

Molecular Weight Distribution in Disulfide Polymers

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Synopsis

The published data on molecular weight distribution in polysulfide are rather contradictory and cannot be correlated with the concept of the existence of thiol-disulfide interchange in these polymers. In the present work the viscosity and molecular weights of liquid thiokols have been investigated (the number-average molecular weight by iodometric titration and by ebulliometry and the weight-average molecular weight by the light-scattering method). When measuring the light scattering in Thiokol solutions a considerable depolarization of the scattered light was observed. This fact must be taken into account in the molecular weight determination. It has been established that in polydisulfides with thiol endgroups thiol-disulfide interchange reactions take place not only during the synthesis, but also in the polymer itself (in bulk). These reactions lead to the formation of polymers with an equilibrium molecular weight distribution. A relation of $\log \eta = f(\bar{M}_w)^{1/2}$ has been found that can be used in determining the weight-average molecular weight of liquid Thiokols.

It is known that organic compounds containing sulfhydryl groups and disulfide bonds (for example cystine, cysteine, etc.) are capable of reactions of thiol-disulfide and disulfide-disulfide interchange.¹⁻³

A linear disulfide polymer undergoing these reactions should have a random molecular weight distribution;⁴ in this case the ratio of the weight-average molecular weight (\bar{M}_w) to the number-average molecular weight (\bar{M}_n) equals 2.

However the data published on molecular weight distribution of disulfide polymers containing terminal sulfhydryl groups are not consistent with this concept and are highly contradictory.

Polymers of narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.1-1.2$) have been obtained by fractionation the low molecular weight Thiokols by eluent chromatography.⁵

On the other hand, Fettes and Mark⁶ determined (by light-scattering and endgroup analysis) molecular weights for liquid Thiokols over the range of $\bar{M}_n = 600-4000$ and obtained values of \bar{M}_w/\bar{M}_n ratio in the range of 3-6.

The authors came to the conclusion that in the synthesis of liquid Thiokols the thiol-disulfide interchange reactions did not take place. Their attempt to reach equilibrium molecular weight distribution by heating polymers for a long period at 100°C., by ultraviolet irradiation, and by introducing certain catalysts did not lead to an appreciable narrowing of molecular weight distribution.

At the same time the sharp fall of the viscosity of Thiokol mixture (without changing the value of \bar{M}_n) on prolonged storage or heating for several hours may be considered as an indication of chain interchange reactions.^{7,8}

The study of the fractional composition of the mixture⁹ also suggested the occurrence of interchange reactions.

In connection with these conflicting results we attempted to investigate the interchange reaction in the linear disulfide polymers and the effects of these reactions on the molecular weight distribution.

EXPERIMENTAL

Polymers

Thiokols having a molecular weight in the range of 600–7000 were prepared by conventional methods of cleavage of high molecular weight polydisulfides by sodium hydrosulfide.^{9–11}

All the investigated polymers were freed from inorganic salts by ultracentrifugation of the benzene solutions at 40,000*g* followed by removal of benzene under vacuum.

Methods

The viscosity of polymers was measured in a Hoesppler viscometer at $25 \pm 0.1^\circ\text{C}$.

Number-average molecular weights were determined by iodometric titration of endgroups as well as by cryoscopic and ebullioscopic methods.

For the latter measurements an ebulliometer with a differential 15-junction thermocouple of the Ray type was used.¹²

Weight-average molecular weights were determined by light-scattering measurements with the use of a Sofica photometer. Benzene was used as the calibration standard. A Rayleigh ratio of $16.3 \times 10^{-6} \text{ cm.}^{-1}$ for 5,461 Å. was applied.

Refractive index increments were measured on the PCL differential refractometer.

Dioxane was employed as solvent. Dust was removed by centrifugation at about 40,000*g* for 1 hr.

Depolarization of the Scattered Light

Investigation of light scattering shows that there is considerable depolarization of scattering, which increases with decreasing molecular weight of the polymers.

