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### **Anionic Copolymerization of Elemental Sulfur with Propylene Sulfide. Equilibrium Sulfur Concentration**

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## Anionic Copolymerization of Elemental Sulfur with Propylene Sulfide. Equilibrium Sulfur Concentration

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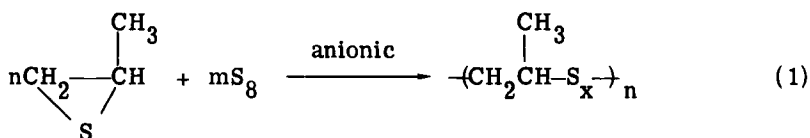
### ABSTRACT

In the anionic copolymerization of elemental sulfur ( $S_8$ ) with propylene sulfide (P) below the floor temperature of elemental sulfur homopolymerization ( $T_f = 159^\circ\text{C}$ ), there is a certain concentration of elemental sulfur left when copolymerization is completed ( $[S_8]_{\text{eq}}$ ). The dependence of  $[S_8]_{\text{eq}}$  on the feed ratio  $[P]_0/[S_8]_0$  and temperature was determined by using laser Raman spectroscopy, and this enabled us to distinguish between the S-S bonds in elemental sulfur and in the linear polysulfide.  $[S_8]_{\text{eq}}$  was found to decrease with increasing temperature and with an increasing  $[P]_0/[S_8]_0$  ratio. The experimental dependence of the average enthalpy and entropy of polymerization ( $\Delta\bar{H}_{\bar{x}}$  and  $\Delta\bar{S}_{\bar{x}}$ ) on  $\bar{x}$ , as described by the equilibrium  $\dots-\text{CH}_2\text{CH}(\text{CH}_3)\text{S}_{\bar{x}}^- + \text{S}_8 \rightleftharpoons \dots-\text{CH}_2\text{CH}(\text{CH}_3)\text{S}_{\bar{x}+8}^-$ , has shown that at  $\bar{x} \geq 9$  the experimental  $\Delta\bar{H}_{\bar{x}}$  and  $\Delta\bar{S}_{\bar{x}}$  approach values determined earlier for the free radical homopolymerization of ele-

mental sulfur  $\dots -S_n^- + S_8 \rightleftharpoons \dots -S_{n+8}^-$ . The corresponding values are 3.1 kcal/mol and 4.76 cal/mol·degree.

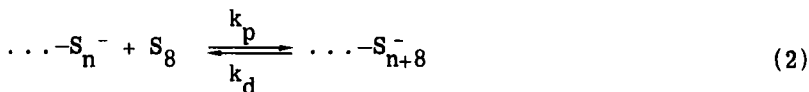
## INTRODUCTION

The anionic copolymerization of elemental sulfur with cyclic sulfides [1-4], e.g., with methylthiirane (propylene sulfide) (P), described by us previously:



(where  $8m = n(x - 1)$ )

has been conducted below the floor temperature of sulfur homopolymerization (i.e., 159°C). At these conditions elemental sulfur would not be able to homopolymerize because the propagation-depropagation equilibrium



is shifted completely to the monomer side.

We observed that in the copolymerization process there is also a certain concentration of  $S_8$  left in the reaction medium when copolymerization is completed. We shall denote this concentration as  $[S_8]_{eq}$ .

In this paper we describe the dependence of  $[S_8]_{eq}$  on the initial feed, i.e., on the ratio  $[P]_0/[S_8]_0$  and on temperature.

## EXPERIMENTAL

Elemental sulfur (Kopalnia Siarki-Grzybów, Poland) for spectroscopy (99.999% pure) was used without further purification.

Propylene sulfide (Fluka AG, chemische Fabrik) was purified as described [3], and distilled in a high vacuum system from a Na mirror just before use.

Sodium thiophenoxide initiator (the sodium cation was complexed with dibenzo-18-crown-6-ether) was prepared from thiophenol and sodium metal.

Crown ether, dibenzo-18-crown-6, was prepared as described [5] and sublimed in vacuo.

Allyl bromide terminating agent (Reakhim, USSR) was purified by distillation and then used.

Benzene (POCh, Poland) was refluxed several days over sodium metal and then fractionated. The middle fraction was dried with  $\text{CaH}_2$ , degassed, and condensed in the vessel with liquid Na/K alloy.

Reaction mixtures, as described by us before [3], were sealed in Pyrex tubes. When all of the propylene sulfide had been consumed and no changes in  $\text{S}_8$  concentration could be observed, the copolymerization was stopped by killing the active centers (thiolate anions) with allyl bromide at the temperature of the copolymerization experiment.

