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# Studies of the Solution Properties of Co-polymer. I. Styrenepolysulfone*

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Styrenepolysulfone was polymerized and then, for its fractionation, tetrahydrofuran and methanol were used as solvent and precipitant respectively. The viscosities and osmotic pressures of fractions of this co-polymer were examined in tetrahydrofuran. The relation between the intrinsic viscosity and the molecular weight, $[\eta]=0.38_9\times 10^{-4}\,\overline{M}_n{}^{0.78}$, was thus obtained. The unperturbed molecular dimension was calculated by the Fixman-Stockmayer method. The results were then compared with the calculated end-to-end distance of the hypothetical freely-rotating chain. The steric parameter, $\sigma=1.53$, was also obtained and compared with that of polystyrene.

The polymerization of styrene and sulfur dioxide has been reported by Staudinger¹⁾ and others²⁾; the co-polymers obtained were called styrenepolysulfones. The synthesis of the co-polymer was examined with various compositions of styrene and sulfur dioxide, and the form of combination of the monomeric units was studied in terms of the head-to-head or head-to-tail combination.³⁾ However, the solution properties of this co-polymer have not been examined as yet.

Recently, the solution properties of hexene-1 polysulfone were examined by Ivin et al.,⁴⁾ and the unperturbed molecular dimensions of this co-polymer were obtained by using two kinds of $\theta$-solvents. Considerably different values of the unperturbed dimensions were obtained in the two $\theta$-solvents. This was a new finding, in contrast to the prevailing view that the unperturbed dimension of flexible polymer chains was practically independent of the solvent nature; the solvent effect observed was interpreted as arising from the dipolar interaction between polar groups contained in the main chain of this molecule.

In the present work, the unperturbed molecular dimensions of styrenepolysulfone and polystyrene will be studied. The viscosities and osmotic pressures of fractions of this co-polymer and those of polystyrene will be examined in tetrahydrofuran as the solvent. The relations between the intrinsic viscosity and the molecular weight will be determined for both styrenepolysulfone and polystyrene. The unperturbed molecular dimensions will be calculated by the Fixman-Stockmayer method.⁵⁾ The results will be compared with the calculated end-to-end distance of the hypothetical freely-rotating chain.

## Experimental

**Materials and Fractionation.**—Styrenepolysulfone was polymerized, with $\alpha$, $\alpha'$-azobis-isobutyronitrile as the catalyzer, from styrene and sulfur dioxide (mole ratio 1 : 1) at 30°C. On the basis of the chemical analysis, the composition of styrenepolysulfone was determined to be $(\text{Styrene})_2\text{SO}_2$. For the fractionation of styrenepolysulfone, tetrahydrofuran and methanol were used as the solvent and the precipitant respectively. The solvent and the precipitant were purified and distilled before use. Ten fractions were obtained by fractional precipitation from a tetrahydrofuran solution (concentration: 10 g./l.) upon the addition of methanol as the precipitant, with the system kept at 40°C. For the fractionation of polystyrene (commercial name: Styron 666), benzene and methanol were used as the solvent and the precipitant respectively. About ten fractions of polystyrene were prepared by fractional precipitation.

**Viscosity and Osmotic Pressure Measurements.**—Tetrahydrofuran was used as the solvent for viscosity and osmotic pressure measurements. The viscosity measurements were carried out with a dilution-type Ubbelohde viscometer at 30±0.005°C. Solutions with a wide variety of concentration were prepared from an

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1) H. Staudinger and B. Ritzenthaler, *Ber.*, **68**, 455 (1935).

2) W. W. Crouch and J. E. Wicklatz, *Ind. Eng. Chem.*, **47**, 160 (1955).

3) F. J. Glavis, L. L. Ryden and C. S. Marvel, *J. Am. Chem. Soc.*, **59**, 707 (1937).

4) K. J. Ivin, H. A. Ende and G. Meyerhoff, *Polymer*, **3**, 129 (1962).

5) W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, Part C, **1**, 137 (1963).

original stock solution by successive dilution with a definite volume of solvent and were then used in the measurements. The concentration of the original stock solution was determined by the evaporation method. The osmotic pressure measurements were made at 30±0.005°C by the semi-dynamic method with a modified Zimm-Meyerson-type osmometer fitted with gelcellophane. The intrinsic viscosities and molecular weights were determined by extraporating the viscosity and osmotic pressure data to zero concentration by the least-square method. The solution density measurements were made with an Ostwald-Sprengel pycnometer.

## Results and Discussion

**The Relation between Intrinsic Viscosities and Molecular Weights.**—The results of the viscosity and osmotic pressure measurements for styrenepolysulfone and polystyrene fractions are collected in Table I. The intrinsic-viscosity-vs.-molecular-weight relationship is illustrated in Fig. 1, where the open circles represent log [$\eta$] for polystyrene fractions plotted against log $\overline{M_n}$, and the closed circles those for styrenepolysulfones. Using these data, the Mark-Houwink equations were calculated by the least-square method. The results are shown by the straight lines in Fig. 1; they are:

$$[\eta] = 1.16_0 \times 10^{-4}\,\overline{M}_n{}^{0.73} \qquad (1)$$

for polystyrene, and:

$$[\eta] = 0.38_9 \times 10^{-4}\,\overline{M}_n{}^{0.78} \qquad (2)$$

for styrenepolysulfone.

