Transport of Penetrants in the Macromolecular Structure of Coals III. Dynamic Swelling of Stiff Polymer Networks That Simulate the Coal Structure

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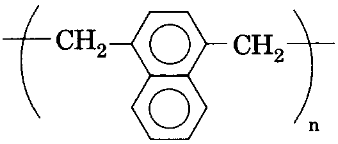
Synopsis

The structure of three cross-linked polymers containing naphthalenic rings in their backbone structure was investigated by dynamic swelling and thermal analytic techniques. It was determined that the pyridine and *n*-proplyamine transport in microparticles (40 μm) of these polymers was non-Fickian, often approaching case II transport and sometimes even super-case II transport. The thermal analysis showed relatively stable structures up to about 350°C.

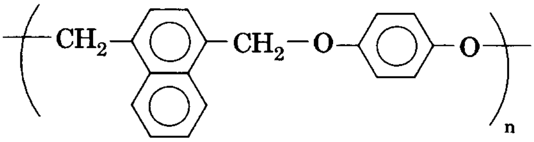
INTRODUCTION

The complex nature of the macromolecular coal network is characterized as insoluble, microporous, and chemically diverse.[1-4] These properties result in numerous limitations when trying to elucidate chemical and physical structures of coal networks. Since the work of Van Krevelen,[5] polymers have been recognized as appropriate models for aiding in the investigation of the coal network structure.

In 1983, Squires et al.[6] synthesized a new class of polymers to aid in this investigation. These polymers contain naphthalene nuclei connected with methylene, ethylene, or oxymethylene linkages.



Polymer I: Poly(1,4-dimethylnaphthalene)



Polymer II: Poly(1,4-dimethylnaphthaleno-1,2-dioxybenzene)

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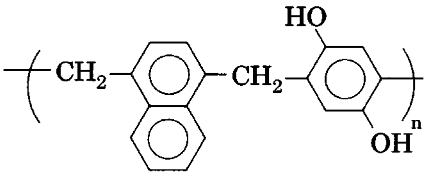

Polymer III: Poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene)

The polymers were cross-linked during polymerization using 1,3,5-trisbromomethylnaphthalene. The naphthalene nucleus was selected because it represents a reasonable average ring size for a bituminous coal; the ethylene and oxymethylene linkages were selected because they are thought to be the most reactive sites in the coal macromolecular network.[7,8]

The results of elemental analysis[6] for polymers I and II are shown in Table I. Similar data for polymer III are not yet available. Polymers I and II were further characterized using pyrolysis mass spectrometry. The base peak for polymer I was found to occur at $m/z = 155$, which is the monomer unit, and the second peak appeared at $m/z = 310$, which is the dimer. A peak at $m/z = 141$ results from cleavage at the benzylaromatic C-C bond. The pyrolysis mass spectrometry for polymer II yielded a more complex spectrum. A peak at $m/z = 262$ represented the repeating unit. The relative distribution between naphthalene, $m/z = 128$, methyl naphthalene, $m/z = 141$ and 142, and dimethylnaphthalene, $m/z = 155$ and 156, is similar to the distribution found in the maceral vitrinite from high-rank bituminous coals. Numerous peaks were also found that contained oxygen.[6]

The initial investigation of Squires et al.[6] shows promise that these coal model polymers can be used to further investigate the physical and chemical nature of the macromolecular coal network. In this contribution, penetrant transport is used as a probe of this structure. In recent publications,[9-11] we have presented results of penetrant transport in unextracted and previously extracted coal particles that show: (1) penetrant transport studies are an excellent analytic tool for the elucidation of the cross-linked structure of coal networks; (2) penetrant transport in coal structures is predominantly anomalous or non-Fickian,[12] and (3) relaxational changes are important in coal structures during dynamic swelling (transport) of penetrants. In addition, we have offered thermoanalytic studies[13-15] that show: (1) the organic coal structure is a highly glassy network at room temperature, and (2) the viscoelastic behavior of coal particles and flat cross sections under compression is similar to that of most glassy polymers at both low and high temperatures.