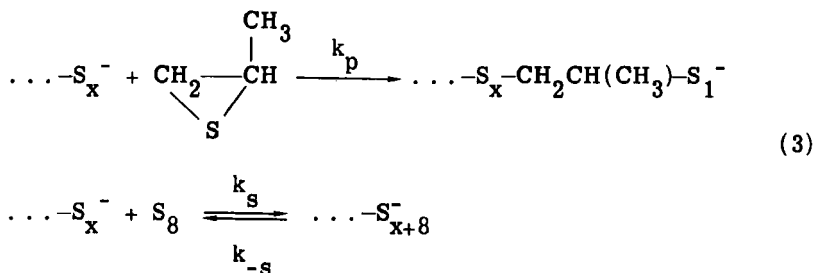
Raman spectra were obtained on the Cary 82 (Varian) Spectrometer with an argon ion laser (Spectra Physics) emitting at  $5145 \text{ \AA}$  (100 mW power at the sample,  $3 \text{ cm}^{-1}$  spectral slit-width). All measurements were performed at  $25^\circ\text{C}$ .

## RESULTS AND DISCUSSION

Copolymerizations were carried out in benzene solutions with sodium thiophenoxide as initiator (sodium cation was complexed with dibenzo-18-crown-6 ether) at 50 to  $90^\circ\text{C}$ . The intensities of the Raman bands at  $217 \text{ cm}^{-1}$  in the laser Raman spectra gave the concentrations of  $\text{S}_8$  (the line at  $607 \text{ cm}^{-1}$  due to the benzene scattering was used as an internal standard).

In Fig. 1 the experimentally-found dependence of  $[\text{S}_8]_{\text{eq}}$  on  $[\text{P}]_0/8[\text{S}_8]_0$  is given. As could be expected, the larger the proportion of propylene sulfide in the feed, the lower the resulting  $[\text{S}_8]_{\text{eq}}$ . These data allow us to relate  $[\text{S}_8]_{\text{eq}}$  to  $[\text{P}]_0/[\text{S}_8]_0$  and thus to predict the copolymer composition as a function of comonomers feed and temperature. (See also Figs. 2 and 3.)

The following kinetic scheme has previously been applied in the description of the copolymerization process:



