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qualitative agreement with substantial temperature independence of the energy per defect ($E = -RT \ln p$).

Acknowledgment. Financial support of Montefluos S.p.A., of the National Research Council (C.N.R.), and of the Ministry of Public Education (Italy) is gratefully acknowledged.

Registry No. PTFE, 9002-84-0.

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Hydrodynamic Radius of Polystyrene in *n*-Butyl Chloride

Y. F. MAA and S. H. CHEN*

Department of Chemical Engineering, University of Rochester, Rochester, New York 14627.

Received July 30, 1987;
Revised Manuscript Received September 2, 1987

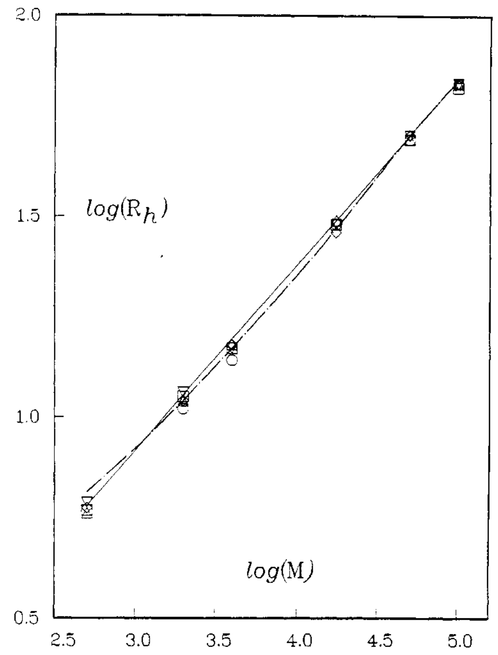

Figure 1. R_h as a function of M. Symbols representing experimentally determined values: (○) at 308 K in cyclohexane; (□) 278 K, (△) 298 K, (◇) 323 K, and (▽) 348 K all in *n*-butyl chloride. Solid line for R_h versus M^ν relationship; dot–dash curve for wormlike chain model prediction.

Table I
Characteristics of Polystyrene Standards from Pressure Chemical

M	$\bar{M}_w/\bar{M}_n$	notation	M	$\bar{M}_w/\bar{M}_n$	notation
503	≤1.03	PS0.5K	17 500	≤1.06	PS17.5K
2000	≤1.06	PS2K	50 000	≤1.06	PS50K
4000	≤1.06	PS4K	100 000	≤1.06	PS100K

Introduction

The conformational dynamics of an isolated macromolecule in solution can be revealed through intrinsic viscosity or translational diffusivity measurements. The macromolecular dimension obtained from transport properties has frequently been interpreted in terms of the chain statistics and the excluded volume and solvent effects, together with the static dimension (e.g., the radius of gyration R_g) derived from light or neutron scattering experiments. For instance, the ratio R_g/R_h was believed to assume a universal value under Θ conditions.[1,2] However, both Fixman[3] and Cherayil et al.[4] have questioned such universality. The failure of the universality might have arisen from the fact that both the excluded volume and solvent perturbations give rise to different quantitative effects on R_h and R_g. Hence, it is important that solvent effects on unperturbed dimensions be clearly understood before the excluded volume effects can possibly be correctly interpreted.

In the present study the translational diffusion coefficients have been determined with the extended Taylor dispersion technique[5] for a series of polystyrene standards with peak molecular weight M from 503 to 10^5 g/mol in cyclohexane at the Θ temperature of 308 K and in *n*-butyl chloride (a good solvent) at temperatures from 278 to 348 K. The hydrodynamic radii R_h calculated from the measured values of translational diffusion coefficients in *n*-butyl chloride will be compared with those in cyclohexane at Θ temperature to examine possible solvent effects. This comparison should furnish new insights into the roles played by phenyl group/solvent interaction and solvent molecular geometry (acyclic versus cyclic) in affecting polystyrene molecular conformation. Both factors have been cited[6,7] to interpret the solvent effects on intrinsic viscosity of polystyrene in a variety of solvents.

Experimental Section

The basis of determining the translational diffusion coefficient of a polymer solute at infinitely dilute solution was presented previously.[5] Note that the dispersion technique results in the diffusivity corresponding to the most probably molecular weight M and that for a nearly monodisperse polymer standard with $\bar{M}_w/\bar{M}_n \leq 1.06$, as was encountered in the present study; the dispersion peak is virtually Gaussian, suggesting that the polystyrene samples as listed in Table I behave like monodisperse solutes. The experimental apparatus and procedures are as described elsewhere.[5] Solvents cyclohexane (99.0 +%, Aldrich Chemical Co.) and *n*-butyl chloride (99.5%, Alltech Associates) were both dried over phosphorus pentoxide (99.2%, J. T. Baker) and then distilled before usage.