The goal of the present investigation is to examime similarities and dif-

TABLE I
Results of Elemental Analysis of Polymers

Element (%)	Polymer I	Polymer II
Carbon	92.6	79.6
Hydrogen	6.70	5.6
Bromine	0.15	3.2
Oxygen	0.59	11.7

ferences between the three novel, stiff polymers and typical coal network structures using penetrant transport and thermoanalytic studies.

EXPERIMENTAL PART

Preparation

The preparation of the model polymeric network particles has been discussed before.[6] As shown in Figure 1, the bis-bromomethyl intermediate was obtained from 1,4-dimethylnaphthalene and converted to polymer I by coupling with phenyl lithium. Polymer II was synthesized from hydroquinone and the bis-bromomethyl intermediate. The cross-linked analogs of polymers I an II were prepared by mixing 5% 1,3,5-tris-bromomethylnaphthalene with the bis-bromomethylnaphthalene starting material. Polymer III was prepared from polymer II reacted with methylene chloride and boron trifluoride.

Dynamic Swelling Studies

Approximately 5 mg of each polymer sample was placed in a platinum pan that was suspended from the lever arm of the balance of the thermodynamic analyzer (Perkin Elmer, model TGA-2, Norwalk, Conn.). The system was emerged in a microfurnace at constant temperature and purged with nitrogen. After 1 hour, the penetrant was allowed to bubble through the system and over the polymer sample. Changes in weight due to sorption were recorded. The penetrants used in these studies were pyridine and

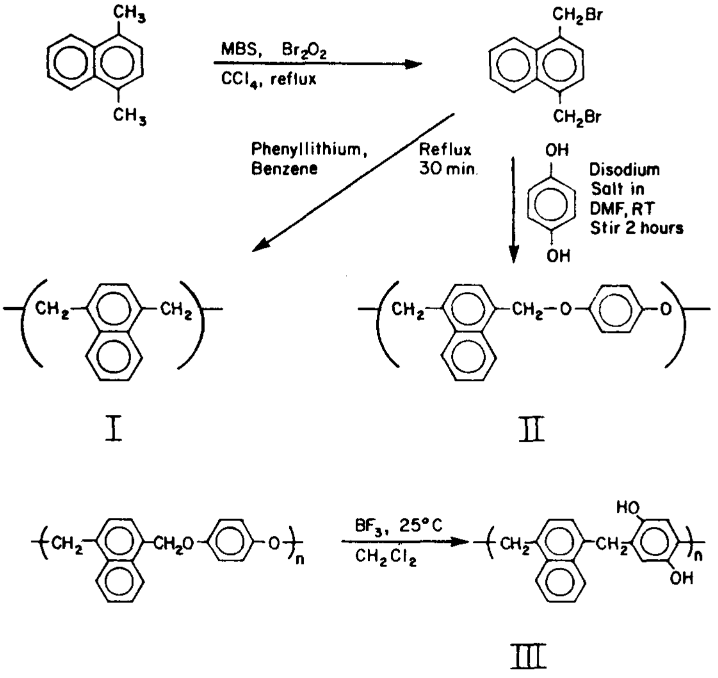

Fig. 1. Synthesis schemes for polymeric coal model particles.

n-propylamine. The sorption experiments were carried out at constant temperatures of 35, 50, 80, and 110°C.

Thermal Analysis

Experiments to determine the glass transition temperature and the heat of melting of the polymers were carried out using a differential scanning calorimeter (Perkin Elmer Model DSC-1B, Norwalk, Conn.). Approximately 5 mg of sample was weighted to ±0.05 mg and enclosed in an aluminum pan. This pan was then set into the sample holder, and at room temperature the system was purged with nitrogen for 45 min. The sample was subsequently heated at a scanning rate of 10°C/min from 30°C up to approximately 480°C. The glass transition temperature and the heat of melting were obtained by analysis of the continuous readout from the calorimeter into a Apple IIe equipped with thermal analysis software.

Thermal degradation studies were carried out using a thermogravimetric analyzer (Perkin Elmer, model TGA2, Norwalk, Conn.). Approximately 5 mg of each polymer sample was heated at a scanning speed of 10°C/min from 35 to 700°C. The weight loss due to the temperature increase was recorded.

