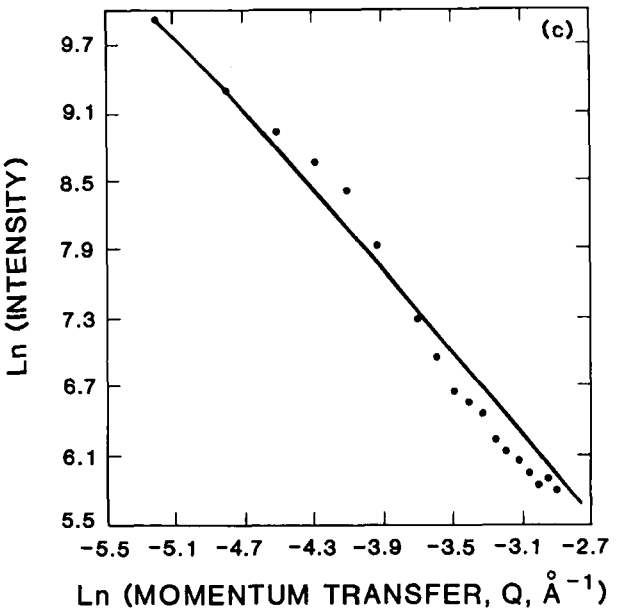

FIGURE 7 [Continued]

can we be sure that the radius has physical significance—the range of Q used for the other samples being inadequate to define a form factor. There is a steady decrease in fractal dimension from 10% to 20% to 30% systems accompanied by increase in aggregate size.

TABLE II

Fractal analysis of power law and form factor scattering from deuterated polyacetylene-polyisoprene copolymers

Sample [6~	Run Number /Instrument	Radius å	Aggregate Size å	Fractal Dimension-ality	Model Fitting Method
30%(CD)$_x$PI	2295/SAD	30.1	1452	1.49	MOD
NEW	"	32.5	1513	1.51	STAT
	"	34.5	1534	1.35	SQR
	"	27.8	288	1.61	LOG
20%(CD)$_x$PI	2294/SAD	4.2	426	2.42	MOD
NEW	"	3.0	455	2.42	STAT
	"	2.0	850	2.40	SQR
	"	1.6	507	2.41	LOG
10%(CD)$_x$PI	(2364+2365)/SAD	3.9	118	2.61	MOD
NEW	"	2.0	119	2.60	STAT
	"	3.0	120	2.60	SQR
	"	1.0	117	2.62	LOG

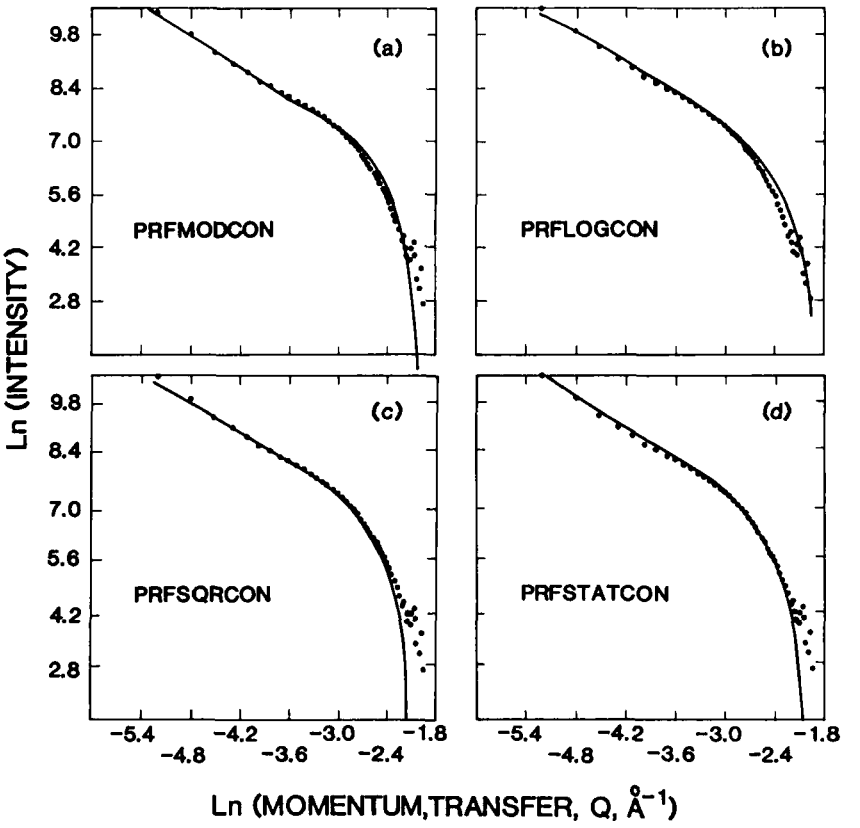

FIGURE 8

DISCUSSION

Within the bounds of our model, different structures are indicated for the 30%, 20% and 10% copolymers. Increase in the polyacetylene fraction leads, initially, to decreased dimensionality for the $(CD)_x$ clusters whose overall aggregate size grows with $(CD)_x$ content. This increase in overall size is consistent with the qualitative increase seen for I_o in Table I—and the 30% $(CD)_x$ system is indeed a very strong scatterer—like fibrous deuterated Luttinger polyacetylene itself.[12] For the 10% $(CD)_x$ and 20% $(CD)_x$ gels the simple measure of radius of gyration (at the lowest Q values) also gives an R_g which increases with $(CD)_x$ content in accord with the above. We conclude that analyses by radius of gyration and using the fractal basis are consistent where they overlap.

