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Hindered Diffusion of Porphyrins and Short-Chain Polystyrene in Small Pores

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Received June 15, 1988; Revised Manuscript Received September 2, 1988

ABSTRACT: The role of configurational effects on diffusion of solutes through pores of comparable dimension has been examined for two molecular geometries: disklike molecules (porphyrins) and short-chain polymers (low-MW polystyrenes). Rates of diffusion were measured as a function of pore size in thin membranes for tetraphenylporphyrin and tetrabiphenylporphyrin in chloroform and for three narrow molecular weight fractions (2000, 3700, and 7000 MW) of polystyrene in tetrahydrofuran. The diffusion properties of the porphyrins resembled those of hard spheres of the same Stokes–Einstein radius. The diffusion of short-chain polystyrenes was hindered to a greater extent than the porphyrins but less than long-chain (10^5–10^6 MW) polystyrenes of equivalent ratio of Stokes–Einstein radius-to-pore radius.

Introduction

The diffusion coefficient of a solute in a small, liquid-filled pore is smaller than the value for bulk (unbounded) solution when the molecule and pore are of comparable dimension. This retardation of diffusion is important to membrane processes associated with cell biology and medical physiology, as well as heterogeneous catalysis in microporous supports. Furthermore, the sharp decline in diffusion rate with increasing ratio of molecule/pore size makes membrane dialysis a potentially useful separation technique for macromolecules.

There are two mechanisms responsible for diffusional hindrance by small pores.[1] First, the mobility of the molecule is smaller because of viscous retardation caused by the pore wall, and second, the molecule is excluded from regions near the pore wall because of its size, so it is partitioned unfavorably within the pores. For diffusion through straight, capillary-like pores, the diffusional transport is parallel to the pore walls, and a diffusion coefficient (D) is defined in terms of the rate of molecular transport (M), the pore area (A_p) and length (l), and the difference in solute concentration (ΔC) of the bulk solutions that bathe opposite ends of the pore:

$$M = D(A_p/l)\Delta C \qquad (1)$$

For a membrane having identical pores, M would be the total rate of transport across the membrane, and C would be the concentration of solute at the membrane/fluid interface. Effects of boundary layers ("unstirred layers") at the membrane surfaces can be minimized by using membranes of low porosity and by vigorous stirring of the fluid.[2]

Of basic interest is the relationship between D/D_0 and λ, where D_0 is the diffusion coefficient in bulk solution and λ is the ratio of molecule-to-pore size. Deen[3] reviews the current state of understanding hindered diffusion. Most of the work to date has focused on spherical, compact solutes. Experiments with polystyrenes of high molecular weight indicate that linear, flexible macromolecules are

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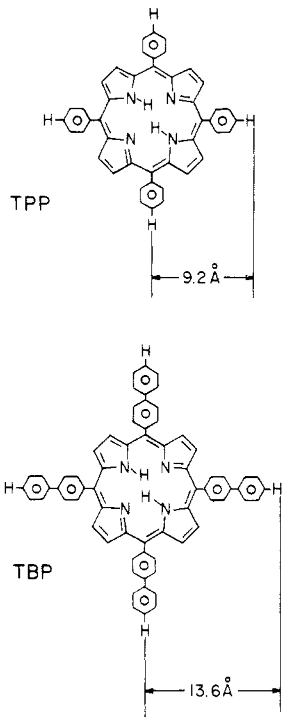

Figure 1. Structure of tetraphenylporphyrin (TPP) and tetrabiphenylporphyrin (TBP).

hindered to a greater extent than compact spheres of the same Stokes–Einstein radius,[4] as predicted from a recent theory based on equilibrium partitioning and mobility of random-flight chains in circular pores.[5] It thus appears that molecular configuration plays a role in determining the relationship between D/D_0 and λ.

