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Probing Pore-Structure within Porous Polymer Particles by NMR

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1. Introduction

The object of the present work is to probe the pore morphology or pore-structure of porous polymer particles by combining NMR cryoporometry and NMR relaxometry.

2. Sample preparation and experimental procedure

The polymer particles were prepared by Dynal Biotech and pre-saturated with water before packed into 10 mm NMR tubes, and sealed. All NMR measurements were performed on a 23.5 MHz MARAN Ultra NMR instrument. The spin-spin relaxation time (T_2) was determined using a CPMG pulse sequence with; $2\tau = 60$ µs, $\pi/2$ rf-pulse = 2.15 µs, dwell time = 0.1 µs, dead time = 5µs, number of transients = 64 and time delay between successive scans = 10 s. The temperature was changed at a rate of 8 K/hour.

3. Results and discussion

The T_2-distribution of pore-confined water (Figure 1) reveals essentially one or two regions (phases “a” and/or “b”) at all temperatures, and is in contrast to what is observed from Cryogenic NMR, which reveals four separate and distinct regions A, B, C and D. From the literature [1, 2], these latter regions may be transformed into corresponding pore size regions with average radius of $R_A = 25$ Å, $R_B = 150$ Å, $R_C = 200$ Å and R_D 1350 Å, respectively

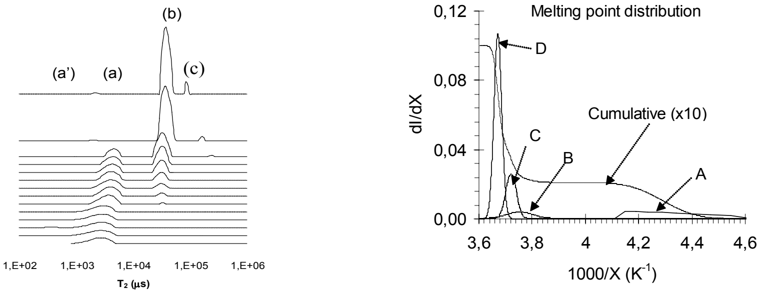

Figure 1. Relaxation time distribution of pore confined water as a function of temperature; 238 K, 242 K, 247 K, 252 K, 257 K, 265 K, 266 K, ….., 271 K (from bottom to top; left). The observed intensity versus temperature curve (IT-curve) and the derived melting point distribution curves A, B, C and D are shown on the right [1, 2].

The different number of components derived from the two NMR techniques is symptomatic of an exchange of water between pore regions A – D [3, 4]. For each region, we may assign an average relaxation rate $1/T_{2X}$ (X = A, B, C and D), according to [3, 4];

$$1/T_{2X} \approx 2\rho / R_X \tag{1}$$

Under the assumption of fast exchange within phases "a" and "b", these relaxation rates ($1/T_{2a}$ and $1/T_{2b}$) may be expressed as a weighted sum of $1/T_{2X}$ (X = A, B, C and D), i.e.;

$$\begin{gathered}1/T_{2Y} = \sum_{x=A,B,C,D} I_X p_X^{(y)} \cdot 1/T_{2X}, I_y = \sum_{x=A,B,C,D} I_X p_X^{(y)}, \quad \sum_{x=A,B,C,D} I_X = 1 \; for\, T = 273K \\ p_X^{(a)} = f_X \; and \; p_X^{(b)} = 1 - f_X \quad for\; X = A, B, C, D \quad and\; x = a, b\end{gathered} \tag{2}$$

The parameter f_X (X = A, B, C and D) reflects the fraction of water which is re-distributed between region X and phase “a”. The model fitted data (Eq. 2) are shown in Figure 2.

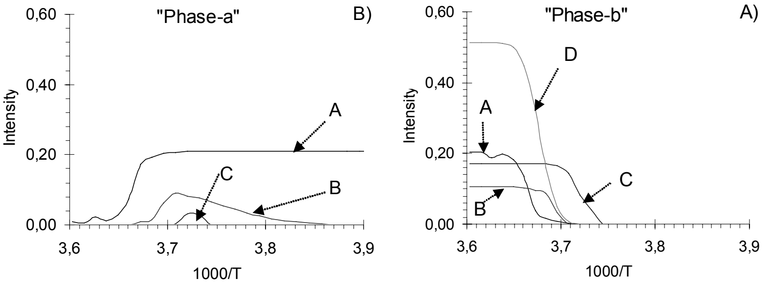

Figure 2. Illustration of how water within regions A – D (Cryogenic NMR) distributes between phases “a” and “b” (Relaxation NMR) as a function of temperature.

By carefully analyzing the intensity distributions presented in Figure 2, the following partial (E and F) and overall pore structure is derived [5].

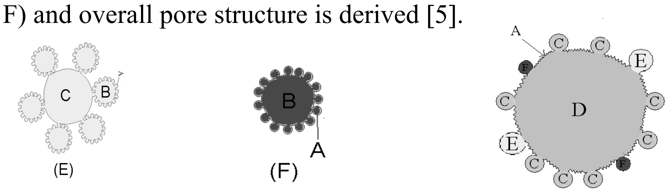

Figure 3. Partial (E, F) and overall pore structure, as derived by combining NMR Cryoporometry and Relaxation NMR.

Conclusion

By combining NMR Cryoporometry and Relaxation NMR on water confined in porous polymer particles, the pore architecture is probed.

References

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