TABLE I.

| Polymer | Fraction | [$\eta$] | $\overline{M}_n \times 10^{-4}$ |
|---|---|---|---|
| Styron 666 | $F_2$ | 1.170 | 26.3 |
| | $F_4$ | 0.902 | 22.3 |
| | $F_6$ | 0.853 | 18.5 |
| | $F_8$ | 0.618 | 12.1 |
| | $F_9$ | 0.508 | 9.2 |
| Styrenepoly-sulfone | $F_1$ | 0.939 | 39.0 |
| | $F_2$ | 0.902 | 38.9 |
| | $F_3$ | 0.861 | 31.8 |
| | $F_6$ | 0.646 | 24.3 |
| | $F_7$ | 0.480 | 17.1 |

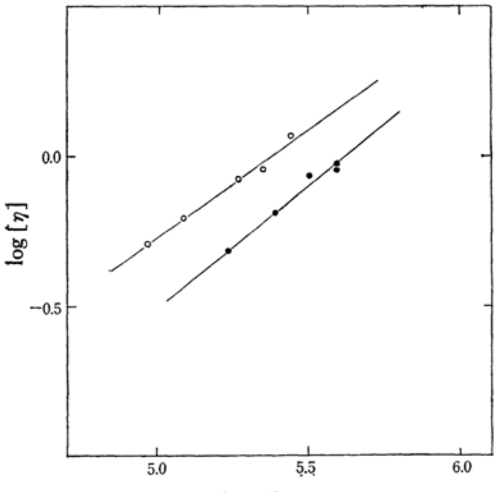

Fig. 1. Relationship between intrinsic viscosity and molecular weight.
○ Polystyrene fractions
● Styrenepolysulfone fractions

**The Estimation of Unperturbed Molecular Dimension Parameters.**—The unperturbed end-to-end distance, $r_0$, may be estimated from the [$\eta$]-vs.-$M$ relationship with the aid of the Fixman-Stockmayer method. We first calculate [$\eta$]$M^{-1/2}$ and $M^{1/2}$ for each fraction. Then the values of [$\eta$]$M^{-1/2}$ are plotted against $M^{1/2}$, as is shown in Fig. 2, and a straight line is obtained for each polymer-solvent system.

According to Stockmayer and Fixman, the [$\eta$]$M^{-1/2}$ ratio is given by:

$$[\eta]M^{-1/2} = K + BM^{1/2} \qquad (3)$$

where $K$ and $B$ are constant, relating to the unperturbed molecular dimension parameter and to the polymer and solvent interaction respectively. Thus, the value of $K$ can be readily determined from the intercept of the straight line shown in Fig. 2. The results are given in Table II. As the value of $K$ for polystyrene in a mixed $\theta$-solvent is essentially identical with our data obtained with the Fixman-Stockmayer method, it seems most reasonable to assume that the value of $K$ for styrenepolysulfone is accurate. The unperturbed end-to-end distance, $r_0$, for styrenepolysulfone and polystyrene can be calculated from

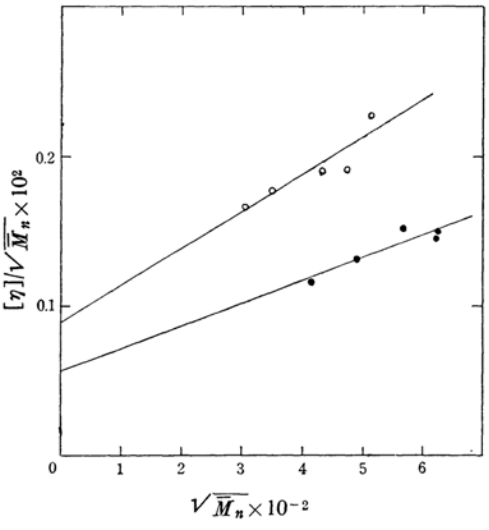

Fig. 2. Relationship between [$\eta$]$M^{-1/2}$ and $M^{1/2}$.
○ Polystyrene fractions
● Styrenepolysulfone fractions

TABLE II.

| Polymer | Solvent | Temp., °C | $K\times10^4$ | $(\bar{r}^2_o/M)\times10^{11}$ | $(\bar{r}^2_o/\bar{r}^2_{of})^{1/2}$ | $\Phi\times10^{21}$ |
|---|---|---|---|---|---|---|
| PS[a)] | A | 30 | 8.6$_{(\theta)}$ | 735 | 2.44 | 2.1 |
| | THF | 30 | 8.99 | 754 | 2.49 | 2.1 |
| SPS[b)] | THF | 30 | 5.74 | 649 | 1.53 | 2.1 |
| HPS[c)] | B | 27 | 4.8$_{(\theta)}$ | | 1.61 | 2.6 |
| | C | 13 | 3.3$_{(\theta)}$ | | 2.1 | 1.8 |

Polymer : a) Polystyrene, b) Styrenepolysulfone c) Hexene-1-polysulfone
Solvents : A Toluene (0.476)-*n*-Heptane (0.524)
B Ethyl methyl ketone (0.37)-Isopropylalcohol (0.63)
C *n*-Hexyl chloride
T. H. F. Tetrahydrofuran

the experimental values of $K$ by the following equation:

$$K=\Phi(\bar{r}^2_o/M)^{3/2} \tag{4}$$

where $\Phi$ is the universal viscosity constant. The results are also given in Table II, with other data given for the sake of comparison.

