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PHYSICO-CHEMICAL PROPERTIES OF SULFUR

III Dissolved State of Sulfur Polymers in Liquid Sulfur

BY TSUNESUKE DOI

The molecular weights of sulfur polymers have not been measured until now because there was no proper solvent for them. Therefore, there is no report concerning the exponent of the intrinsic viscosity-molecular weight relationship of sulfur polymers in liquid sulfur. Nevertheless, the author found a method which could assume the exponent without measuring the molecular weight of sulfur polymer.

He obtained satisfactory results by applying this method to the data which referred to the viscosities of liquid sulfur, already reported by the author in this journal1). The exponent obtained for sulfur polymer, in the temperature range 120 to 150°C, lies between 0.4 and 0.7 and is dependent on the temperatures of the viscosity determinations and increases gradually with temperature.

Introduction

It is known that the length of S–S bonds in sulfur and sulfur compounds ranges generally from 1.89Å to 2.39Å. Therefore, it is suggested that the length of S–S bonds of S_8 ring and of polysulfide implies a slight double-bond character2), because it is 2.08Å. From this point of view, it can readily be realized that the chains of sulfur polymers would be more or less rigid and less coiled. On the other hand, the chains of pure sulfur polymers have no other kind of atoms and atomic groups bound to them. Thus, it can be understood that the chains of sulfur polymers are easy to coil. It is significant to solve this problem.

There is no report on the dissolved state of sulfur polymers in liquid sulfur. This dissolved state is explained by the exponent of the intrinsic viscosity-molecular weight relationship. Gee3) adopted $2/3$ as such an exponent for sulfur polymer in his paper with reference to the paper of Scott and Magat4) on natural rubber hydrocarbon.

In order to find the exponent of the intrinsic viscosity-molecular weight relationship experimentally, the molecular weight determination of the polymers by the known methods as by osmotic pressure, light scattering or centrifugal force etc. is usually taken into consideration at first. But such methods can not be applied to sulfur polymers because there is no proper solvent.

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1) T. Doi, *This Journal*, **33**, 41 (1963),
2) A. F. Wells, "Structural Inorganic Chemistry", 1962, Oxford
3) R.L. Scott, W.C. Carter and M. Magat, *J. Am. Chem. Soc.*, **71**, 220 (1949)
4) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1962)

The purpose of this paper is to find a method by which the exponents can be obtained without measurements of molecular weight of sulfur polymers. The author obtained satisfactory results by applying this method to the data related to the viscosities of liquid sulfur, already published by the author in this journal[1].

Calculation of Constants of Intrinsic Viscosity-Molecular Weight Relationship

As the author has already reported[1], the viscosities of liquid sulfur, below the critical transition temperature (169°C) of polymerization of pure liquid sulfur, increase with addition of halogen and dibenzothiazyl disulfide. In this case, chlorine and bromine are more reactive than others, and it is found that the greater part of them react with sulfur and bound to one end of sulfur polymers. It is convenient to take this example, especially to take chlorine, in order to derive the equations to be able to find the degree of polymerization of sulfur with reference to the method of Tobolsky *et al.*[5], because chlorine can be added to sulfur as sulfur monochloride, and this fact can simplify the derivation of the equations.

$$S^* + M \overset{K_x}{\rightleftharpoons} M_1^*, \qquad M_1^* = K_x S^* M \tag{1}$$

where S^* is ClS· radical which has been produced by the cleavage of sulfur monochloride, M is S_8 ring, and M_1^* is ClS_9· radical.

$$M_1^* + M \overset{K_x}{\rightleftharpoons} M_2^*, \qquad M_2^* = K_x M_1^* M = K_x^2 S^* M^2 \tag{2}$$

$$M_{n-1}^* + M \overset{K_x}{\rightleftharpoons} M_n, \qquad M_n^* = K_x M_{n-1}^* M = K_x^n S^* M^n \tag{3}$$

where M_n^* is $ClS(S_8)_n$· radical (as a matter of fact, there would be the molecules obtained by bonding different M_n^* with each other or the radicals obtained by cleaving M_n^* itself).