Finally, thermomechanical studies were carried out in a thermomechanical analyzer (Perkin Elmer, model TMS-2, Norwalk, Conn.) using approximately 5 mg of each polymer, which was placed under the probe of the device and compressed under applied stress of 0.316 MPa, while at 10°C/min, starting from 35°C.

RESULTS AND DISCUSSION

The model polymers were studied to aid in the understanding of the physical and chemical nature of coal networks. It is important to remember, however, that the coal networks contain inhomogeneities and mineral matter that cannot be accounted for by the coal model polymers, and therefore similarities obtained during these studies cannot be related entirely to coal on a one-to-one basis. It was hoped that the studies of the coal model polymers would, instead, result in some general guidelines about the structure of coal networks.

Dynamic Swelling Studies

Dynamic swelling experiments yield information on the mechanisms of solvent transport, diffusion coefficients, and relaxation constants that can be compared to similar results from dynamic swelling studies[10] of coal networks.

The three coal model polymers were subjected to pyridine vapor at 35, 50, 80, and 110°C. The mass of solvent uptake per mass of sample was determined as a function of time. Results from these studies are shown in Figures 2 through 4 for poly(1,4-dimethylnaphthalene), poly(1,4-dimethylnaphthaleno-1,2-dioxybenzene), and poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene), respectively. Experimental error for these studies was of the order of 0.5%.

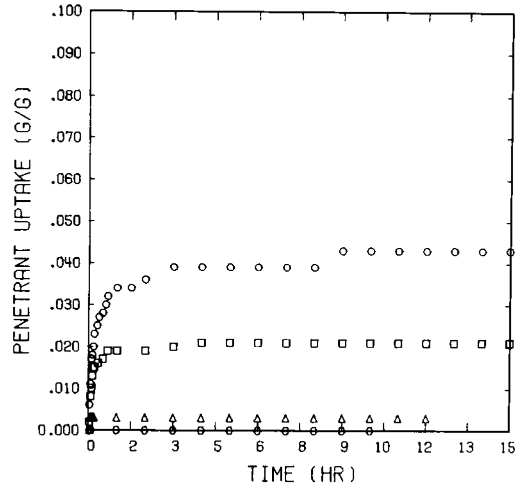

Fig. 2. Pyridine uptake per mass of sample as a function of time at an activity of 0.002 for poly(1,4-dimethylnaphthalene) at 35°C (○), 50°C (□), 80°C (△), and 110°C (○).

The first major observation from these studies was that, as the temperature of swelling increased, the penetrant uptake decreased from all three samples. This may be the result of induced crystallinity at the higher temperatures in the presence of penetrant. The induced crystallinity reduces the free energy of mixing, thereby decreasing the solvent uptake. Information available on the coal model polymers[6] indicates that crystallinity may be induced in these polymer networks. The equilibrium swelling values from these studies are given in Table II.

The other major observation from these studies is that polymer III swelled the most in pyridine followed by polymer II, and finally polymer I swelled

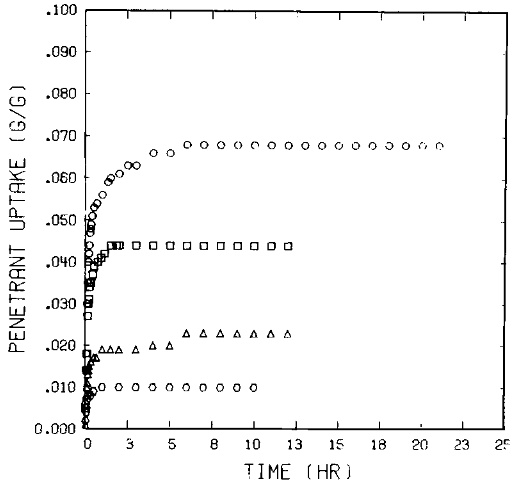

Fig. 3. Pyridine uptake per mass of sample as a function of time at an activity of 0.002 for poly(1,4-dimethylnapthaleno-1,2-dioxybenzene) at 35°C (○), 50°C (□), 80°C (△), and 110°C (○).