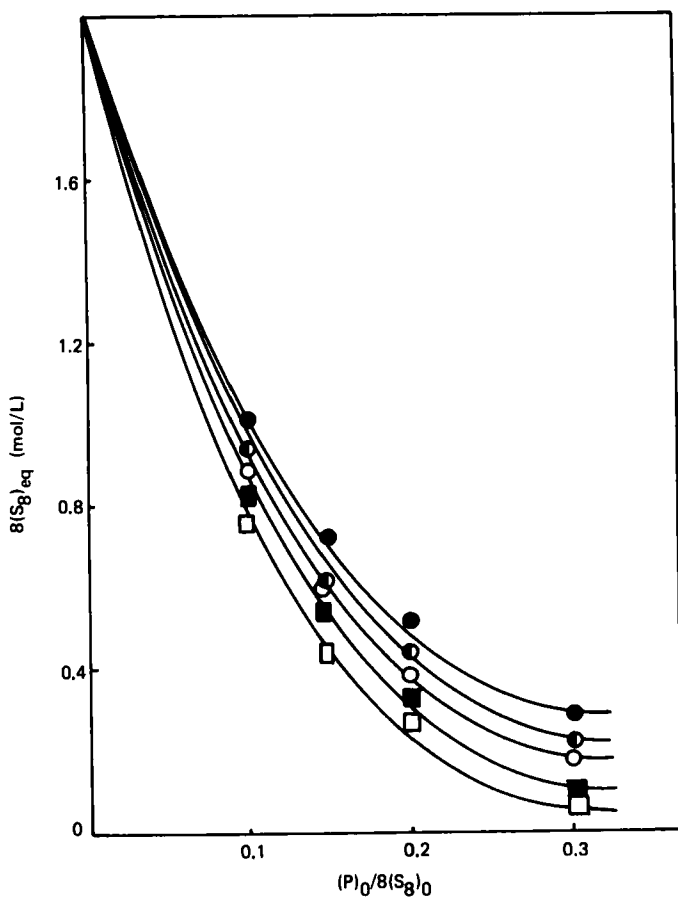


FIG. 1. Dependence of the equilibrium concentration of elemental sulfur ( $[S_8]_{eq}$ ) on the initial concentrations of propylene sulfide and elemental sulfur ratio  $([P]_0/8[S_8]_0)$  in  $C_6H_6$  solution. Initiator (I): sodium thiophenoxide (sodium cation complexed with dibenzo-18-crown-6 ether).  $[I]_0 = 1 \times 10^{-3}$  M,  $8[S_8]_0 = 2$  M. Temperature: ( $\bullet$ ) =  $50^\circ\text{C}$ , ( $\circ$ ) =  $60^\circ\text{C}$ , ( $\square$ ) =  $70^\circ\text{C}$ , ( $\blacksquare$ ) =  $80^\circ\text{C}$ , ( $\square$ ) =  $90^\circ\text{C}$ .

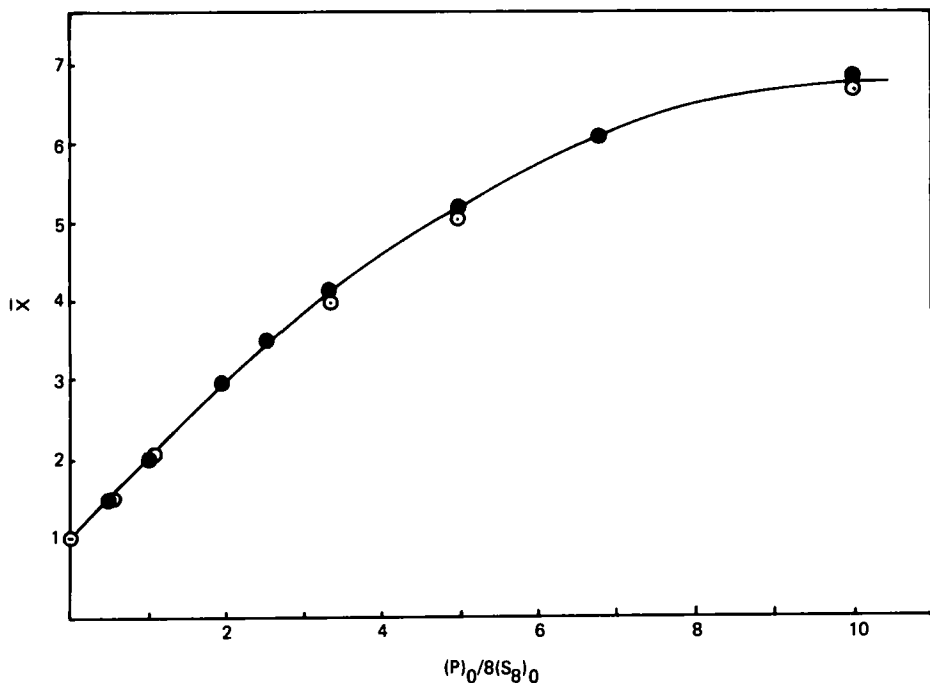
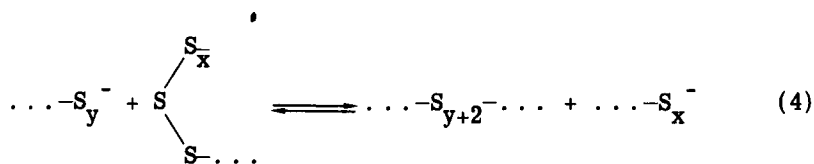


FIG. 2. The average number of sulfur atoms in the polysulfide bridges (sulfur rank),  $\bar{x}$  in  $-(CH_2-CH(CH_3)-S_x-)_n$ , as a function of a feed composition of the reaction mixture  $1/y_0 = 8[S_8]_0/[P]_0$ . (●) Calculated from Raman spectra. (○) Based on elemental analysis of copolymers extracted with methyl alcohol until complete  $S_8$  removal. Points experimental, line plotted according to the equation  $\bar{x} = y_0^{-1} [1 - \exp(-9.4 y_0)] + 1$ . Conditions of copolymerizations:  $C_6H_6$  solution at  $80^\circ C$  initiator: sodium thiophenoxide,  $[I]_0 = 10^{-3} M$ ,  $8[S_8]_0 = 2 M$ .

