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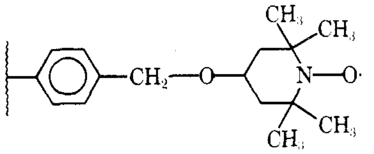
Motion of Molecules within Solvent Channels of Polystyrene Matrices[1]

Polystyrene matrices show considerable promise as support material for transition-metal catalysts, photochemical sensitizers, organic substrates, and organic reagents.[2] At present, the precise physical and chemical nature of molecules covalently bound to polystyrene resins remains poorly defined. In addition, it is not clear how molecules contained within the solvent channels differ from those residing in the liquid phase outside the lattice. We have recently applied the spin-labeling technique to this problem and have demonstrated that the degree of swelling of polystyrene resins, as determined by the swelling solvent and cross-link density, has a substantial influence on the mobility of a nitroxide covalently attached to the resin.[3,4]

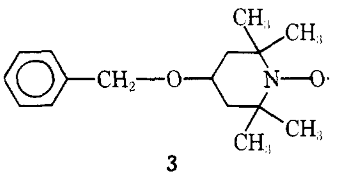
We now wish to report data which establish (1) the degree of swelling of cross-linked polystyrene beads (200–400 mesh) in benzene has a significant influence on the rotational motion of a nitroxide *imbibed* in the solvent channels of the polymer and (2) the magnitude of the effect is nearly equivalent to that observed for the same spin label incorporated into the polymer backbone.

The nitroxide 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (1) was covalently attached to cross-linked polystyrene yielding 2.[5] The benzyl ether 3 of nitroxide 1 was prepared using procedures similar to that described previously.[7] Benzene solutions of 3 were imbibed into unfunctionalized polystyrene resins; excess solution was then removed by rapid suction filtration. Rotational correlation times, τ, were calculated from observed room-temperature electron paramagnetic resonance (EPR) spectra.[8,9] The degree of swelling values, q (swelled volume/dry volume), was determined from the measured density of the dry resin and the weight of the imbibed benzene.[10]



nitroxide polystyrene
(<0.02% ring substitution)

2



3

In order to ensure the absence of any specific binding of 3 to cross-linked polystyrene, we measured the nitroxide concentration in the liquid phase above one of the swelled resins. After swelling 0.35 g of Bio-Rad S-X2 with 2.5 ml of a benzene solution of 3 (1.22×10^{-4} *M*) for 24 hr, analysis of the external liquid phase indicated a slight *increase* in concentration of the label (1.31×10^{-4} *M*).[11] Based on the external concentration and degree of swelling of the resin, the calculated concentration of the nitroxide in the solvent channels was 1.08×10^{-4} *M*. These results show that 3 prefers to reside outside the lattice.

Table I
Motion Within Solvent Channels of Polystyrene Matrices[a,f]

Resin[5]	2[b] 10^{10} τ, sec	3[c] 10^{10} τ, sec	q	$\eta_{\text{"internal"}}$, cP
		0.19[d]		0.6[e]
S-X1	2.9	0.22	5.4	0.7
S-X2	3.1	0.31	3.7	1.0
S-X4	5.5	0.49	2.8	1.5
S-X8	15.0	1.3	2.0	4.1
S-X12	17.0	1.9	1.9	6.0

[a] Rotational correlation times, τ, are accurate to ±10%; degree of swelling values, q (swelled volume/dry volume), are accurate to ±5%. [b] Nitroxide 1 covalently bound to chloromethylated supports which were swelled with benzene at room temperature. [c] Benzene solutions of 3 (1.22 ± 10^{-4} *M*) imbibed in unfunctionalized polystyrene resins. [d] Benzene solution of 3 in the absence of polystyrene. [e] Viscosity of benzene at 25°. [f] NOTE: The extent of chloro methylation for S-X1, S-X2, S-X4, S-X8, and S-X12 was 0.75, 1.0, 0.90, 0.80, and 0.75 mmol of chlorine/g of resin as determined by established procedures; J. M. Stewart and J. D. Young, "Solid Phase Peptide Synthesis", W. H. Freeman, San Francisco, Calif., 1969, p 55.