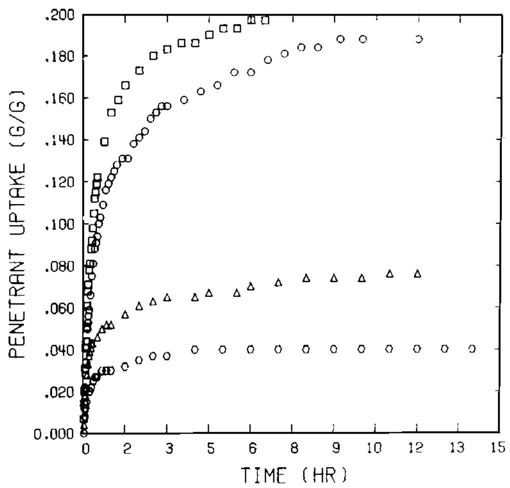

Fig. 4. Pyridine uptake per mass of sample as a function of time at an activity of 0.002 for poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) at 35°C (○), 50°C (□), 80°C (△), and 110°C (○).

the least. The pyridine uptake of polymer III appeared most to resemble the pyridine uptake in coal networks.[10]

To determine the mechanism of penetrant transport in the polymer structures, the dynamic swelling results of Figures 2 through 4 were fitted to eq. (1).

$$\frac{M_t}{M_\infty} = kt^n \tag{1}$$

Here M_t is defined as the mass of penetrant uptake at time t, M_∞ is the mass of penetrant uptake at long times, k is a constant dependent on the structural characteristics of the network, and n is the exponent that indicates the type of solvent uptake. Table III relates the exponent n to the

TABLE II

Equilibrium Pyridine Uptake Per Mass of Sample at Activity of 0.002

Polymer	Temperature (°C)	Pyridine uptake (g/g)
I	35	0.043
	50	0.021
	80	0.003
	110	0.000
II	35	0.068
	50	0.044
	80	0.023
	110	0.010
III	35	0.188
	50	0.197
	80	0.048
	110	0.040

TABLE III
Analysis of Diffusional Behavior in Spheres Using Eq. (1)

Exponent n	Type of diffusion
0.43	Fickian diffusion
$0.43 < n < 0.85$	Anomalous transport
0.85	Case II transport
$n > 0.85$	Super-Case II transport

various types of diffusion. Equation (1) is valid only in the analysis of the first 60% of the final mass of penetrant uptake. It cannot be used to analyze inflections or overshoots typically observed with penetrant transport in glassy polymers.[12,16]

The results from this analysis are presented in Table IV. As the swelling temperatures increased from 35 to 80°C, the exponent n increasased, which indicated a shift from anomalous transport to super-case-II transport. However, at 110°C, the mechanisms shifted back to anomalous transport for polymer II and polymer III. No penetrant transport was observed at 80 or 100°C for polymer I. Polymer III exhibited transport mechanisms that most closely correspond to the transport mechanisms obtained from the coal networks.[10]

The average particle size was determined using a microscope equipped with a micrometer. The average particle diameter for poly(1,4-dimethylnaphthalene) was 52.3 $\mu \pm 11.6$, and for poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) was 40.5$\mu \pm 10.8$. Once the particle size was determined, penetrant diffusion coefficients and network relaxation constants were calculated using the model of Berens and Hopfenberg[16] given by eq. (2).

$$1 - \frac{M_t}{M_\infty} = \phi_F \left[\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-4\pi^2 n^2 \frac{Dt}{d^2}\right) + \phi_R \exp(-kt) \right] \qquad (2)$$

TABLE IV
Analysis of the Pyridine Uptake by the Coal Model Polymers at an Activity of 0.002 Using Eq. (1)

Polymer	Temperature (°C)	k	Exponent n	Correlation coefficient
I	35	1.50	0.66	0.97
	50	10.69	1.35	0.97
	80	—	—	—
	110	—	—	—
II	35	5.82	1.19	0.98
	50	6.66	1.18	0.99
	80	9.35	1.48	0.99
	110	3.66	0.85	0.99
III	35	0.89	0.71	0.97
	50	1.40	0.84	0.98
	80	1.40	1.04	0.98
	110	1.32	0.67	0.98

Here, ϕ_F and ϕ_R are the fractions of transport contributed by Fickian diffusion and the relaxation process, respectively, D is the transport diffusion coefficient for the Fickian portion of the transport, and k is the first-order relaxation constant of the network. If diffusion occurs rapidly in comparison with relaxation, both D and k can be determined from the transport data.[17]

The results from this analysis are shown in Table V. The diffusion studies marked with the symbol * were characterized by super-case II transport. However, the Berens and Hopfenberg[16] model is valid only for anomalous transport. The data available for poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) allow calculation of the activation energy of the diffusion process and the relaxation process assuming Arrhenius-type relationships. From these studies, the activation energy of relaxation process was calculated as 1.8 kcal/mol.