Results and Discussion

Summarized in Table II are the translational diffusion coefficients D measured with the extended Taylor dispersion technique[5] for polystyrene in cyclohexane and

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* Author to whom correspondence should be addressed.

0024-9297/88/2221-1176$01.50/0

Table II
Translational Diffusion Coefficients (10^6D, cm^2/s) and Hydrodynamic Radii (R_h, Å) of Polystyrene Standards in *n*-Butyl Chloride and Cyclohexane at Infinite Dilution

T, K		PS0.5K	PS2K	PS4K	PS17.5K	PS50K	PS100K
			n-Butyl Chloride Solvent				
278	10^6D	6.61	3.47	2.59	1.28	0.778	0.586
	R_h	5.83	11.1	14.9	30.2	49.5	65.7
298	10^6D	8.93	4.67	3.40	1.67	1.05	0.761
	R_h	5.74	11.0	15.1	30.6	48.9	67.3
323	10^6D	12.2	6.59	4.77	2.50	1.43	1.07
	R_h	5.91	11.0	15.1	28.9	50.4	67.6
348	10^6D	15.6	8.45	6.48	3.17	1.91	1.44
	R_h	6.10	11.4	14.9	30.5	50.6	67.1
			Cyclohexane Solvent				
308[a]	10^6D		2.81	2.13	0.981	0.603	0.457
	R_h		10.5	13.9	30.2	49.1	64.8

[a] Data taken from ref 15.

n-butyl chloride. Each reported value is the mean of three or four measurements, and the standard deviation is usually ±2% of the mean. The hydrodynamic radii calculated from $R_h = kT/6\pi\mu_0 D$, where k is Boltzmann's constant and T the absolute temperature, are also given in Table II. The values of solvent viscosity μ_0 as a function of temperature were collected from relevant literature.[9,10] Plotted as solid straight line in Figure 1 is the scaling relationship, R_h versus M^ν, where ν was found to be 0.46. For an unperturbed Gaussian chain[10] ν is equal to 0.5, suggesting the non-Gaussian nature of the relatively short chain polystyrene conformation.

First of all, it is observed that the hydrodynamic radii of polystyrene chains in *n*-butyl chloride stay constant to within ±3% over the temperature range from 278 to 348 K. Moreover, the R_h values in *n*-butyl chloride are equal to those in cyclohexane at the Θ temperature within experimental uncertainties in diffusivity and solvent viscosity. Both observations seem to suggest that the excluded volume perturbations on R_h in *n*-butyl chloride are absent. Second, one would have expected the unperturbed R_h values in *n*-butyl chloride to be less than those observed in cyclohexane, judging from the interaction between the phenyl group and the moderately polar *n*-butyl chloride molecule (2.05 D), which was proposed based on the intrinsic viscosity data.[6,7] From the geometric considerations alone,[6,7] one could also have predicted lower values for unperturbed R_h in acyclic *n*-butyl chloride than in cyclohexane. The results reported in Table II suggest that both effects that could possibly be caused by solvent play no role in affecting the unperturbed R_h values over the molecular weight range studied here.

To interpret the R_h versus M relationship as plotted in Figure 1, we employed the Yamaka–Fujii theory for a wormlike chain as summarized in eq 49 and 51 of ref 11. Zimm's computation results[12] were also included to correct for possible error due to Kirkwood's approximations. As for the three parameters involved in the theory, macromolecular mass per unit chain length M_L, the cross-sectional diameter d, and the persistence length q, we adopted the values reported in the literature. Hence, $M_L = 390$ nm^{-1} and $q = 1.0$ nm, both from ref 13, and $d = 0.94$ nm from ref 14. We also scaled the R_h value predicted with the Yamaka–Fujii theory with a factor of 1.11 according to Zimm's computations[12] intended to correct for the error due to Kirkwood's approximations. The so determined R_h value as a function of M is plotted as a dot-dash curve in Figure 1; the absolute average error of prediction is 4%. For the relatively short polystyrene chains under present investigation there is little surprise that the Gaussian statistics is not a good representation.[15] However, the wormlike chain model appears to be adequate for representing the relationship between R_h and M with independently determined parameter values.

Summary

From the comparison of R_h values in *n*-butyl chloride and cyclohexane, we conclude that the excluded volume effect on R_h expected of a good solvent is not observed for polystyrene chains with molecular weights up to 10^5. Higher molecular weight is required for the coil expansion due to excluded volume perturbation to be observed. Moreover, solvent molecular geometry and polarity do not appear to affect the unperturbed hydrodynamic radius. The experimentally determined hydrodynamic radius follows the wormlike chain model representation very closely.

Acknowledgment for partial support of this work is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society. The other source of support came from the National Science Foundation under Grant CBT-8500974. The authors appreciate helpful suggestions made by one of the reviewers.

Registry No. Polystyrene, 9003-53-6.

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