Porous structure of electrosynthesized poly(*p*-phenylene) films characterized by the standard porosimetry technique

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Both the internal and external porous structure of poly(*p*-phenylene) films, synthesized electrochemically via oxidation of benzene in concentrated H_2SO_4, was shown to be highly regular, possessing two characteristic ranges of pore radii, up to 2.5 and 80–200 nm.

(Keywords: poly(*p*-phenylene); electrochemical synthesis; standard porosimetry; regular and highly crystalline structure)

Application of the standard porosimetry technique (SPT) for the characterization of total porosity, specific surface area, pore shape, etc. is based on the thermodynamic treatment of the capillary equilibrium between the porous sample under study and well characterized standard samples in contact with each other[1]. The most important advantage of this technique over the well known and widely used mercury porosimetry technique is that the former can easily be used for characterization of readily compressible or easily swelled materials, or those prone to amalgamation. Different wetting liquids can also be used, thus allowing their porometric behaviour to be observed *in situ*. Here we present preliminary results on the porometric behaviour of highly crystalline poly(*p*-phenylene) (PPP) films obtained by electrochemical synthesis in concentrated H_2SO_4[2]. This seems to be the first application of SPT for examining the morphology of an electronically conducting polymer. Both non-polar and polar impregnating liquids, namely decane and acetonitrile, were used in order to show different *in situ* porometric properties of PPP.

PPP films were deposited onto a square glassy carbon electrode (visible surface area was about 4 cm^2) according to ref. 2. The resulting films (10 μm thick) were peeled off the electrode surface and put into a clamping cylinder in contact with a standard porous sample[1] under an axial pressure of about 8 MPa. Both doped and undoped films, typically of 29 mg, were used following this procedure.

Figure 1 shows differential pore radius distribution curves (porometric curves) for the doped (1, 1′) and undoped (2, 2′) PPP films measured on evaporation of decane (1, 2) or acetonitrile (1′, 2′). Curves 1 and 2 of this figure may be suggested to be characteristic of the unswelled ('dry') porous structure of PPP. Comparison between the curves 1, 1′ and 2, 2′ leads to the conclusion that the pore volume of doped and undoped PPP in acetonitrile is larger than that in decane. This result can reasonably be attributed to ion solvation and hence to the presence of bisulfate counterions and some residual sulfuric acid in the doped and undoped states, respectively. Total porosity of undoped PPP turned out to be larger than that of doped PPP, which is not unusual for fibrous polymers, in particular for polyacetylene[3].

Figure 1 also shows two peaks on the porometric curves in the two ranges of pore radius (r), namely between 80 and 200 nm and between 10^3 and 10^5 nm. The first reflects the internal structure of PPP fractions (very fine pores) whereas the second refers to the external macrostructure of the film. Two ranges of pore radius of the internal structure, namely up to 2.5 nm and between 80 and 200 nm, cover approximately 70 and 80% of the internal pore volume of doped and undoped PPP, respectively. One can reasonably assume that the finest pores characterize the distances between the polymer chains, whereas the second pore range can be ascribed to the distances between the polymer fibrils.

It was observed that the total porosity of the samples increases during successive courses of impregnation with acetonitrile and its subsequent evaporation. In particular, specific surface area, S, increases from 70 to 270 $m^2\,g^{-1}$ for the doped PPP while for undoped PPP the corresponding values were 80 and 360 $m^2\,g^{-1}$ (S was calculated from the porometric curves following the procedure described in ref. 1). Assuming a cylindrical shape of PPP fibrils, a simple formula can be used to estimate the mean fibril radius, $R = 2/S\rho$, where ρ is the density of the PPP (in the first approximation this can be taken as 1). On the other hand, R is equal to the maximum diffusion length of counterions inside the polymer phase. In some cases[4] it is diffusion that controls the overall doping–undoping kinetics. According to our data, R decreases from 22 to 6 nm and from 19 to 4 nm during consecutive courses of impregnation and evaporation of doped and undoped PPP, respectively.