Table II shows that the molecular dimension of styrenepolysulfone is smaller than that of polystyrene in a tetrahydrofuran solution.

According to the results of chemical analysis and other evidence,[6)] the molecular formula, $-CH_2CH(C_6H_5)SO_2CH_2CH(C_6H_5)-$, seems appropriate for the repeating units of styrenepolysulfone. To the distance from phenyl-to-phenyl groups in this molecule is larger than that in polystyrene, the steric interaction between phenyl groups, and consequently the hindrance to the rotation of the main chain, would be less significant than with the polystyrene chain. With the model defined by the above molecular formula or shown in Fig. 3, the mean-square end-to-end distance of free rotation for the monomer unit of styrenepolysulfone may be calculated by Flory's method as:[7)]

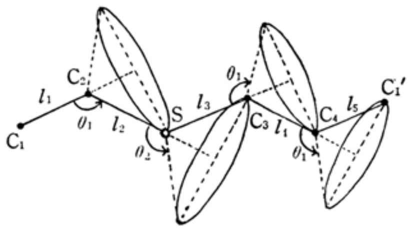

Fig. 3. Spatial representation of styrenepolysulfone monomer for free rotation.
$l_1, l_4, l_5$: C-C bond length 1.54 Å
$l_2, l_3$: C-S bond length 1.82 Å
$\theta_1$: ∠C-C-C, ∠C-C-S 109.5°
$\theta_2$: ∠C-S-C 115°

$$(\bar{r}^2{}_m)=\left|\begin{array}{l}\overline{l_1\cdot l_1}+\overline{l_1\cdot l_2}+\cdots\cdots+\overline{l_1\cdot l_5}\\ +\overline{l_2\cdot l_1}+\overline{l_2\cdot l_2}+\cdots\cdots+\overline{l_2\cdot l_5}\\ +\overline{l_3\cdot l_1}+\overline{l_3\cdot l_2}+\cdots\cdots+\overline{l_3\cdot l_5}\\ +\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\ +\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\end{array}\right| \tag{5}$$

where $l_1$, $l_4$ and $l_5$ are the bond lengths of C–C, and $l_2$ and $l_3$ are the bond lengths of C–S. The result is:

$$\begin{aligned}(\bar{r}^2{}_m)&=l_1{}^2[1+2(1-\cos\theta_1)(1-\cos^2\theta_1\cdot\cos\theta_2)]\\&\quad+2l_2{}^2(1-\cos\theta_2)\\&\quad-2l_1l_2\cos\theta_1(2-\cos\theta_1)(1-\cos\theta_2)\end{aligned} \tag{6}$$

where $\theta_1$ is the bond angles of C–C–C and C–C–S, and $\theta_2$ is the bond angle of C–S–C. For the polymer with the polymerization degree of $x$, the mean-square end-to-end distance of free rotation in the main chain is obtained as:

$$(\bar{r}^2{}_{of})=x\cdot(\bar{r}^2{}_m)(1-\cos\theta_1)/(1+\cos\theta_1) \tag{7}$$

where $\theta_1$ is the bond angle of C–C–C (monomer)–(monomer). On the other hand, for the freely-rotating state of polystyrene, $\bar{r}^2{}_{of}$ is given as:

$$(\bar{r}^2{}_{of})=n\cdot l^2(1-\cos\theta_1)/(1+\cos\theta_1) \tag{8}$$

where $l$ is the bond length of C–C. Therefore, the steric parameter, $(\bar{r}^2{}_o/\bar{r}_{of})^{1/2}$, can be calculated for styrenepolysulfone and for polystyrene by using Eq. 7 and Eq. 8 respectively. The results are shown in Table II. It is notable that the values of $(\bar{r}^2{}_o/M)$ and $(\bar{r}^2{}_o/\bar{r}^2{}_{of})^{1/2}$ for styrenepolysulfone are considerably smaller than those of polystyrene. This clearly shows that the internal rotation around the bond axis in the main chain can occur with less hindrance in styrenepolysulfone than in polystyrene. Finally, if it is compared with that for hexen-1-polysulfone, the steric parameter for styrenepolysulfone is approximately identical with that for hexen-1-polysulfone obtained from mixed $\theta$-solvent (ethyl methyl ketone and isopropylalcohol).

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6) N. Tokura and M. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sect* (*Kogyo Kagaku Zasshi*), **64**, 501 (1961).

7) P. J. Flory, Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y. (1953).