In this paper we report experimental determinations of hindered diffusion for two molecular configurations: disklike molecules (porphyrins) and short-chain polymers (low molecular weight polystyrene). Porphyrins are essentially planar macrocycles with only slight out-of-plane ruffling of the pyrrole units. The porphyrin π-system has a van der Waals thickness of 3.4 Å, but the overall molecular thickness is somewhat larger due to the *meso*-phenyl groups, which are rotated about 60° with respect to the porphyrin plane in biphenyl-type conformations.[6] The structures of the two molecules studied here, tetraphenylporphyrin (TPP) and tetrabiphenylporphyrin (TBP), are shown in Figure 1. The dimensions given in the figure were obtained from Corey–Pauling–Koltun space-filling models. With respect to Brownian diffusion, we consider these molecules to be infinitely thin, circular disks of radius R_D, which we determine from the bulk-solution diffusion coefficient. The polystyrenes (2000 < MW < 7000) are considered here to be stiff chains whose transport properties are described by the wormlike chain model.[7,8] There are three parameters of this model: contour length (L), persistence length (α), and diameter (d) of the chain; for each molecular weight fraction of polystyrene, we assume values for L and d and determine α from the bulk-solution diffusion coefficient.

Experiments

Porphyrins. Tetraphenylporphyrin (TPP, MW = 615) was synthesized by standard techniques.[9] Tetrabiphenylporphyrin (TBP, MW = 9169) was prepared similarly by adding samples of pyrrole (139 μL, 10^{-2} M) and 4-biphenylcarboxaldehyde (364 mg, 10^{-2} M) to 200 mL of CH_2Cl_2 with magnetic stirring at room temperature. The condensation process to form the porphyrinogen was initiated upon addition of trifluoroacetic acid (308 μL, 2×10^{-2} M). After 30 min, the process to oxidize the porphyrinogen in situ to the porphyrin was initiated by addition of p-chloranil (369 mg, 7.5×10^{-3} M) in powder form. The oxidation was allowed to proceed at room temperature for 1 h, at which point porphyrin cyrstals were clearly visible in the dark reaction mixture. (Unlike many porphyrins, TBP is relatively insoluble in CH_2Cl_2.) One equivalent of triethylamine (560 μL) was added to neutralize the acid. The mixture was filtered and washed with methanol, affording 128 mg of purple crystals. The filtrate was concentrated to 75 mL and allowed to stand overnight, affording a second crop of crystals (29 mg). Overall yield was 34%. Absorbance peaks in $CHCl_3$ were at 424, 520, 554, 594, and 648 nm. ^1H NMR (CF_3CO_2D, 300 MHz) 7.19, (m, 1 H), 7.28 (m, 2 H), 7.66 (m, 2 H), 8.06 (m, 2 H), 8.42 (m, 2 H), 8.61 (s, 2 H). ^{252}Cf fission fragment mass spectrum ($C_{68}H_{46}N_4$) calcd M, 918.37; obsd 919.6 (M + H^+).

TBP is insoluble in dimethyl sulfoxide, acetone, or benzene and only weakly soluble in tetrahydrofuran. The solubility in $CHCl_3$ ($\approx 2 \times 10^{-4}$ M) is 3–4 times that in CH_2Cl_2. The large extinction coefficient at 424 nm (ϵ 4.76×10^5 M^{-1} cm^{-1}) permitted us to monitor very dilute concentrations, so that diffusion experiments could be performed well below the onset of molecular aggregation; the maximum concentration in our experiments was 27 μM in the high-concentration side of the diffusion cell.

The solvent was HPLC-grade $CHCl_3$ (stabilized with 0.75% ethanol). The base N,N-diisopropylethylamine was added (3.6 mM) to neutralize the HCl in chloroform, because protonation of the porphyrins would result in new spectral bands, thereby complicating the analysis.

Polystyrene. Three polystyrene fractions of weight-average MW 2000, 3700, and 7000 were purchased from the Pressure Chemical Co. (Pittsburgh, PA). They were synthesized by anionic polymerization, which typically gives a narrow MW distribution ($M_w/M_n < 1.1$) in this MW range. The solvent was tetrahydrofuran (THF) without peroxide inhibitor. In the diffusion experiments, the polymer concentration was determined by absorption spectroscopy at 260 nm. The maximum concentration of polymer in any diffusion experiment was below 20 mg/cm^3 in the high-concentration side of the diffusion cell.

Membranes. The membranes were made from sheets of muscovite mica about 7 μm thick by the track-etch process.[10] In a given membrane, the pores are parallel capillaries of the same size with a rhomboidal cross section (60° angle); the pore radius (R) is defined as the radius of a circle having the same areas as the pore. Figure 2 shows electron micrographs of large and small pores. The porosity of the membranes was always below 0.15%, and boundary layer effects were found to contribute less than 1% of the diffusional resistance. The number of pores per irradiated area (n) was determined from irradiation calibrations. The pore length (l), which equals the membrane thickness because of proper collimation during irradiation, was found by weighing the membrane prior to irradiation.

