

## NMR IMAGING OF ANOMALOUS SOLVENT TRANSPORT IN MACROMOLECULAR MATERIALS\*

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### INTRODUCTION

The phenomenon of solvent transport into polymers has fascinated researchers for decades. Significant insight into the character of solvent transport has been obtained through time resolved direct imaging of concentration gradients during solvent uptake. Early on, optical microscopy revealed that systems in which a change in state accompanies solvent transport exhibit a sharp solvent front that penetrates the sample like a shock wave;<sup>1</sup> such behavior has been referred to as case II transport to distinguish it from Fickian transport. Subsequent analysis of concentration profiles accompanying solvent transport has been accomplished using X-ray absorption<sup>2</sup> and Rutherford backscattering.<sup>3,4</sup> Recently, NMR imaging<sup>5,6,7</sup> has verified the behavioral characteristics of this transport mechanism.

Case II transport behavior has been observed in a wide variety of macromolecule/solvent systems, including complex systems such as bituminous coals swollen in pyridine.<sup>8</sup> The only requirement necessary for case II behavior is that the sample exist in a glassy state when dry, but cross a phase boundary to a rubbery state during the solvent uptake event. Two characteristics which typify case II behavior are the presence of a sharply defined solvent front and a constant front velocity.

The search for a theoretical basis for this type of non-Fickian behavior has been irresistible for both experimentalists and theorists; to date numerous theories abound. Although there are many unique approaches to this problem, it is universally recognized that the general causes of case II behavior are related to the relative magnitudes of characteristic diffusion times and molecular relaxation times in polymer/solvent systems.<sup>9,10</sup> In the present paper, these generalities are exploited for the purpose of simplifying the quantification of case II transport. An experimental analysis of case II transport of methanol in polyethylmethacrylate and pyridine in coal using both optical and NMR imaging techniques is included as a test case for quantifying the transport behavior.

## RESULTS AND DISCUSSION

For the present purposes 2-D images using conventional techniques<sup>11</sup> are sufficient to address the question at hand, and their acquisition is suitably fast. In order to ensure that the transport process was also two-dimensional, the upper and lower sample surfaces were protected from solvent infiltration by glass coverslip which restricted the flow of solvent to cross only the exposed faces of the sample. Each sample is rectangular with initial dimensions on the order of 2 x 2 x 1 mm. The experimental protocol involved immersing the sample in the solvent for a period of time, removing it from the solvent bath, acquiring an image, and re-immersing it.

Figure 1 presents transient images together with one-dimensional projections for each of the three macromolecular systems. The first (a) illustrates the swelling behavior of isobutyl rubber in toluene. In the case of a rubbery material, the transport behavior is anticipated to be Fickian. Analysis of the dynamic behavior of the isobutyl rubber confirms this: during the swelling interval a steep solvent gradient observed in the frame rapidly evolves into a smooth and shallower gradient indicative of a transport mechanism which is essentially Fickian.

The second (b) illustrates the swelling behavior of PEMA in methanol. Clearly evident is a sharply defined solvent front which separates a swollen region from the glassy core. Swelling is essentially complete when the solvent fronts meet at the object center. In general, this behavior is typical of all polymers which pass through a glass to rubber transition during solvent uptake.<sup>12</sup> The term case II has been used to describe such transport phenomena.<sup>1</sup> Analysis of the transport of pyridine during the swelling of a sample of high volatile bituminous coal (c) clearly reveals a sharp concentration profile during the uptake process which is indicative of case II type transport behavior.

In order to quantify the transient aspects of case II transport, a phenomenological transport model was designed which incorporates the essential characteristics of swelling of materials that exhibit a glass transition accompanying solvent uptake. Solvent induced dilation of a macromolecular network, in either the glassy and or the rubbery states, results from osmotic stresses. Kinetically, the character of transport, hence dilation, is different in the two states. In the glassy state the characteristic relaxation time for diffusion is very long relative to the relaxation time for molecular motion. In the rubbery state, however, diffusion is very rapid relative to molecular relaxation. The point of inversion in the relative magnitudes of the characteristic relaxation times occurs when crossing the phase boundary from the glassy to the rubbery state.

The presence of this osmotic stress is a thermodynamic driving force for rapid expansion at the phase boundary. The net effect of the relaxation at the glass to rubber transition is to convert the problem of solvent transport into a moving boundary value problem; the rate of relaxation in the rubbery region drives the diffusion in the glassy region.

Any useful model constitutes a balance between the need to accurately describe a physical process and the desire to remain simple with a minimum number of parameters. Ideally, these parameters have a direct connection with fundamental molecular scale characteristics of the macromolecule. In the case of solvent transport in a system undergoing a glass transition, we can define the uptake behavior using three parameters: a characteristic cooperative diffusion

coefficient,  $D_c$ , governing dilation of the network; a molecular relaxation rate constant,  $\beta$ , which is given by the relationship  $\beta = K_{os}/\eta_l$ , where  $\eta_l$  is the bulk viscosity and  $K_{os}$  is the osmotic modulus; and a critical solvent concentration,  $C^*$ , above which there is a transformation of the network from a glass to a rubber.