This is obviously related to the great anisotropy of the low molecular weight Thiokol macromolecules and should be taken into account in determining their molecular weights. Accordingly, for all the polymers investigated the value of depolarization of scattered light was measured and molecular weights were calculated by using eqs. (1) and (2) for natural (unpolarized) incident beam and vertically polarized light, respectively.

$$1/\bar{M}_w = (H_c/R_{90})_{c \rightarrow 0} [(6 + 6\Delta_u)/(6 - 7\Delta_u)] \quad (1)$$

$$1/\bar{M}_w = (2H_c/R_{90})_{c \rightarrow 0} [(3 + 3\Delta_v)/(3 - 4\Delta_v)] \quad (2)$$

Here, H is a known optical constant, R_{90} is the Rayleigh ratio, c is the concentration (in grams per milliliter), and Δ_u , Δ_v are the ratios of the horizontal component of scattered light to its vertical component for natural and vertically polarized incident light, respectively.

Values of Δ_u and Δ_v are shown in Table I as well as values of \bar{M}_w , calculated for several polymers investigated without taking into account depolarization of scattering. The data of Table I indicate that if the polarization is not accounted for when working in normal light in the case of the lowest molecular weight polymers, the results are overestimated by a factor of two.

TABLE I
Effect of Depolarization of Scattered
Light on the Molecular Weight Determination

| \bar{M}_n | Natural light | | Vertically-polarized light | | | |
|-------------|-------------------|---------------------------------|-------------------------------|--------------|---------------------------------|-------------------------------|
| | Δ_u | \bar{M}_w uncor- rected | \bar{M}_w cor- rected | Δ_v^a | \bar{M}_w uncor- rected | \bar{M}_w cor- rected |
| 635 | 0.28 | 3,160 | 1,650 | 0.16 | 2,040 | 1,600 |
| 1,620 | 0.08 | 4,000 | 3,300 | 0.04 | 3,600 | 3,300 |
| 7,100 | 0.06 ₈ | 16,000 | 14,500 | — | — | — |

^a The Δ_v -value was not measured directly, but calculated from the known relation $\Delta_u = 2\Delta_v/(1 + \Delta_v)$.

The \bar{M}_w values used in our work are the mean values from data obtained in natural and vertically polarized light.

It is also necessary to consider that the refractive index of Thiokols in the range of molecular weights investigated depends on the molecular weights. Therefore the increment of the refractive index was measured for each of the polymers studied.

RESULTS AND DISCUSSION

The results of viscosity and molecular weight determinations of Thiokols are summarized in Table II and graphically represented in Figure 1.

Figure 1 shows that the linear relationship between $\log \eta$ and $\bar{M}_w^{1/2}$ derived by Flory¹³ for linear polyesters is also valid in the case of liquid Thiokols.

By using the data obtained, the relationship for $\eta = f(\bar{M}_w)$ was derived for these polymers at a temperature of 25°C. as

$$\log \eta = -0.19 + 0.0313\bar{M}_w^{1/2}$$

This relation can be used to determine the weight-average molecular weight.

TABLE II
Molecular Weights of Thiokols

| No. | Viscosity, poises | n_D^{20} | Number-average molecular weights | | | Weight-average molecular weights | | | \bar{M}_w/\bar{M}_n |
|-----|----------------------|------------|----------------------------------|-----------------|----------------------|-------------------------------------|-----------------|-----------|-----------------------|
| | | | By end groups | By cryoscopy | By ebulli- ometry | By light scattering | By viscosity | | |
| 1 | 4.0 | 1.559 | 640 | — | — | 1,600 | — | 2.5 | |
| 2 | 7.4 | 1.563 | 700 | 700 | — | — | 1,200 | 1.7 | |
| 3 | 16.0 | — | 940 | — | — | 1,900 | — | 2.0 | |
| 4 | 34.0 | — | — | — | 1,620 | 3,300 | — | 2.0 | |
| 5 | 83.5 | 1.572 | 1,770 | — | 2,130 | 4,500 | — | 2.5 (2.1) | |
| 6 | 470 | — | 3,850 | — | — | — | 8,200 | 2.1 | |
| 7 | 680 | — | 4,950 | — | 5,170 | 8,800 | — | 1.8 | |
| 8 | 728 | 1.579 | 4,480 | — | 4,630 | 9,100 | — | 2.0 | |
| 9 | 755 | 1.579 | 4,480 | 4,450 | 5,170 | — | 9,400 | 2.1 | |
| 10 | 3880 | 1.579 | 7,100 | — | — | 14,500 | — | 2.0 | |