After irradiating and etching a membrane, the pore radius was obtained by measuring the diffusion rate (M_B) of benzene in either THF or chloroform and using a modified version of (1):

$$M_B = D_0[1 + (9/8)\lambda \ln \lambda - 1.54\lambda](A_0 n\pi R^2/l)\Delta C \qquad (2)$$

A_0 is the area of the membrane that was exposed to radiation, D_0 is the bulk-solution value of the benzene diffusion coefficient which we determined with membranes having very large pores (R > 2000 Å), and $\lambda = a_s/R$ where a_s is the Stokes–Einstein radius:

$$a_s = kT/6\pi\eta D_0 \qquad (3)$$

The term in square brackets in (2) is the ratio of D/D_0 expected for hard spheres diffusing in circular pores when $\lambda < 0.1$;[11] the maximum value of λ for the benzene diffusion experiments was 0.044. The values of a_s for benzene in THF and chloroform were determined to be 1.74 and 1.70 Å, respectively.

Diffusion Experiments. A continuously purged, well-stirred diaphragm cell was used for the diffusion experiments. The apparatus and procedure are described by Kathawalla and Anderson.[4] The diffusion rate was determined by continuously monitoring the low-concentration side of the membrane by absorption spectroscopy at 260 nm for polystyrene and at 418 and 424 nm for TPP and TBP, respectively, using a flow-through spectrophotometer. The concentration–time data were used in a material balance for the diffusing solute to obtain $M/\Delta C$, and D was computed from (1) with A_p ($=A_0 n\pi R^2/l$) determined from

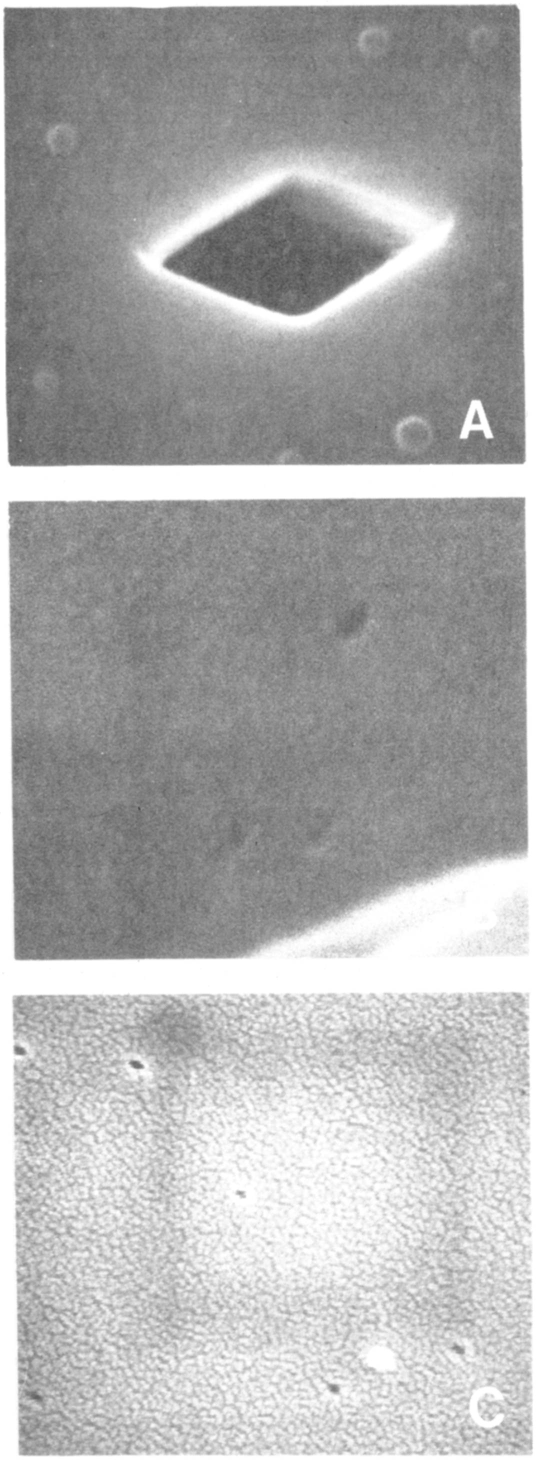

Figure 2. Electron micrographs of pores in muscovite mica. Pore radius (R): (A) 2410 Å; (B) 112 Å; (C) 67 Å.

