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Fractal Behaviour of the Polyaniline Surface

By

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Introduction Polyaniline (PANI) can be synthesized chemically or electrochemically and made electrically conductive by doping. It has good chemical and thermal stability. Thus, this material has attracted considerable attention in both basic research and commercial development [1].

It is well known that the structure of conducting polymers is difficult to characterize for understanding their electronic and optical properties. Although electron micrographs have shown a richness in behaviour of conducting polymers, the rich information is difficult to quantify. Small-angle X-ray scattering (SAXS) is a useful technique for investigating the structure of materials on a scale from about 0.5 to 200 nm. The external fractal surface behaviour can be determined by measurement of the SAXS intensity [2, 3].

In this note we present the SAXS study of the PANI and its surface behaviour is discussed in the light of fractals.

Experimental The PANI sample used in the present study was synthesized chemically using techniques described earlier [4]. The infrared spectra of the PANI indicate that the molecular structure of the PANI was in agreement with literature. For the direct SAXS measurements the powdered reaction product of PANI was compressed into cylindrical pellets having a diameter of 10 mm and a thickness which varied from 0.5 to 1 mm. The SAXS measurements were made using a position sensitive detector, a small-angle goniometer, and a step-by-step scanning technique. Nickel-filtered CuKα (λ = 0.154 nm) radiation and slit collimation were employed in all the measurements.

Results and discussion The scattered intensity $I(q)$ from a surface fractal is given by [5, 6]

$$I(q) = NI_0(qa), \tag{1}$$

where $q = 4\pi\lambda^{-1} \sin(\theta/2)$ is the modulus of the scattering vector, λ the X-ray wavelength, θ the scattering angle, $I_0(qa)$ is the scattered intensity from one scatterer, and a the diameter of a randomly oriented aggregate with N surface fractals in the scattering sample. In the two-phase approximation from (1) and $qa \gg 1$ we obtain

$$I(q) \sim q^{-(6-D_s)}, \tag{2}$$

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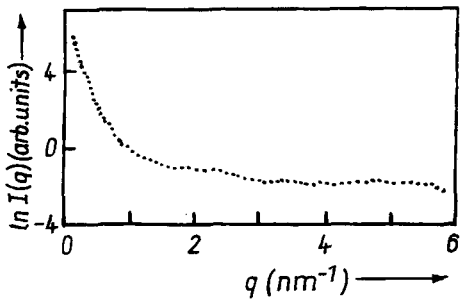

Fig. 1. $\ln I(q)$ as a function of the modulus of the scattering vector

where D_s is the surface fractal and $2 \leqq D_s \leqq 3$. Equation (2) describes power-law scattering. Thus the magnitude of the power-law exponent from SAXS measurement allows to conclude whether the scatterer is a surface fractal or not. If $D_s = 2$, so $I(q) \sim q^{-4}$, which is the familiar Porod law. The logarithm of the SAXS intensity $I(q)$ as a function of the modulus of the scattering vector q is shown in Fig. 1. From Fig. 1 we can see that first the scattering intensity decreases rapidly with increasing q, and the decreases slowly. The SAXS intensity $I(q)$ as a function of the modulus of the scattering vector $\boldsymbol{q}$ is shown in Fig. 2. It shows that the scattering intensity decreases rapidly with increasing q. Fig. 3 shows the straight line relation between $I(q)$ and q in a log–log plot from 0.25 to 1.25 nm^{-1}. The relation follows the power law (2) and the slope of the straight line is $\alpha = -3.38$, corresponding for a fractal dimension $D_s = 2.62$. It is in agreement with surface fractals. If $q \geqq 1.25$ nm^{-1}, there is no straight line because $\boldsymbol{q}$ has become so large that the scattering process deals with the problem of the size of individual atoms and the two-phase approximation is no longer valid. As we can see from Fig. 2, in a wide range of $\boldsymbol{q}$ the intensity is proportional

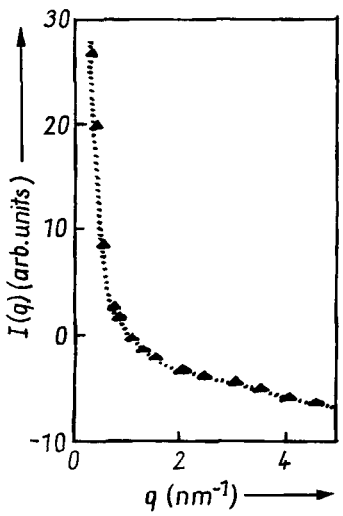

Fig. 2

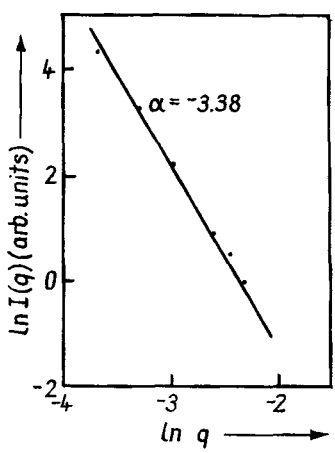

Fig. 3

Fig. 2. SAXS intensity as a function of the modulus of the scattering vector

Fig. 3. SAXS intensity as a function of q (in 10 nm^{-1})

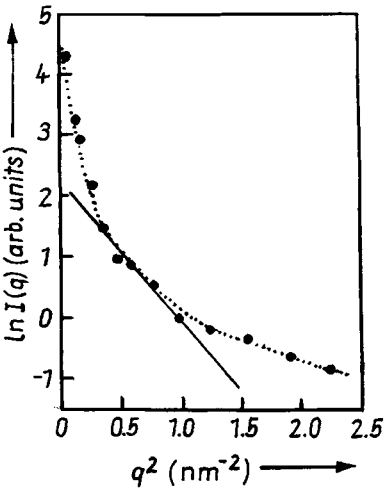

Fig. 4. Plot of ln $I(q)$ vs. q^2 of the SAXS curve

to $q^{-3.38}$. This kind of curve can be explained by the fractal behaviour of the PANI surface with a fractal dimension of 2.62. A rough order of magnitude estimate of fractal surface lengths can be obtained from the condition that the scattering at a given value of q is associated with a distance π/q. Since the curve is linear for q between approximately 0.25 and 1.25 nm^{-1}, we conclude that the fractal surfaces have a fractal dimension 2.62 on a length from about 15.7 nm down to at least 2.6 nm.

Fig. 4 shows the change of ln $I(q)$ with the square of the scattering vector q^2 for the PANI sample. From Fig. 4, a linear region within a more or less extended q domain can be observed. If it is assumed that the system is composed of identical particles, the intensity change of X-rays scattered at low angles follows Guinie's law [7],

$$I(q) = B \exp(-\tfrac{1}{3} R^2 q^2), \tag{3}$$

where B is a constant and R is the average (electronic) radius of gyration of the particles, respectively. While using this equation and the linear portion of Fig. 4 we can calculate $R \approx 2.04$ nm.

Conclusions In conclusion, the experimental results of SAXS demonstrate that the PANI surface shows fractal behaviour. From a measurement of the fractal dimension we found a value of 2.62 in agreement with surface fractals. The SAXS technique is therefore applicable to the optimization of PANI and can be used to study the nonlinear optical properties of PANI.

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