Once again, poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) exhibited a behavior that most closely corresponded to the behavior of the coal networks. The values of the relaxation constants were found to be similar. However, the penetrant diffusion coefficients for the polymer were found to be approximately one order of magnitude lower. It can also be seen that the relaxation constants increased as the temperature increased. The diffusion coefficients, however, remained fairly constant.

Similar swelling studies were carried out on the three coal model polymers using n-propylamine vapor as the penetrant at an activity of 0.007 an temperatures of 35, 50, 80, and 110°C. The mass of penetrant uptake per mass of sample was determined as a function of time. The results from these studies are shown in Figures 5 through 7 for polymers I, II, and III, respectively. Experimental error for these studies was of the order of 0.5%. The equilibrium n-propylamine uptake values for these studies are found in Table VI. As shown in Figure 7, there was again a decrease in the penetrant uptake as the temperature of swelling increased.

The mechanisms of solvent transport were determined by fitting these data to eq. (1). The results from this analysis are shown in Table VII. The

TABLE V

Analysis of the Pyridine Sorption Data from Dynamic Swelling Studies of Coal Model Polymers at an Activity of 0.002 Using Eq. (2) to Determine Diffusion Coefficients and Relaxation Constants

Polymer	Temperature (°C)	Relaxation constant k(s^{-1})	Diffusion coefficient D(cm^2/s)
I	35	$1.58 \times 10^{-4} \pm 2.0 \times 10^{-6}$	$3.49 \times 10^{-10} \pm 4.4 \times 10^{-12}$
	50	*	*
II	35	*	*
	50	*	*
	80	*	*
	110	$6.86 \times 10^{-4} \pm 1.8 \times 10^{-5}$	$8.28 \times 10^{-10} \pm 2.1 \times 10^{-11}$
III	35	$8.50 \times 10^{-5} \pm 4.3 \times 10^{-7}$	$2.05 \times 10^{-10} \pm 1.1 \times 10^{-12}$
	50	$14.5 \times 10^{-5} \pm 2.3 \times 10^{-6}$	$2.49 \times 10^{-10} \pm 4.0 \times 10^{-12}$
	80	*	*
	110	$17.1 \times 10^{-5} \pm 22.2 \times 10^{-6}$	$2.05 \times 10^{-10} \pm 2.6 \times 10^{-12}$

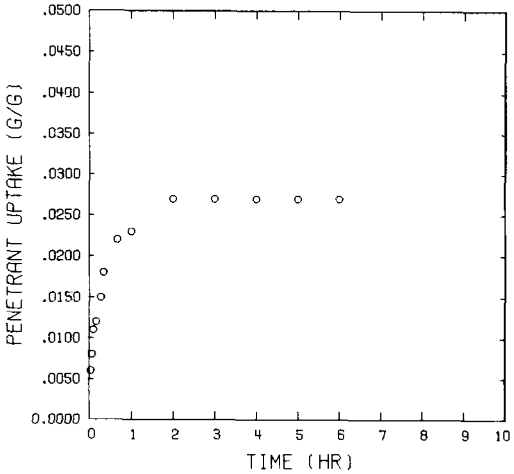

Fig. 5. *n*-Propylamine uptake per mass of sample as a function of time for poly(1,4-dimethylnaphthalene) at 35°C (○), and an activity of 0.007.

exponent *n* values of below 0.5 are indicative of some type of diffusion into pores. At 35°C, diffusion into poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) appeared to be approaching Fickian diffusion. Of the three coal model polymers, studies for poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) most closely corresponded to the coal network studies.[10]

Propylamine diffusion coefficients and network relaxation constants were determined using eq. (2) and are given in Table VIII. All the studies showed relaxation constants larger and diffusion coefficients smaller than those of the coal networks studies. For poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene), the studies showed a decrease in the relaxation constant with an increased temperature of swelling, a trend opposite the trend in the pyridine studies. The diffusion coefficients had no correlation with the temperature of swelling.