the benzene diffusion experiments. All experiments were performed in a constant-temperature room at 20 ± 0.5 °C. A more complete description of the experimental procedure can be found in the thesis by Kathawalla.[12]

It is important to note that benzene diffusion experiments performed before and after the porphyrin and polystyrene experiments showed no change of pore radius, indicating that there had been negligible adsorption of solute during the diffusion experiments.

Results and Discussion

The bulk-solution coefficients of the two porphyrins were obtained by measuring their diffusion rates through pores having $R = 1450$ Å. Because λ was less than 0.005, the measured diffusion coefficient gives an accurate value for D_0. The results for D_0 are presented in Table I. The equivalent radius (R_D) of a thin disk having the same diffusion coefficient as the porphyrin was calculated from

$$D_0 = kT/12\eta R_D \tag{4}$$

This formula was obtained by averaging the mobility of a disk over all its orientations assuming a random distribution.[13] Our R_D values compare quite favorably with the molecular dimensions shown in Figure 1, thus supporting our assumption that these porphyrins behave as disklike molecules.

Table I
Diffusion of Porphyrins through Large Pores (R = 1450 Å) at 20 °C in Chloroform[a]

porphyrin	$10^6 D_0$, cm²/s	a_s, Å	R_D, Å
TPP	5.75	6.5	10.2
TBP	4.44	8.4	13.3

[a] a_s from (3), R_D from (4).

Table II
Experimental Diffusion Coefficient versus Pore Radius for Porphyrins in Chloroform at 20 °C[a]

R, Å	$10^6 D$, cm²/s	D/D_0	λ
	TPP		
39	2.72	0.47	0.17
55	3.13	0.55	0.12
67	3.61	0.63	0.097
101	3.80	0.66	0.064
133	4.32	0.75	0.049
	TBP		
39	1.68	0.38	0.22
55	1.95	0.44	0.15
67	2.19	0.49	0.13
101	2.77	0.62	0.083
133	3.03	0.68	0.065

[a] $\lambda = a_s/R$. Values of D_0 and a_s are given in Table I.

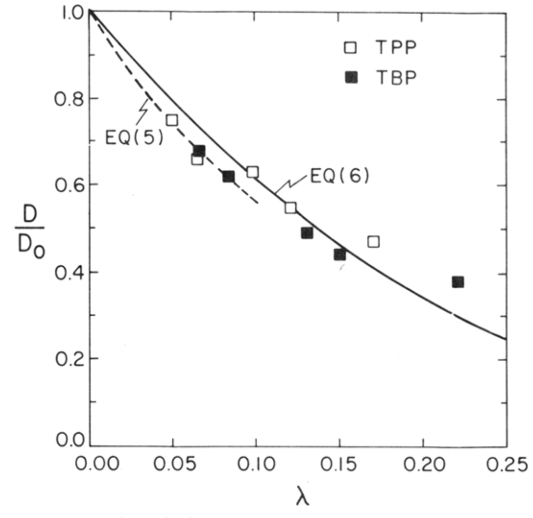

Figure 3. Hindered diffusion of porphyrins. The symbols correspond to the data listed in Table II. In plotting (5) and (6), $\lambda = a_s/R^*$ where a_s and R^* are given by (3) and (7), respectively.

The experimental results for the diffusion coefficients are listed in Table II and plotted in Figure 3. Also plotted are predictions from the following two equations:

$$D/D_0 = 1 + (9/8)\lambda \ln \lambda - 1.54\lambda \tag{5}$$

$$D/D_0 = (1 - \lambda)^2[1 - 2.1044\lambda + 2.0888\lambda^3 - 0.948\lambda^5] \tag{6}$$

Equation 5 is valid when λ is small (<0.1) and is the most accurate theory for hard spheres diffusing through circular pores.[11] Equation 6 was derived by Pappenheimer et al.[14] for hard spheres assuming that the average pore wall effect

Table III
Experimental Diffusion Coefficient versus Pore Radius for Polystyrene in Tetrahydrofuran (THF) at 20 °C[a]