Let N=total concentration of sulfur polymers.

$$N = \sum_{n=1}^{\infty} M_n^* \tag{4}$$

$$N = K_x S^* M + K_x^2 S^* M^2 + K_x^3 S^* M^3 + \cdots\cdots$$

$$= K_x S^* M (1 + K_x M + K_x^2 M^2 + \cdots\cdots)$$

$$N = \frac{K_x S^* M}{1 - K_x M} \tag{5}$$

Let S_0^* be concentration of ClS· radicals (assuming that all molecules decompose to ClS· radicals, the concentration of S_0^* radicals becomes twice the concentration of S_2Cl_2 molecules).

$$S_0^* = S^* + \sum_{n=1}^{\infty} M_n^* \tag{6}$$

$$= S^* + K_x S^* M + K_x^2 S^* M^2 + K_x^3 S^* M^3 + \cdots\cdots$$

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[5] A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.*, **81**, 780 (1959)

$$=S^*(1+K_xM+K_x^2M^2+K_x^3M^3+\cdots\cdots)$$

$$S_0^*=\frac{S^*}{1-K_xM} \tag{7}$$

$$S^*=S_0^*(1-K_xM) \tag{8}$$

Let W=total concentration of monomer segments (S_8 units) incorporated in the sulfur polymer

$$W=\sum_{n=1}^{\infty} nM_n^* \tag{9}$$

$$=K_xS^*M+2K_x^2S^*M^2+3K_xS^*M^3+\cdots\cdots$$

$$=K_xS^*M(1+2K_xM+3K_x^2M^2+\cdots\cdots)$$

$$W=\frac{K_xS^*M}{(1-K_xM)^2}=\frac{K_xS_0^*M}{(1-K_xM)} \tag{10}$$

Let P_x be number average chain length (in terms of S_8 units)

$$P_x=\frac{W}{N}=\frac{K_xS^*M}{(1-K_xM)^2}\Big/\frac{K_xS^*M}{1-K_xM}=\frac{1}{1-K_xM} \tag{11}$$

Let M_0 be total concentration of monomer segments (S_8 units) incorporated in this reaction.

$$M_0=M+W=M+\frac{K_xS_0^*M}{1-K_xM} \tag{12}$$

$$M=\frac{M_0+S_0^*+\frac{1}{K_x}-\sqrt{\left(M_0+S_0^*+\frac{1}{K_x}\right)^2-\frac{4M_0}{K_x}}}{2} \tag{13}$$

Inserting eq. (13) into eq. (11), we can calculate P_x. The author adopted the numerical values of K_x obtained by Tobolsky *et al.* in order to calculate P_x. K_x is shown in mole kg^{-1} unit. In this case, the author assumes that the initiating functions of polymerization of both ClS· radicals and S_n· radicals produced by ring opening of pure S_8 rings are the same. The calculating results of P_x are shown in Table 1. Table 1 shows that the more the reagent is added the more the degree of polymerization of sulfur decreases, and that the more the reaction temperature rises the more the degree of polymerization of sulfur increases.

The author assumed that Baker's equation[6] was applicable for this polymerized liquid. The equation is

$$\eta_r=\left(1+\frac{[\eta]}{\alpha}\cdot C\right)^{\alpha} \tag{14}$$

This can be written in the form

$$[\eta]=\frac{\alpha(\eta_r^{\frac{1}{\alpha}}-1)}{C} \tag{15}$$

where η_r is relative viscosity, α is constant, C is the concentration of sulfur polymers and $[\eta]$ is intrinsic viscosity.

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6) W. E. Davis and J. H. Elliott, *J. Colloid Sci.*, **4**, 313 (1949)