A striking result was observed on integral porometric curves of undoped PPP when varying the compression of the samples from 8.2 to 100.0 MPa (*Figure 2*). The external structure of the sample is almost entirely independent of the compression at pore radii larger than 3×10^3 nm. Note that materials possessing rather large pores are characterized, as a rule, by less rigid structure. Thus the effect observed is likely connected with the rigidity of the external polymer structure. It is challenging to ascribe this behaviour to the highly crystalline structure of as-prepared PPP, which was in evidence

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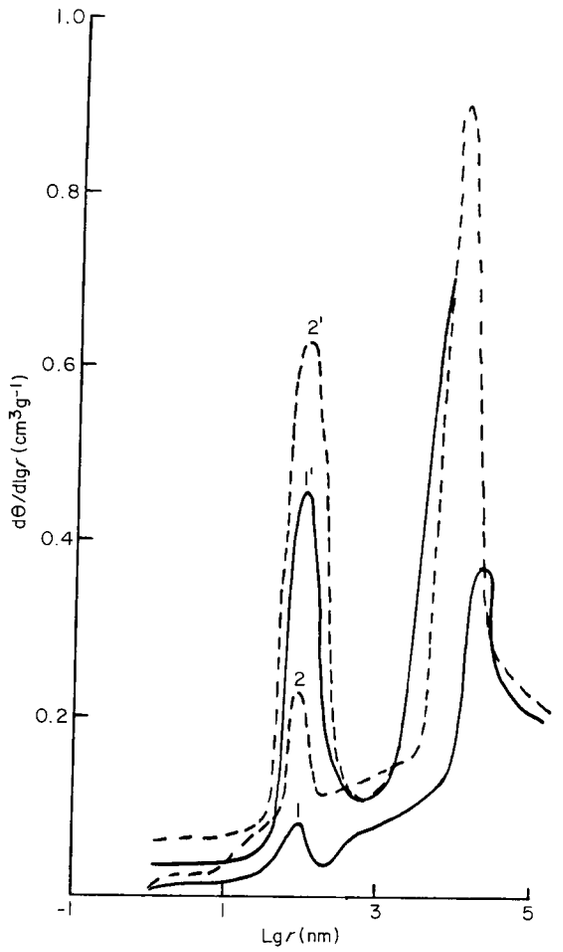

Figure 1 Differential pore radius distribution of doped (1, 1') and undoped (2, 2') PPP using different impregnating liquids: decane (1, 2) and acetonitrile (1', 2')

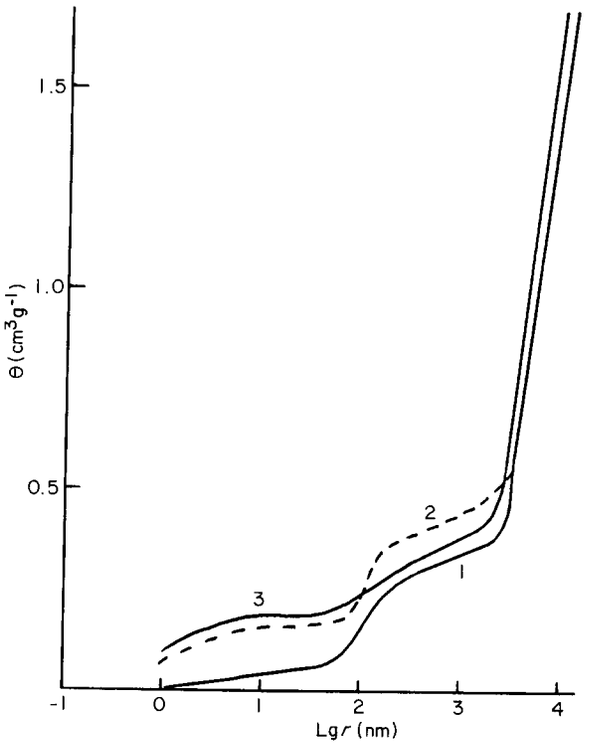

Figure 2 Integrated porometric curves of doped PPP using acetonitrile as working liquid at different values of compression (kg cm^{-2}): 1, 80; 2, 200; 3, 1000

under TEM, SEM or X-ray diffraction studies[2]. Some diversion of curves 1, 2 and 3 in the fine pore region (*Figure 2*) is apparently accounted for by increasing the total porosity during consecutive processes of sample impregnation with a solvent and its subsequent evaporation.

In conclusion, both the internal and external structure of PPP films, deposited by electrooxidation of benzene in concentrated H_2SO_4, is characterized by a highly regular structure as evidenced by two distinct peaks on the differential porometric curves obtained with the standard porosimetry technique.

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References

1 Vol'fkovich, Yu. M., Bagotski, V. S., Sosenkin, V. E. and Shkolnikov, E. I. *Sov. Electrochem.* 1980, **6**, 549
2 Levi, M. D., Pisarevskaya, E. Yu, Molodkina, E. V. and Danilov, A. I. *J. Chem. Sòc., Chem. Commun.* 1992, **N2**, 149
3 Jow, T. K. and Shacklette, L. W. *J. Electrochem. Soc.* 1988, **135**, 541
4 Vol'fkovich, Yu. M., Bobé, S. L. and Bagotski, V. S. *Sov. Electrochem.* in press