FRACTAL STRUCTURE OF A CROSS-LINKED POLYMER RESIN.A PULSED FIELD GRADIENT, PARAMAGNETIC RELAXATION AND SMALL ANGLE X-RAY SCATTERING STUDY.

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ABSTRACT

The diffusion of small solvent molecules in poly(4-vinylpyridine) resins (P4VP) crosslinked by divalent ions has been studied by pulsed field gradient and relaxation rate measurements,evidencing a distribution of pore size in the 3 nm-50 μm range with a surface fractal dimension of 2.6 well confirmed by small-angle X-ray scattering.

PACS N°

INTRODUCTION

The microscopic structure of crosslinked polymer resins is an essential factor in their applications as catalysts or in the separation of chemical species since governing the diffusion of solvent molecules. The poly(4-vinylpyridine) resins have been subjected to a number of studies motivated by their chemical properties involving either conventional chemical analysis or ESR when crosslinked by paramagnetic ions. To get more insight in their structure, we have recently performed a longitudinal relaxation study of solvents such as methanol and nitromethane in P4VP resins crosslinked by VO^{2+}, Cu^{2+} and Cd^{2+} . When the divalent ion is paramagnetic, the relaxation functions are no longer monoexponential.They have been simulated assuming a fractal distribution of pore size with a surface dimension $d_f = 2.65 \pm 0.05$[(1)]. However this method by itself is not sufficient to determine the range of pore sizes as well as the solvent diffusion coefficients so that we have performed ^1H pulsed field gradient spin-echo (PGSE) and small angle X-ray scattering (SAXS) experiments.

RESULTS AND DISCUSSION

The PGSE experiments have been done on methanol adsorbed on P4VP-Cd^{2+} resin. For a delay Δ between two gradient pulses of amplitude G, the echo attenuation A(G)/A(0) is of the form $\exp(-kG^2D)$ or $\exp(-k'G^2R^2)$ according as $\Delta \ll R^2/6D$ (free diffusion) or $\Delta \gg R^2/6D$ (bounded diffusion), D being the solvent self diffusion coefficient and R the pore radius. The echo attenuation curves are therefore dependent upon the size distribution of the pores.This is such that there are $n(\in 0,1,\ldots n_{max})$ categories of pores of radius $R_n = R_0\,\alpha^{-n}$,R_0 being the maximum pore radius and $\alpha > 1$, a constant.For each of these categories, the number of pores is proportional to α^{nd_f} .Fitting the echo attenuation curves for different Δ values yields $d_f = 2.6$ and a self-diffusion coefficient of ca. 5×10^{-10} m^2/s for methanol inside the pores (Figure 1). The proton transverse relaxation

M. Mehring et al. (eds.), *25th Congress Ampere on Magnetic Resonance and Related Phenomena*

function is a weighted sum of exponentials $\exp(-t/T_{2n})$, T_{2n} depending on the surface to volume ratio of pores of radius R_n. The PGSE experiments sample the pores where Δ is not much larger than T_{2n} i.e. the biggest ones, in the 1 μm - 50 μm range.The surface longitudinal and transverse relaxations being much faster than the bulk one, especially in resins crosslinked by paramagnetic ions, their contributions become predominent for smaller pore sizes and are obtained from the fits of relaxation curves at short times (Figure 2). These fits show that the same fractal hierarchy of pore size with d_f = 2.6, and $\alpha \simeq 2$ holds down to 3 nm (n_{max} = 14). SAXS experiments confirm the validity of this model, giving d_f = 2.5-2.6 between 4 and 17 nm. There are evidences for the roughness of the pore surface : the self-diffusion coefficient of the solvent is much smaller than in the pure liquid and its effective adsorption thickness corresponds to ca. 10 molecular diameters. The structure of the resins under study can be depicted as a wide distribution of void pores separated at the interface by $\sim$ 4 nm thick regions of dense crosslinked polymer whose mass fractal dimension given by SAXS is 2.7-2.75.

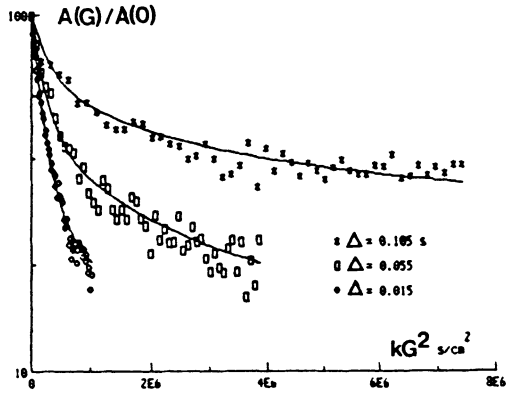

Figure 1. ^{1}H spin-echo attenuation curves for $CH_3OH/P4VP-Cd^{2+}$ resin.

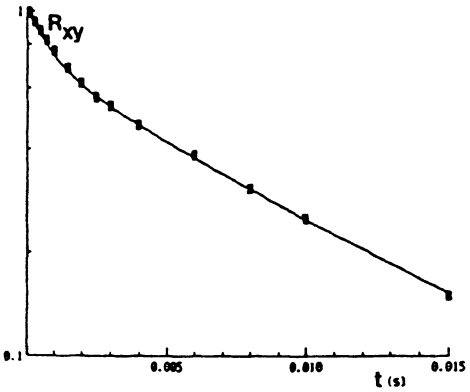

Figure 2. ^{2}H transverse relaxation curve for $CD_3NO_2/P4VP-VO^{2+}$ resin.

CONCLUSION

This study provides an example of crosslinked resin which behaves as a porous solid whose fractal structure has been verified over four order of magnitude, a rather unusual result. This is a very good model for further studies of molecular diffusion and chemical kinetics in organic disordered systems.

REFERENCE

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