The fractal dimensionality, D, gives an interesting perspective of these copolymers, D, consistently *decreasing* as the $(CD)_x$ content is increased. The tendency of the $(CD)_x$ clusters is to elongate to a habit which is seen fully developed in pure $(CD)_x$ fibres. This results from the strong interchain $(CD)_x$ – $(CD)_x$ cohesive

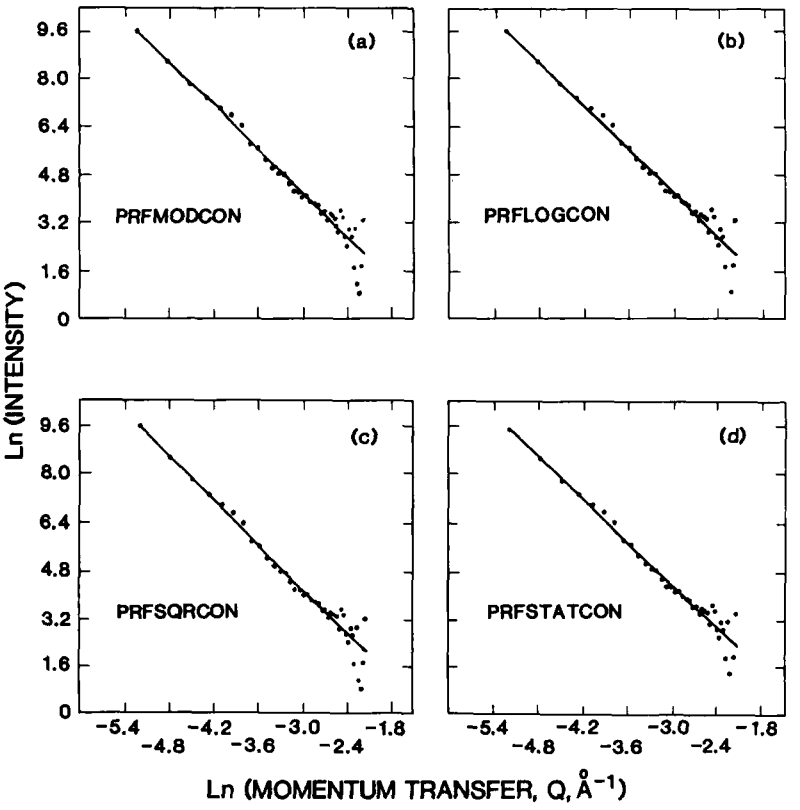

FIGURE 9

forces which compete with entropic and surface tension terms in the free energy responsible for mixing the two polymer constituents.

Domain formation in AB block copolymers has been discussed by Meier[13,14] in terms of the relative stability of different shaped domains as a function of volume fraction and polymer molecular weight. This stability is determined by the interplay between the surface free energy and negative entropic terms resulting from, the restriction in A-B covalent bonds, the requirement that A and B segments remain in their own domain spaces and from the perturbation of chain dimensions in domains compared to their random flight values.[15] For the systems considered, by Meier spherical domains were preferred at volume fractions (ϕ) below 20%, cylindrical domains for $20\% < \phi < 30\%$ and lamellar structures at higher concentrations.

Our results show that $(CD)_x$/polyisoprene at low volume fractions 10% and possibly 20% and room temperature, is most probably micellar with the micelle becoming more elliptical in the 20% region but that for 30% $(CD)_x$ the domains are elongated—approaching cylindrical form. This evolution is in accord with the striking increase in electrical conductivity with $(CH)_x$ volume fraction when these

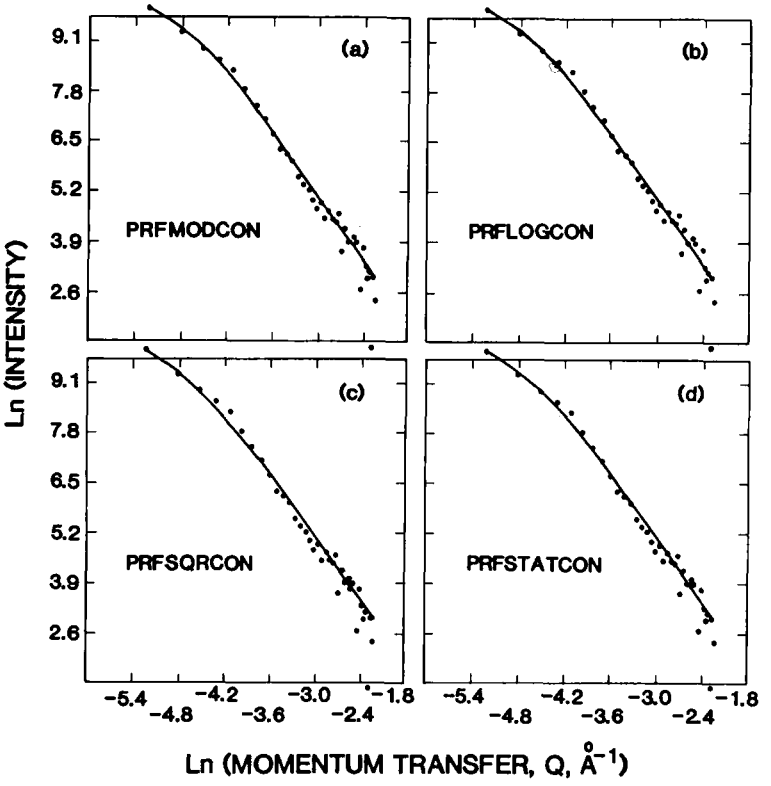

FIGURE 10

materials are doped. Even if the shape of $(CD)_x$ domains did not change—a percolation threshold appropriate to that for say the 10% system ($D = 2.6$) would be approached as the volume fraction increases. But with a change in domain shape to near cylindrical form ($D = 1.5$) this threshold is itself lowered. The onset of conductivity as a function of volume fraction thus becomes a very steep function of V.

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