R, Å	$10^6 D$, cm^2/s	D/D_0	λ
MW = 2000			
39.3	0.98	0.25	0.28
49.5	1.12	0.28	0.23
67.2	1.41	0.35	0.17
108	1.97	0.50	0.10
112	1.83	0.46	0.099
380	3.44	0.87	0.030
2410	3.88	0.98	0.0046
MW = 3700			
39.3	0.47	0.16	0.39
49.5	0.37	0.13	0.31
57.2	0.62	0.22	0.27
67.2	0.70	0.25	0.23
108	0.99	0.35	0.14
112	0.95	0.33	0.14
375	2.38	0.83	0.041
2410	2.80	0.97	0.0064
MW = 7000			
39.3	0.19	0.091	0.54
49.5	0.19	0.091	0.43
57.2	0.28	0.13	0.37
67.2	0.28	0.14	0.32
108	0.59	0.28	0.20
112	0.51	0.30	0.19
370	1.50	0.71	0.057
2410	1.98	0.94	0.0087

[a] D_0 was obtained by extrapolating the data to infinite pore size (see Table IV). $\lambda = a_s/R$, and a_s was calculated from (3).

on the mobility of a sphere is approximated by the effect when the sphere is on the centerline of the pore. This approximation, given by the term in square brackets in (6), applies for $\lambda < 0.5$; Paine and Scherr[15] have calculated the centerline mobilities of hard spheres at larger values of λ. In plotting these two expressions in Figure 3, we have taken $\lambda = a_s/R^*$ where R^* is the geometric mean of the radius of the area-equivalent circle (R) and the inscribed circle of the actual 60° rhomboidal pore ($R/1.21$):

$$R^* = 0.91R \tag{7}$$

The rationale for choosing this intermediate radius is that the inscribed circular radius is the correct dimension for the partitioning effect for hard spheres (term $(1 - \lambda)^2$ in (6)), while the area-equivalent radius is probably a better measure of size for the mobility effect.

Diffusion of TPP and TBP appears to agree with the hard-sphere theory over the range of λ studied here. In fact, the porphyrins appear to be hindered to a slightly less extent than hard spheres of the same Stokes radius. Of course, a weak long-range (van der Waals) attraction between the porphyrins and the mica pore wall could have resulted in a more favorable partitioning between bulk and pore solutions, which would give a larger diffusion coefficient than expected for strictly entropic (excluded volume) interaction. A more critical evaluation of these results must await development of a theory for diffusion of disklike molecules in small pores.

The experimental results for the diffusion of the polystyrenes are shown in Table III. Because the λ values were significant even at the largest pore sizes, we extrapolated the diffusion coefficients to $R \to \infty$ to obtain D_0; these values are given in Table IV. A least-squares fit of the extrapolations gives

$$D_0 = 1.918 \times 10^{-4}(\mathrm{MW})^{-0.511} \tag{8}$$

which is within ±5% of the diffusion coefficients measured by Barooah et al.[16] in a different solvent (1,4-dioxane) after adjusting their results by assuming $D_0\eta/T$ is independent of solvent and temperature.

Table IV
D_0 for Polystyrene in THF at 20 °C, As Determined by Extrapolating Plots of ln D versus R^{-1} to $R \to \infty$[a]

MW	$10^6 D_0$, cm^2/s	L, Å	α, Å	D_0/D_0^{rr}
2000	3.97	49	16.8	1.08
3700	2.88	90	16.9	1.12
7000	2.08	170	16.6	1.23

[a] $L = 0.0243$ MW and $d = 9.6$ Å, where L is the contour length and d the diameter of the polymer chain. The persistence length of the chain (α) was calculated from D_0 and the theory of wormlike chains developed by Yamakawa and Fujii[7] with Zimm's correction[8] for preaveraging the hydrodynamic interactions ($D_0 = D_{\mathrm{YF}}/1.085$). D_0^{rr} was calculated from (9).