Higher conversions have to be complemented with the reaction between sulfide ions and polysulfide junctions in the copolymer:



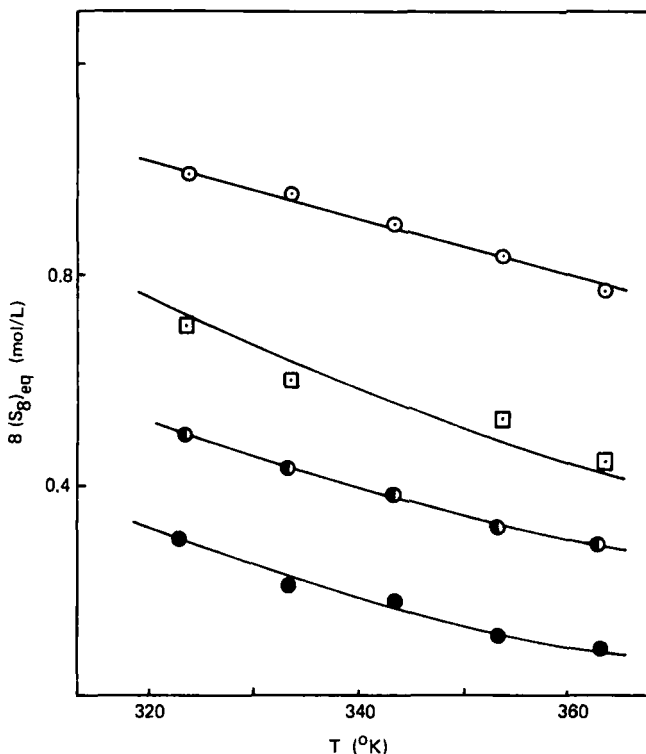
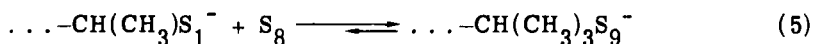


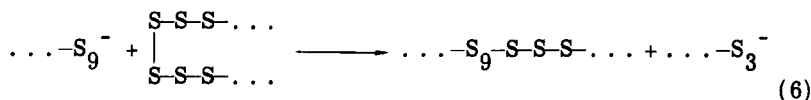
FIG. 3. Dependence of  $[S_8]_{eq}$  on the absolute temperature.  $[P]_0/8[S_8]_0$ : ( $\circ$ ) = 0.1, ( $\square$ ) = 0.15, ( $\bullet$ ) = 0.2, ( $\blacklozenge$ ) = 0.3. (Conditions of copolymerization as given in Fig. 1.)

The distribution of the discrete  $x$  values (e.g., 1, 2, . . . , 7, 8, . . .) changes during copolymerization, depending on the relative proportions of comonomers built in the copolymer. However, once equilibrium is reached, a certain distribution of active species in the system is established. These species, which differ in  $x$ , are in equilibrium with  $S_8$ , and the overall equilibrium position depends on the distributions of  $x$  and the values of the individual equilibrium constants  $K_x$ . It can be assumed that when  $x = 1$ , the addition of  $S_8$  is practically irreversible, because, as it is illustrated in Eq. (4), the reformation of . . .  $-\text{CH}(\text{CH}_3)-S_1^-$  from . . .  $-\text{CH}(\text{CH}_3)S_9^-$  is highly improbable due to the large difference in the internal energies of both species:



This difference is caused by interaction of the lone electron pair of thiolate anion with the nearby sulfur atoms. This interaction, which lowers the internal energy of the ion, is not possible for  $\dots -\text{CH}(\text{CH}_3)\text{S}_1^-$ .

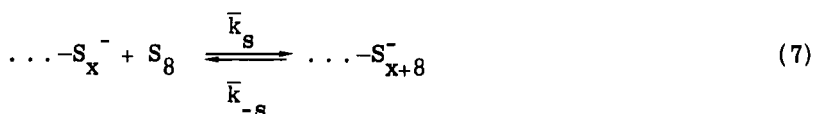
However, there is another mechanism by which the  $\dots -\text{S}_9^-$  species can lose sulfur. This is the scrambling process:



Thus, the  $\dots -\text{S}_{12}^- \dots$  unit is formed (for instance) in this way within a chain, and another attack of  $\dots -\text{S}_x^-$  into this unit can provide, in the way shown in Eq. (5), a thiolate anion, e.g.,  $\dots -\text{S}_y^-$ , in which  $y > 9$ . This one is now able to depropagate. Thus, if the scrambling process is fast enough, then, formally, any of the active species is eventually in equilibrium with  $\text{S}_8$ .