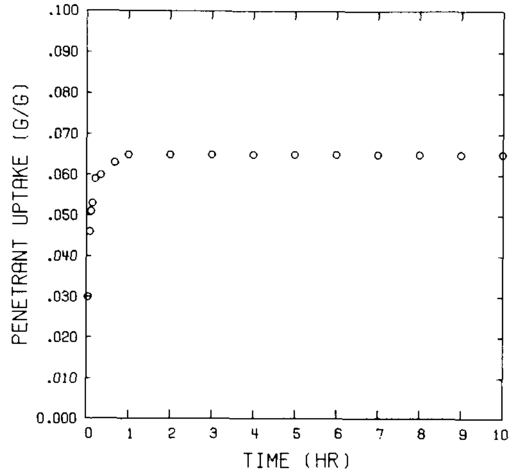

Fig. 6. *n*-Propylamine uptake per mass of sample as a function of time for poly(1,4-dimethylnaphthaleno-1,2-dioxybenzene) at 35°C (○) and at an activity of 0.007.

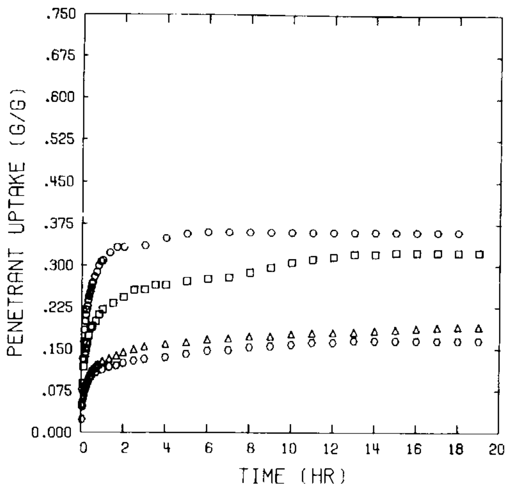

Fig. 7. *n*-Propylamine uptake per mass of sample as a function of time for poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) at 35°C (○), 50°C (□), 80°C (△), and 110°C (○) and at an activity of 0.007.

Thermal Analysis

Thermal analysis of the coal model polymers was carried out to determine the effect of temperature on the structures. Differential scanning calorimetry studies were carried out to determine the glass transition temperatures of the coal model polymers. It is known from previous work[14] that the glass transition temperature of coal is 350–400°C, depending on the carbon content. For polymer I the T_g was 376°C, and for polymer III it was 358°C. However, polymer II exhibited an endotherm at 265°C, and the ΔH_f of the endotherm was calculated as 155 J/g.

Thermogravimetric analysis was carried out on the three coal model polymers under a continuous nitrogen purge. The results of percentage weight loss as a function of temperature are given in Figures 8 through 10 for polymers I, II, and III, respectively.

TABLE VI

Equilibrium *n*-Propylamine Uptake per Mass of Sample at an Activity of 0.007

Polymer	Temperature (°C)	*n*-Propylamine uptake (g/g)
I	35	0.027
II	35	0.065
III	35	0.360
	50	0.324
	80	0.190
	110	0.165

TABLE VII
Analysis of the *n*-Propylamine Uptake by the Coal Model Polymers Using Eq. (1) at an Activity of 0.007

Polymer	Temperature (°C)	k	Exponent n	Correlation coefficient
I	35	1.014	0.440	0.985
I	35	—	—	—
III	35	1.543	0.559	0.985
	50	0.926	0.464	0.964
	80	0.750	0.290	0.993
	110	1.066	0.527	0.970

For poly(1,4-dimethylnaphthalene) with a T_g of 376°C, degradation appeared to become very important at approximately 440°C. For poly(1,4-dimethylnaphthaleno-1,2-dioxybenzene) with an endotherm at 265°C, the weight loss behavior due to temperature occurred in two steps, the first at roughly 280°C and the second at approximately 420°C. This was unlike anything observed in coal analysis.[14] Finally, for poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) with a T_g of 358°C, degradation became important at approximately 440°C. Of the three coal model polymers, poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) exhibited thermal degradation most like the thermal degradation exhibited by coal.[14]

Thermomechanical Analysis

Thermomechanical analysis was carried out on the three coal model polymers with an applied stress of 0.316 MPa and under a nitrogen purge. The results of compressive strain versus temperature are found in Figure 11. All three coal model polymers exhibited little compressive strain up to a temperature of 100°C. Then polymers I and II showed a much steeper compressive strain as a function of temperature in comparision with polymer III. Again, poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) exhibited behavior most comparable with the coal networks.