The comparison of number-average molecular weights and weight-average molecular weights represented in Table II shows that the ratio \bar{M}_w/\bar{M}_n for all polymers studied (having a viscosity of 4-4000 poises), practically equals 2.

Thus, in synthesizing liquid Thiokols, polymers with an equilibrium molecular weight distribution are formed; this can evidently be explained by chain interchange reactions.

In order to confirm the existence of such reactions in liquid Thiokols and to elucidate the conditions under which they take place we studied 1:1 mixtures (by weight) of Thiokols, having molecular weights (\bar{M}_n) of 640

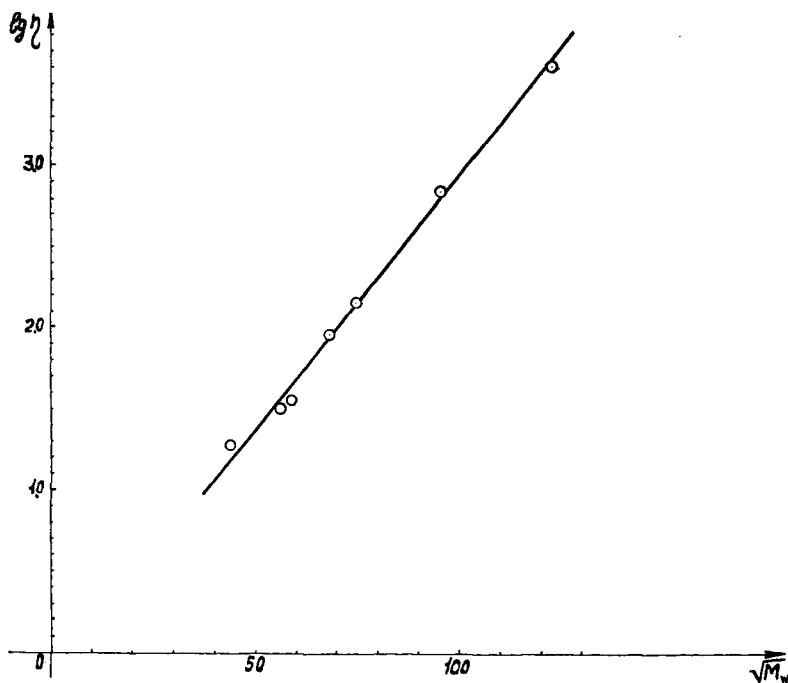


Fig. 1. Plot of $\log \eta$ against $\bar{M}_w^{1/2}$.

and 4480. The mixing of these polymers was achieved at room temperature by intense stirring for 3 hr.

The viscosity measurements made after this treatment gave a value of 64 poises as compared to the calculated value of 117 poises (in the absence of interchange).

The following viscosity reduction at room temperature without stirring is very slow. Therefore the mixture was subjected to heating for 36 hr. at 100°C. under argon. Figure 2 shows the viscosity changes with time at 100°C.

