Molar Volume of Polystyrene in Solution

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Introduction

Osmotic pressure measurements have been made on fractions of polystyrene in toluene, benzene and methylethylketone at 20°C, and the maximum molar volume $b_{\max}$ of solute have been calculated by the relation (1), which has already been reported by us[1],

$$A_2 = \frac{b_{\max}}{M^2} \qquad (1)$$

where A_2 represents the second virial coefficient of osmotic pressure, M the molecular weight, and $b_{\max}$ is the volume occupied by the solute molecule at its highest degree of expansion.

Many attempts have been made to deduce the relation between the degree of expansion and the molecular weight of chain molecules in dilute solutions. For example Flory[2] has shown that special interferences between distantly connected segments of a chain lead to the relation

$$R \propto M^{\alpha}, \qquad (2)$$

where R is the average radius of the expansion of chain molecules in dilute solution, and the parameter α changes between 0.5 and 0.6 with varying solvent-polymer systems.

We have examined the relation between $b_{\max}$ and M, and obtained values of α for polystyrene in toluene, benzene and methylethylketone at 20°C.

Experimental

Preparation of Polymer Samples.—Styrene monomer was sealed in tubes in atmosphere. The tubes were placed in a thermostat at 120°C for nine and a half hrs. The contents were taken up in benzene and then monomer and benzene were removed from the mixtures by the method of vacuum sublimation.

The polystyrene was separated into 19 fractions by fractional precipitation, vaporizing benzene and butanol mixture solution[3]. These fractions were reprecipitated with CH_3OH from benzene solutions and finally dried by vacuum sublimation of benzene from benzene solutions frozen by dry ice.

Measurement of Osmotic Pressure.—Osmotic pressure measurements were made in Zimm and Meyerson type osmometers, kept in a thermostat regulated to 20.000±0.003°C. Denitrated collodion was used as membranes. A static method of measurement was employed. Equilibrium was attained in about 10 hrs. The values of the osmotic pressure were accepted only when it remained constant for 12 hrs.

Results and Discussion

The osmotic pressure measurements were made on six fractions in toluene, and three fractions in both benzene and methylethylketone. Some of the plots of π/c against c are shown in Fig. 1. The unit of concentration is g.×cm^{-3} and that of pressure is g.×cm^{-2} and hence π/c is in cm.

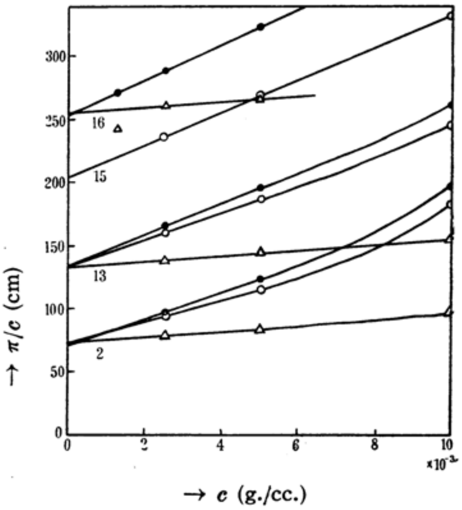

Fig. 1. Variation of π/c with c for polystyrene at 20°C; ○ toluene, ● benzene, △ methylethylketone.

Extrapolation to c=0 was made by freehand drawing, and the molecular weight M was calculated from the intercept, and the second virial coefficient A_2 from the initial slope of the curve. The $b_{\max}$ was calculated by the relation (1) using the values of M and A_2. These results are summarized in Table I.

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[1] G. Meshitsuka, This Bulletin, **25**, 309 (1952).

[2] P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

[3] T. Titani, G. Meshitsuka, and Y. Matsui, *Chem. High Polym., Japan*, **10**, 175 (1953).

TABLE I
THE MOLECULAR WEIGHTS M, THE SECOND VIRIAL COEFFICIENTS A_2 AND THE MAXIMUM MOLAR VOLUMES b_{max}

Fraction No.	$M\times10^{-4}$	$A_2\times10^4$ (cc/g²)			$b_{max}\times10^{-4}$ (1/mole)		
		Toluene	Benzene	Methyl-ethyl-ketone	Toluene	Benzene	Methyl-ethyl-ketone
2	33.6	3.25	4.25	0.80	3.7	5.4	0.93
5	27.2	3.95	—	—	2.9	—	—
11	21.8	4.28	—	—	2.0	—	—
13	18.7	4.28	5.02	0.94	1.5	1.8	0.33
15	12.2	4.98	—	—	0.74	—	—
16	9.8	—	5.62	1.07	—	0.54	0.10
17	6.0	6.02	—	—	0.22	—	—

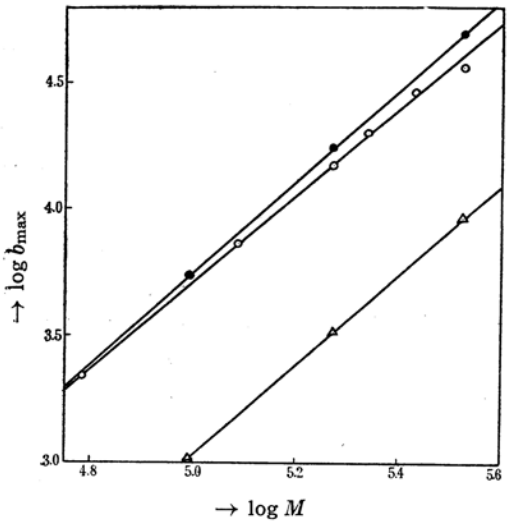

Fig. 2. Variation of log b_{max} with log M for polystyrene at 20°C; ○ toluene, ● benzene, △ methylethylketone.

Assuming the molecules to be sphere, b_{max} must be expressed as

$$b_{max}=4/3\pi\ R^3 \tag{3}$$

Inserting the equation (2), it follows that

$$b_{max}=KM^{3\alpha}, \tag{4}$$

or

$$\log b_{max}=\log K+3\alpha\log M, \tag{5}$$

where K is a constant.

Fig. 2 is the plots of log b_{max} against log M for our results on the polystyrene in toluene, benzene and methylethylketone, which shows straight lines. The values of K and α determined are shown in Table II.

TABLE II
K AND α FOR POLYSTYRENE

Solvent	$K\times10^5$	α
Toluene	1.46	0.57
Benzene	0.69	0.60
Methylethyl-ketone	0.17	0.59

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