Data obtained for a benzene solution of 3 imbibed in S-X1, S-X2, S-X4, S-X8, and S-X12, along with data for the corresponding benzene-swelled nitroxide polymers, are presented in Table I. Examination of the observed rotational correlation times reveals two important facts. First, the imbibed nitroxide has approximately ten times more motional freedom than the same label incorporated into a resin having the identical cross-link density. Second, both the imbibed and the "immobilized" labels have correlation times that span almost one order of magnitude for the range of swelling investigated. It is evident from the results cited here that the degree of swelling of the polystyrene matrix in benzene, as defined by the cross-link density, influences not only the mobility of bound molecules, but also the motion of molecules located within the solvent channels. In order to obtain a crude estimate of the "internal viscosity" of the various benzene-swelled resins, we have used the relationship: $\tau \simeq \eta/T$, where η is the macroscopic solution viscosity and T is the temperature.[12,13] At constant temperature, a change in τ corresponds to a proportional change in η. Based upon the measured values of τ and η for 3 dissolved in benzene and the values of τ for 3 imbibed in the various supports at 25°, $\eta_{\text{"internal"}}$ values have been obtained and are included in Table I.

References and Notes

(1) Supported by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Marquette University Committee on Research.

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(5) Commercially available resins (S-X1, S-X2, S-X4, S-X8, and S-X12, Bio-Rad Laboratories) were chloromethylated[6] and the spin label was then attached using procedures previously described.[3] The number following the letter, X, indicates the percent of divinylbenzene incorporated into the polymer beads. Although we have found that this displacement reaction proceeds quantitatively for much higher percent

ring substitution, our method of analysis (chlorine content) was not sufficiently sensitive to determine how complete these displacement reactions were. Nonetheless, based upon the proportions of spin label and chloromethylated polymer used, these resins contain <0.02% ring substitution. At these low concentrations the observed correlation times showed no significant concentration dependence.

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(8) Each polymer sample was swelled with benzene for 24 hr in an EPR tube sealed with a No-Air stopper, and then purged with nitrogen for 10 min.

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(10) Swelling measurements were made after the polymers were equilibrated with benzene for at least 48 hr; swelling equilibrium was usually attained within a 2-hr period. In this calculation it was assumed that the volumes of the polymer and the solvent are additive.

(11) The external concentration remained unchanged after an additional 100 hr of contact time with the swelled resin.

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Erratum. Shape of Random Flight Chains

The statistical behavior of the inertial tensor for random flight chain molecules of different structures, with applications to theories of the excluded-volume effect and the osmotic second virial coefficient, has been investigated in a series of papers[1–6] by both Monte-Carlo and analytical methods. It has recently come to our attention that the representation of flexible-chain molecular shape in terms of the ellipsoid of inertia was previously used in several papers by Koyama.[7,8] Here we comment briefly on the similarities and differences between the two groups of papers.

In his first paper on the excluded volume effect,[7] Koyama calculated the exact average ellipsoidal volume of a random flight chain, and using it together with a distribution of molecular radius which is the same as that used by Flory and Fisk,[9] he constructed a distribution function of molecular radius of gyration for expanded polymer. As compared to the experimental data, the Koyama theory appears to underestimate the excluded volume effect. Our efforts on this problem[4] were somewhat similar. We also obtained an underestimation when the distribution of molecular volumes was treated by assuming a Flory–Fisk type of distribution for each principal component of the radius. In consequence, we preferred to use directly an ensemble of Monte-Carlo lattice chains to represent the distribution, and the results then showed a better agreement with experiment.

In his second paper,[8] dealing with intrinsic viscosity (a problem we have not treated by use of the inertial tensor), Koyama formulated the average principal components of the radius for an infinitely long linear random flight chain. His procedure is attractive in its simplicity, though it is restricted to the second moments of the principal-component distribution and preaverages the coefficients of the cubic equation for the three components. His values for the average second moments are in quite good agreement with ours.

A main objective of our work was the detailed investigation of the shape distribution as such, and we therefore avoided preaveraging. We investigated higher moments, and in one case[6] succeeded in obtaining analytically the shape distribution itself. We also give results for finite chain lengths and for nonlinear molecules.[2,3,6]

We offer our regrets to Dr. R. Koyama for our previous ignorance and oversight of his prior work.

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