TABLE VIII
Analysis of the *n*-Propylamine Sorption Data (Activity of 0.007) from Dynamic Swelling Studies of Coal Model Polymers Using Eq. (2) to Determine Diffusion Coefficients and Relaxation Constants

Polymer	Temperature (°C)	Relaxation constanst k (s^{-1})	Diffusion coefficient D (cm^2/s)
I	35	$7.33 \times 10^{-4} \pm 2.0 \times 10^{-4}$	$5.24 \times 10^{-9} \pm 1.5 \times 10^{-11}$
II	35	$2.12 \times 10^{-3} \pm 8.7 \times 10^{-6}$	$2.44 \times 10^{-9} \pm 1.0 \times 10^{-11}$
III	35	$2.37 \times 10^{-4} \pm 2.1 \times 10^{-6}$	$6.98 \times 10^{-10} \pm 6.1 \times 10^{-12}$
	50	$1.03 \times 10^{-4} \pm 8.4 \times 10^{-8}$	$5.21 \times 10^{-10} \pm 4.2 \times 10^{-13}$
	80	$1.03 \times 10^{-4} \pm 3.3 \times 10^{-8}$	$10.6 \times 10^{-10} \pm 3.1 \times 10^{-12}$
	110	$0.82 \times 10^{-4} \pm 6.6 \times 10^{-8}$	$5.21 \times 10^{-10} \pm 4.2 \times 10^{-13}$

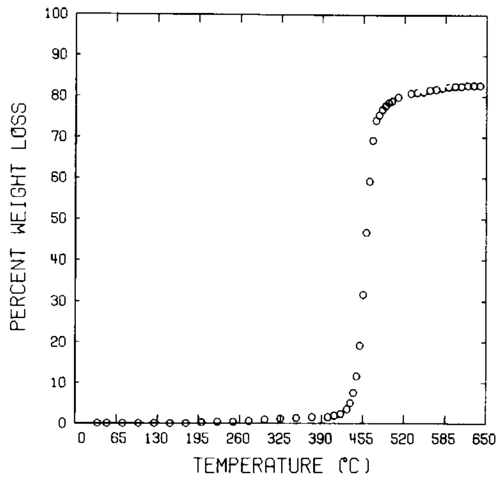

Fig. 8. Percentage weight loss as a function of temperature for poly(1,4-dimethylnaphthalene) under nitrogen purge.

Comparison of Results

Analysis of dynamic swelling of macromolecular networks swollen by thermodynamically compartible solvents yields important information about the structure of the networks. The purpose of this research was to compare transport mechanisms of penetrants into coal networks with those of penetrants into cross-linked synthetic macromolecular structures that allegedly simulate the coal network structure.

Results from several diffusion studies using pyridine vapor as the penetrant at 35°C are collected in Table IX for the coal model polymers and coals with carbon contents similar to the coal model polymers obtained

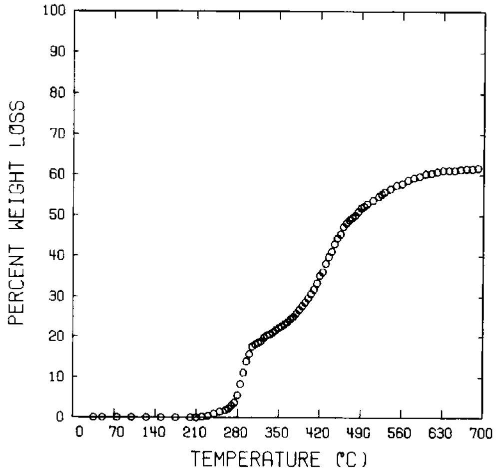

Fig. 9. Percentage weight loss as a function of temperature for poly(1,4-dimethylnaphthaleno-1,2-dioxybenzene) under nitrogen purge.