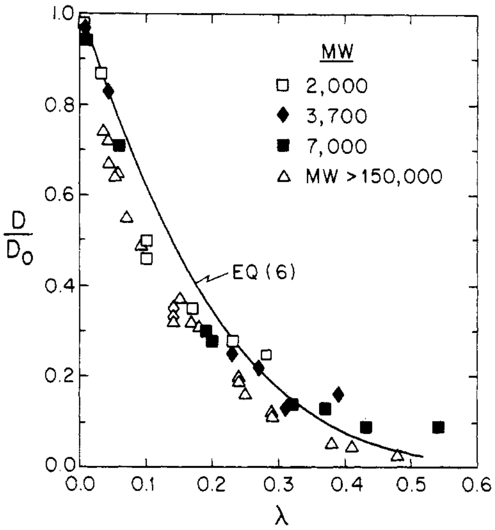

Figure 4. Hindered diffusion of polystyrenes. The symbols correspond to the data listed in Table III. The high-MW data (MW > 150000) are from Kathawalla and Anderson.[4] In plotting (6), we set $\lambda = a_s/R^*$.

The fact that the exponent of MW is close to −0.5 indicates that these low-MW polystyrenes exhibit small excluded volume effects. We choose the wormlike model of Yamakawa and Fujii,[7] as corrected by Zimm[8] for preaveraging the hydrodynamic interactions, to model the diffusion properties. In interpreting our results for D_0 in terms of this model, we accept the value of 0.0243 Å/dalton to compute the contour length of each MW fraction[17] and 9.6 Å for the chain diameter.[18] From (8) we find $\alpha = 16.7 \pm 0.2$ Å over the range $2000 < \mathrm{MW} < 7000$, which is in good agreement with the value $\alpha = 18$ Å reported by Huber et al.[19] for polystyrene in toluene over the MW range 3000–11000. For a perfectly *straight* chain (rigid rod) of length L and diameter d, the diffusion coefficient would be given by

$$D_0^{\mathrm{rr}} = (kT/3\pi\eta L)[\ln (L/d) + 0.3863] \tag{9}$$

which is derived from the two principal mobility coefficients of a long cylinder.[20] For the 2000 MW polystyrene, this formula predicts $D_0^{\mathrm{rr}} = 3.66 \times 10^{-6}$ cm^2/s, compared to the experimental value of 3.97×10^{-6}. The last column of Table IV compares the experimental value to the rigid-rod prediction of the bulk diffusion coefficient for each MW. The fact that D_0/D_0^{rr} is close to unity does not mean that these chains are rigid rods; rather it shows that the chains are elongated coils with limited hydrodynamic screening.

The diffusion data for polystyrene are plotted in Figure 4, along with data for high MW (1.5–9.0×10^5) polystyrene in THF.[4] Comparison of these data indicates that the short chains (low MW) are hindered to a lesser extent than the long chains (high MW); furthermore, the 2000 MW polymer seems to be hindered slightly less than the 3700 and 7000 MW polymer at the same value of λ, although the data are perhaps too limited to make a firm conclusion. Thus, contrary to the high-MW data which are well correlated by using λ alone, two parameters might be necessary to correlate the hindrance of short chains. There is as yet no hydrodynamic theory available for comparison with our experimental results for the short-chain polystyrene; however, the smaller hindrance of the short chains may be explained by a more favorable partitioning between the pores and bulk solution as predicted from Monte Carlo calculations for the partitioning of ideal chains.[21]

In summary, our data show that disklike porphyrins and short-chain polystyrenes exhibit different hindered diffusion characteristics. The porphyrins behave similarly to hard spheres, while the short-chain polystyrenes are hindered to a greater extent than the porphyrins. The hindrance of short-chain polystyrene may depend on both λ and MW, whereas the diffusion of long-chain polystyrenes, which exhibit significant excluded volume effects, can be correlated using only the parameter λ. To gain further insight into configurational effects on hindered diffusion, there is a definite need to synthesize more model compounds of high purity and controlled three-dimensional shapes.

Acknowledgment. Support for this work came from the National Science Foundation (CBT-8613212), the National Institutes of Health (GM-36238), the Petroleum Research Fund, administered by the American Chemical Society, and the IBM Corporation through the Center for Thin Film Sciences at Carnegie Mellon University. We are grateful to N. T. Nuhfer who made the TEM's shown in Figure 2. The mass spectrometric analysis was performed by Brian Chait of the Rockefeller University Mass Spectrometric Research Resource supported by the Division of Research Resources, NIH.

Registry No. TPP, 917-23-7; TBP, 81566-83-8; polystyrene, 9003-53-6; muscovite, 1318-94-1.

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