Table 1 Calculations of P_x

	S_2Cl_2 mole/kg	M_0 mole/kg	S_0^* mole/kg	K_x mole/kg	$1/K_x$ mole/kg	$\frac{4M_0}{K_x}$	M mole/kg	P_x S_8 unit
120°C	0.0138	3.89	0.0276	0.1805	5.54	86.2	3.824	3.23
	0.0274	3.88	0.0548	0.1805	5.54	86.0	3.752	3.10
	0.0546	3.87	0.1092	0.1805	5.54	85.7	3.649	2.93
	0.0816	3.86	0.1632	0.1805	5.54	85.5	3.566	2.80
	0.1083	3.85	0.2166	0.1805	5.54	85.3	3.473	2.68
	0.1349	3.83	0.2698	0.1805	5.54	84.8	3.395	2.58
130°C	0.0138	3.89	0.0276	0.1992	5.02	78.1	3.794	4.10
	0.0274	3.88	0.0548	0.1992	5.02	77.9	3.708	3.83
	0.0546	3.87	0.1092	0.1992	5.02	77.7	3.590	3.51
	0.0816	3.86	0.1632	0.1992	5.02	77.5	3.497	3.29
	0.1083	3.85	0.2166	0.1992	5.02	77.3	3.389	3.08
	0.1349	3.83	0.2698	0.1992	5.02	76.9	3.310	2.94
140°C	0.0138	3.89	0.0276	0.2205	4.54	70.6	3.734	5.68
	0.0274	3.88	0.0548	0.2205	4.54	70.5	3.643	5.10
	0.0546	3.87	0.1092	0.2205	4.54	70.3	3.505	4.41
	0.0816	3.86	0.1632	0.2205	4.54	70.1	3.392	3.97
	0.1083	3.85	0.2166	0.2205	4.54	69.8	3.262	3.71
	0.1349	3.83	0.2698	0.2205	4.54	69.5	3.185	3.37
150°C	0.0138	3.89	0.0276	0.2410	4.15	64.6	3.689	9.01
	0.0274	3.88	0.0548	0.2410	4.15	64.4	3.572	7.20
	0.0546	3.87	0.1092	0.2410	4.15	64.2	3.375	5.37
	0.0816	3.86	0.1632	0.2410	4.15	64.0	3.257	4.65
	0.1083	3.85	0.2166	0.2410	4.15	63.9	3.114	4.03
	0.1349	3.83	0.2698	0.2410	4.15	63.6	3.070	3.85

By the definition, we obtain

$$C=\frac{P_xN}{M_0} \tag{16}$$

and

$$\eta_r=\eta_{sp}+1 \tag{17}$$

where η_{sp} is specific viscosity. From eqs. (5) and (7), N is given by

$$N=\frac{K_xS^*M}{1-K_xM}=K_xS_0{}^*M\,. \tag{18}$$

Finally, eq. (15) becomes

$$P_x[\eta]=\alpha[(\eta_{sp}+1)^{\frac{1}{\alpha}}-1]\frac{M_0}{K_xS_0{}^*M}\,. \tag{19}$$

The value of α is not known. But fortunately, it has been confirmed[7] that the intrinsic viscosity scarcely-

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[7] A. Odera, "Jikken Kagaku Koza", Vol 6, p. 146, Maruzen

deviates from its true value, if the value of α is not quite in correct. Therefore, the author adopted 10 for α. For the calculation of the specific viscosity (η_{sp}) of the polymerized liquid sulfur, both the viscosity values of the polymerized liquid sulfur and the viscosity values (η_0) of the pure liquid monomer sulfur are necessary. The former was obtained from the paper[5] by the author, and the latter was obtained from Gee's formula as follows,

$$-\ln \eta_0 = 9.67 - 2940/T \tag{20}$$

The calculated results of the product $P_z[\eta]$ are shown in Table 2. The well known relationship between the intrinsic viscosity and the degree of polymerization is

$$[\eta] = AP^a . \tag{21}$$

Eq. (21) is of general applicability for various types of polymers. It is also well known that the constant A and a depend on the types of polymers, the types of solvents and the temperatures of measurements, but are independent of the degree of polymerization of polymer.

By transferring P of eq. (21) to P_z and multiplying both sides of eq. (21) by P_z, we obtain