The values of the weight- and number-average molecular weights of the mixture were simultaneously obtained immediately after the preparation

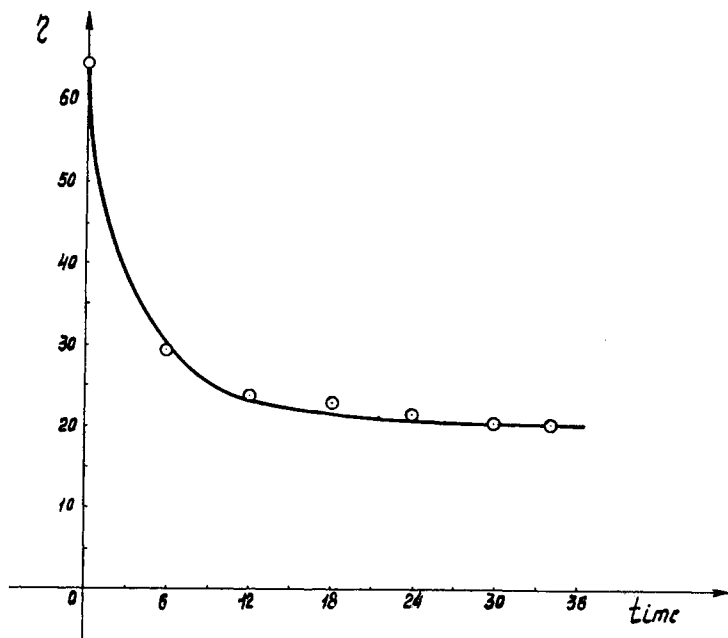


Fig. 2. Viscosity change with time.

and after the equilibrium was attained: the latter was established by the constancy of the viscosity values.

The results obtained are summarized in Table III, along with the molecular weight values calculated from \bar{M}_w and \bar{M}_n values of the original polymers (cf. Table II). The values of \bar{M}_w and \bar{M}_n for the mixture immediately after mixing were calculated by using common formulas; in calculating these values after the equilibration the distribution was assumed to correspond to the Flory case with $\bar{M}_w = 2\bar{M}_n$.

These data show that in the mixing process an equilibrium molecular weight distribution is reached, which is considered as evidence of interchange reactions in bulk.

Thus chain interchange takes place in liquid Thiokols not only during their synthesis, but also in the polymer itself (in bulk) even at room temperature.

TABLE III
Molecular Weights of Thiokol Mixture

| | \bar{M}_n | | M_w | |
|---------------------------------|-------------|-------|------------|-------|
| | Calculated | Found | Calculated | Found |
| Immediately after mixing | 1,100 | 1,160 | 5,140 | 6,000 |
| After attainment of equilibrium | 1,100 | 1,160 | 2,200 | 2,300 |

In polysulfides having thiol endgroups, exchange reactions between thiol and disulfide groups, as well as between two disulfide groups, can take place.

As interchange reactions are observed even at room temperature it could be suggested that thiol-disulfide interchange proceeds essentially by an ionic mechanism of nucleophilic substitution.

In order to confirm this assumption we have investigated the viscosity and molecular weight of mixtures of Thiokols having different molecular weights and containing terminal thioacetyl groups. The data of Table IV show that in polysulfides containing no terminal thiol groups the reactions of chain interchange do not take place, even on prolonged heating at 100°C.

TABLE IV

| Polymer | Viscosity at 25°C., poises | \bar{M}_n | | \bar{M}_w | |
|-----------------------------|----------------------------------|-------------|-----------------|-------------|---------------------|
| | | Calculated | By ebulliometry | Calculated | By light scattering |
| No. 1 | 9.5 | — | 900 | — | 1,600 |
| No. 2 | 453 | — | 4,700 | — | 6,900 |
| Immediately after mixing | 74.5 | 1,500 | 1,300 | 4,300 | 4,600 |
| After 6 hr. at 100°C. | 77 | — | 1,500 | — | — |
| After 36 hr. at 100°C. | 71.5 | — | 1,300 | — | — |

Thus it may be considered as established that in polysulfides with thiol endgroups, reactions of thiol-disulfide interchange proceed during the synthesis as well as in the polymer in bulk.

These reactions ensure the possibility of obtaining polymers with an equilibrium molecular weight distribution.