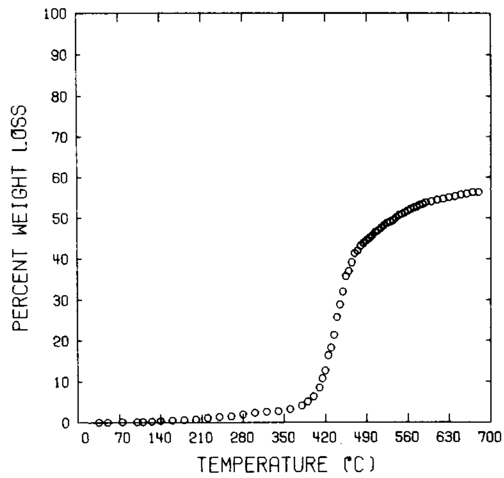

Fig. 10. Percentage of weight loss as a function of temperature for poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) under nitrogen purge.

earlier by Lucht et al.[14] There are several characteristics common to both the coal networks and the coal model polymers. It is important to note that the penetrant activities for these studies are not the same; however, they do fall within a low range, from 0.002 to 0.18. For the highly cross-linked glassy macromolecular structures studied here, these variations should not greatly affect the results.

Poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) (polymer III) exhibited a similar mechanism of penetrant transport to that observed with coal networks, as judged by the value of the exponent n of eq. (1). Similarly,

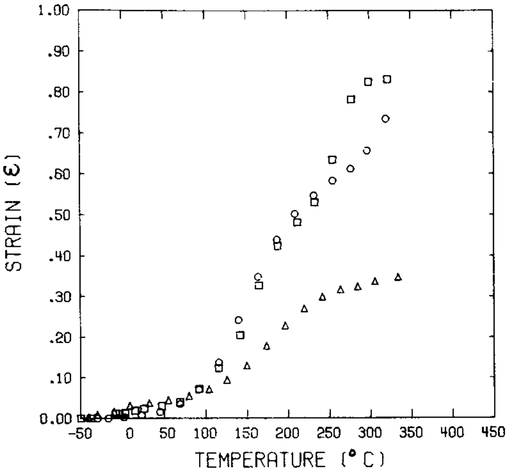

Fig. 11. Compressive strain as a function of temperature for poly(1,4-dimethylnaphthalene) (○), poly(1,4-dimethylnaphthaleno-1,2-dioxybenzene) (□), and poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) (△) under a continuous nitrogen purge and an applied stress of 0.316 MPa.

TABLE IX

Collected Results from Dynamic Swelling Studies of Pyridine-Extracted Coal Particles and Coal Model Polymers Swollen with Pyridine Vapor at 35°C

Sample	Carbon content	Exponent n	k (s^{-1})	D (cm^2/s)	k_o (g/cm^2-s)
Polymer I	93.5	0.66	158.0×10^{-6}	0.35×10^{-9}	0.67×10^{-8}
Polymer II	82.4	1.19	—	—	0.60×10^{-8}
Polymer III	80.0	0.71	85.0×10^{-6}	0.21×10^{-9}	1.07×10^{-8}
Coal 853	80.12	0.84	5.51×10^{-6}	6.21×10^{-9}	6.02×10^{-8}
Coal 402	82.48	0.75	23.9×10^{-6}	112.0×10^{-9}	16.5×10^{-8}
Coal 989	88.19	0.85	53.9×10^{-6}	56.0×10^{-9}	4.02×10^{-8}

the network relaxation constant k for polymer III was comparable to that of coal. The pyridine diffusion coefficient was one to two orders of magnitude lower for polymer III than for coals with similar carbon content.

Poly(1,4-dimethylnaphthalene) (polymer I) also exhibited a similar (anomalous) mechanism of diffusion. However, the network relaxation constant was considerably larger and the penetrant diffusion coefficient was lower in comparison with the coal networks. Poly(1,4-dimethylnaphthaleno-1,2-dioxybenzene) (polymer II) showed no similarities with the coal networks.

The coal model networks exhibited limited degradation below their glass transition temperatures. Poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene) exhibited thermal degradation most comparable to that of coal.

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