$$P_z[\eta] = AP_z^{a+1} . \tag{22}$$

Table 2 Calculations of $P_z\cdot[\eta]$

	η_{sp} Centipoise	$(\eta_{sp}+1)^{\frac{1}{10}}$	$\frac{M_0}{K_z\cdot M\cdot S_0{}^*}$	$P_z\cdot[\eta]$
120°C	0.024	1.0023	223.0	5.13
	0.047	1.0047	104.0	4.90
	0.086	1.0082	53.7	4.40
	0.122	1.0114	36.7	4.19
	0.148	1.0140	28.4	3.92
	0.175	1.0162	23.2	3.76
130°C	0.037	1.0036	254.0	9.15
	0.092	1.0088	96.0	8.45
	0.150	1.0141	49.6	6.99
	0.209	1.0190	34.0	6.46
	0.256	1.0230	26.3	6.05
	0.305	1.0269	21.5	5.77
140°C	0.080	1.0078	263.0	20.5
	0.218	1.0200	88.0	17.6
	0.337	1.0295	45.8	14.2
	0.426	1.0360	31.6	11.4
	0.495	1.0410	24.7	10.3
	0.552	1.0450	20.2	9.1
150°C	0.450	1.0379	158.5	60.0
	0.598	1.0480	82.2	39.5
	0.755	1.0578	42.4	24.5
	0.858	1.0640	30.1	19.3
	0.920	1.0673	23.7	15.9
	0.980	1.0708	19.2	13.6

The log−log plots of $P_x[\eta]$ against P_x are shown in Fig. 1. The straight lines are obtained at each temperature, and the values of A and a are obtained from the intercept and the slope of each straight line, respectively. They are shown in Table 3.

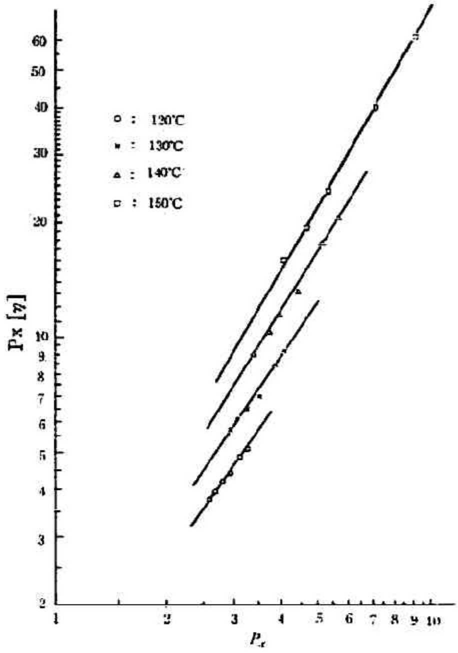

Fig. 1 $P_x[\eta]$ against P_x

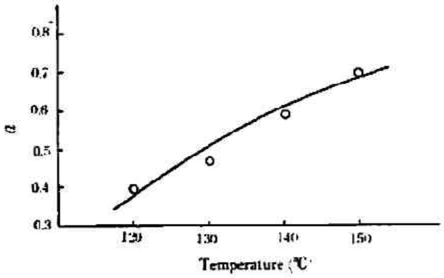

Fig. 2 Temperature dependence of a

Table 3 Temperature dependence of A and a

temperature (°c)	$A \times 10^2$	a
120	0.0	0.40
130	7.2	0.47
140	11.4	0.59
150	14.6	0.70

Plots of a against temperature are shown in Fig. 2.

Considerations

By analysing the viscosity curves obtained by measuring the liquid sulfur added with sulfur monochloride, it was observed that the exponents of the intrinsic viscosity-degree of polymerixation relationship for the polymerized liquid sulfur, in the temperature range 120 to 150°C, are between 0.4 and 0.7, depending on the temperature of the viscosity determinations and that they gradually increase with the temperature. These results agree with the measurements[8] in the case of the other types of polymer.

The result suggests that the sulfur polymer molecules assume a compact shape at low temperature and become a rather loosely extended shape with rising temperature. But in this analysis, as already mentioned, it must be kept in mind that the degree of polymerization of polymer sulfur has been found by an independent method. It must be also kept in mind that the author assumed what follows.

a) Sulfur monochlorides added to liquid sulfur completely change into ClS· radicals by the cleavage.

b) The equilibrium constants for the polymerizations of pure liquid sulfur obtained by Tobolsky *et al.* were taken as the equilibrium constants for the sulfur polymerizations initiated by ClS· radicals.

c) Baker's equation was used for the viscosities of sulfur polymer in spite of the high concentrations of sulfur polymer ranging from 0 to 20 weight % (in general, Baker's equation is well known because it is useful even if concentrations of the polymer solutions are high up to about 10 weight %).

This analysis contains many assumptions, as mentioned above. Nevertheless, the results excellently agree with the theory of high polymer chemistry. Conversely speaking, the results suggest the propriety of the assumptions taken in this analysis.

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8) T. Fox and P. Flory, *J. Phys. and Colloid Chem.*, 53, 197 (1949)