References

1. A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).
2. N. Kharasch, Ed., *Organic Sulfur Compounds*, Pergamon, New York, 1961, p. 83.
3. E. N. Guryanova, "Isotope interchange and structure of organic sulfur compounds," Thesis for Doctor's degree, L. Y. Karpov Physico-Chemical Institute, Moscow, U.S.S.R., 1956.
4. P. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936); *ibid.*, **64**, 2205 (1942).
5. A. N. Genkin, T. P. Nassonowa, I. Ya. Poddubnyi, *Vysokomolekul. Soedin.*, **4**, 1088 (1962).
6. E. M. Fettes and H. Mark, *J. Appl. Polymer Sci.*, **7**, 2239 (1963).
7. *Thiokol Liquid Polymer*, LP-3 (1952), Thiokol Chemical Corporation, No. A300.
8. R. A. Shlyakhter, N. P. Apukhtina, and T. P. Nassonowa, *Dokl. Akad. Nauk SSSR*, **149**, 345 (1963).
9. E. M. Fettes and J. S. Jorczak, *Ind. Eng. Chem.*, **42**, 2217 (1950).
10. J. S. Jorczak and E. M. Fettes, *Ind. Eng. Chem.*, **43**, 336 (1951).

11. N. P. Apukhtina, R. A. Shlyakhter, F. B. Novoselok, *Kautschuk i Resina*, **6**, 7 (1957).

12. P. W. Allen, Ed., *Techniques of Polymer Characterisation*, Butterworths, London, 1959.

13. P. Flory, *J. Am. Chem. Soc.*, **62**, 1057 (1940).

Résumé

Les résultats publiés dans la littérature relatifs à la distribution des poids moléculaires dans les polysulfures sont en opposition avec le concept traditionnel d'existence d'une réaction d'interchange thio-disulfure dans ces polymères. Dans ce travail nous avons étudié la viscosité et le poids moléculaire de thiokols liquides (le poids moléculaire exprimé en nombre a été déterminé par titration iodométrique et par ebulliométrie et le poids moléculaire exprimé en poids par la diffusion de lumière). En mesurant la diffusion de lumière de solutions thiokols on a constaté l'existence d'un phénomène de dépolarisation important de la lumière diffusée. On a tenu compte de ce phénomène pour déterminer les poids moléculaires. On a établi que la réaction d'interéchange qui se produit dans les polydisulfures possédant des groupements thiols terminaux se produit non seulement durant la synthèse mais continue dans le polymère lui-même (en bloc). Ces réactions entraînent la formation de polymères avec une distribution des poids moléculaires résultant d'un équilibre. On a trouvé une relation $\log \eta = f(\bar{M}_w^{1/2})$; cette relation peut être utilisée pour déterminer le poids moléculaire exprimé en poids des thiokols liquides.

Zusammenfassung

Die über die Molekulargewichtsverteilung in Polysulfiden veröffentlichten Angaben sind recht widerspruchsvoll und lassen sich mit dem Konzept des Bestehens eines Thiol-Disulfidaustausches bei diesen Polymeren nicht in Einklang bringen. In der vorliegenden Arbeit wurden Viskosität und Molekulargewicht flüssiger Thiokole untersucht und zwar das Zahlenmittelmolekulargewicht durch jodometrische Titration und Ebullioskopie und das Gewichtsmittelmolekulargewicht nach der Lichtstreuungsmethode. Bei der Messung der Lichtstreuung von Thiokollösungen wurde eine starke Depolarisation des Streulichtes beobachtet. Dieser Umstand muss bei der Molekulargewichtsbestimmung berücksichtigt werden. Es wurde festgestellt, dass bei Polydisulfiden mit endständigen Thiolgruppen ein Thiol-Disulfidaustausch nicht nur während der Synthese sondern auch im Polymeren selbst (in Substanz) stattfindet. Diese Reaktion führt zur Bildung von Polymeren mit einer Gleichgewichts-Molekulargewichtsverteilung. Eine Beziehung $\log \eta = f(\bar{M}_w^{1/2})$ wurde aufgefunden, die zur Bestimmung des Gewichtsmittelmolekulargewichts flüssiger Thiokole benutzt werden kann.

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