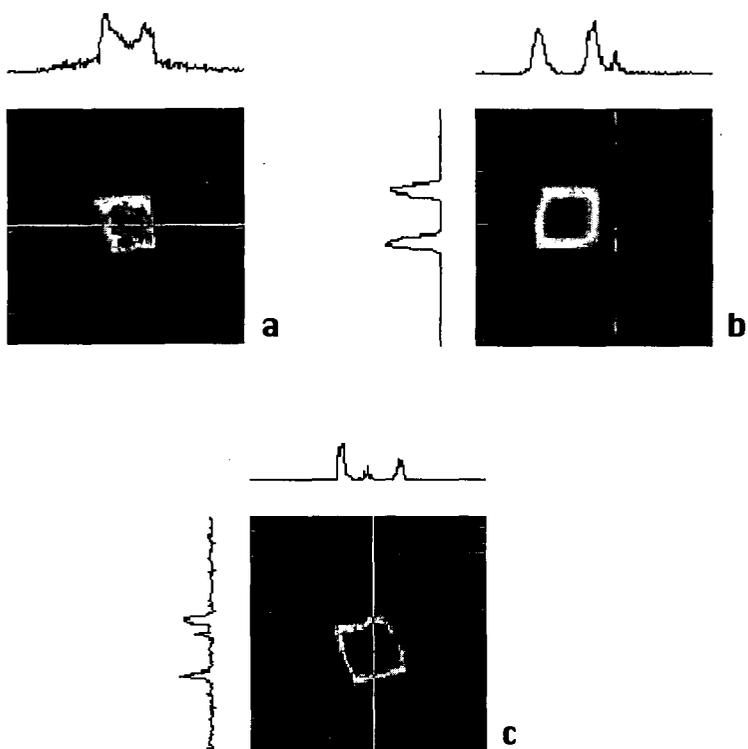
Figure 2 illustrates the time dependent uptake,  $L/L_0$ , vs. the square root of dimensionless time,  $\tau$ , for PEMA and the hv bituminous A coal. Depending on the magnitude of  $\beta$ , the characteristic shape of the uptake curve plotted as normalized dilation vs. the square root of dimensionless time is observed to evolve from an essentially convex shape at high values to sigmoid shaped uptake curve at the lower values. The convex curves are indicative of constant velocity of solvent front with time; this is consistent with case II behavior and clearly distinguishable from Fickian transport behavior. The cooperative diffusion coefficient and absolute magnitude of  $\beta$  calculated for PEMA and the coal using  $C^* = 0.25$  are  $D_c = 9.4 \times 10^{-8}$  cm<sup>2</sup>/s,  $\beta = 4.2 \times 10^6$  s<sup>-1</sup> and  $D_c = 7.4 \times 10^{-8}$  cm<sup>2</sup>/s,  $\beta = 3.5 \times 10^6$  s<sup>-1</sup>, respectively. Quantifying these parameters and searching for the relationship between molecular structure and transport behavior will be the focus of future work.

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**Figure 1.** 2-D transient proton NMR images and 1-D projections of solvent transport in three macromolecular networks: (a) toluene in isobutyl rubber, (b) methanol in polyethylmethacrylate, and (c) pyridine in hv bituminous A vitrain.

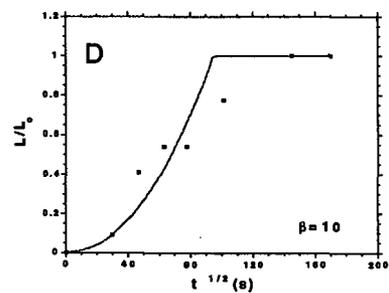
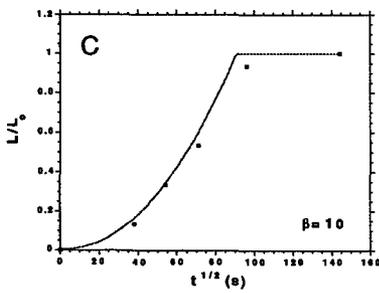
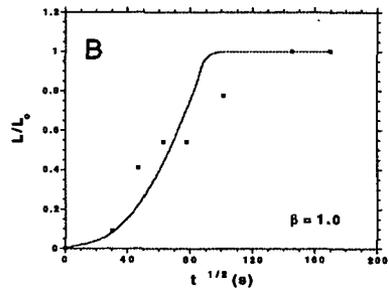
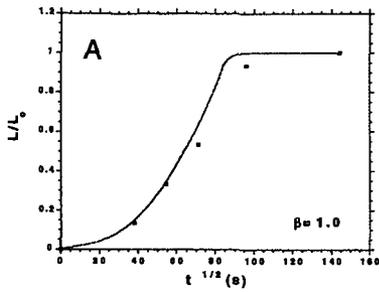


Figure 2. Dilation data for hvA bituminous vitrain swollen in pyridine and polyethylmethacrylate (PEMA) swollen in methanol fit to case II model with  $C^* = 0.25$ : (A) PEMA,  $\beta = 1.0$ ; (B) vitrain,  $\beta = 1.0$ ; (C) PEMA,  $\beta = 10$ ; (D) vitrain,  $\beta = 10$ .