We can now introduce an average value  $\bar{x}$ , and an equilibrium coefficient  $K_{\bar{x}}$ , which for a given system (i.e.,  $[\text{P}]_0$ ,  $[\text{S}_8]_0$ , and temperature) incorporates a set of equilibrium constants  $K_1, K_2, \dots, K_5, \dots, K_8, \dots$ , with subscripts giving the number of S atoms in the thiolate anion.  $K_{\bar{x}}$  also incorporates the distribution of the length of sulfur chains preceding the thiolate anions.

Thus, we can write as a unique formal equilibrium:



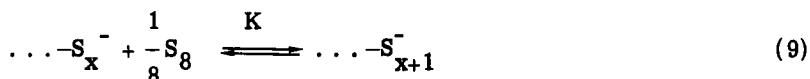
where  $\bar{k}_s$  and  $\bar{k}_{-s}$  are the average "rate constants" of propagation and depropagation involving elemental sulfur, respectively, and  $\bar{x}$  is an average number of sulfur atoms in the polysulfide bridges preceding the active species. This number is equal to those in the thiolate anion, provided that scrambling, as we have assumed, is indeed faster than propagation.

It follows from Eq. (7) that



$$K_{\bar{x}} = \frac{\bar{k}_s}{\bar{k}_{-s}} = \frac{[\dots - S_{x+8}^-]}{[\dots - S_x^-]} \frac{1}{[S_8]_{\text{eq}}} \quad (8)$$

Considering the hypothetical equilibrium



we have

$$K = \frac{[\dots - S_{x+1}^-]}{[\dots - S_x^-]} \frac{1}{[S_8]_{\text{eq}}^{1/8}} \quad (10)$$

Assuming further that the  $[\dots - S_{x+1}^-]/[\dots - S_x^-]$  ratio is constant and independent of the  $x$  value, we can write the equilibrium coefficient  $K_{\bar{x}}$  in terms of the equilibrium constant  $K$  as

$$K_{\bar{x}} = K^8 \quad (11)$$

and

$$K_{\bar{x}} = \alpha^8 \frac{1}{[S_8]_{\text{eq}}} \quad \left( \text{where } \alpha = \frac{[\dots - S_{x+1}^-]}{[\dots - S_x^-]} \right) \quad (12)$$

According to an earlier assumption that fast scrambling reactions govern similarity of distributions for  $x$  values in the thiolate anions and in the polysulfide bridges of the copolymer,  $\alpha$  can be expressed as the  $[\dots - S_{x+1}^- \dots]/[\dots - S_x^- \dots]$  ratio (cf. Eq. 4).

Reacted elemental sulfur is built into the linear polysulfide linkages of the copolymer:

$$8[S_8]_0 - 8[S_8]_{\text{eq}} = [\dots - S_2^- \dots] + 2[\dots - S_3^- \dots] + \dots (x-1)[\dots - S_x^- \dots] + \dots \quad (13)$$

Introducing  $\alpha$ , we obtain

$$\begin{aligned} 8[S_8]_0 - 8[S_8]_{\text{eq}} &= [\dots - S_2^- \dots] (1 + 2\alpha + \dots + (x-1)\alpha^{x-2} + \dots) \\ &= [\dots - S_2^- \dots] \sum_{x=2}^{\infty} (x-1)\alpha^{x-2} \quad (14) \end{aligned}$$

Taking into account that below  $T_f$  the inequality  $\alpha < 1$  holds,

$$8[S_8]_0 - 8[S_8]_{eq} = [\dots - S_2 - \dots] \frac{1}{(1 - \alpha)^2} \quad (15)$$

Thus, for sufficiently large  $[S_8]_0/[P]_0$  ratios, the diads of P are practically not produced and the concentration of the polysulfide sequences is equal to  $[P]_0$ :

$$[P]_0 = [\dots - S_2 - \dots] + [\dots - S_3 - \dots] + \dots + [\dots - S_x - \dots] + \dots \quad (16)$$

Introduction of  $\alpha$  yields

$$\begin{aligned} [P]_0 &= [\dots - S_2 - \dots] (1 + \alpha + \dots + \alpha^{x-2}) \\ &= [\dots - S_2 - \dots] \sum_{x=2}^{\infty} \alpha^{(x-2)} \end{aligned} \quad (17)$$

And further:

$$[P]_0 = [\dots - S_2 - \dots] \frac{1}{1 - \alpha} \quad (18)$$

From a comparison of Eqs. (18) and (15):

$$\frac{8[S_8]_0 - 8[S_8]_{eq}}{[P]_0} = \frac{1}{1 - \alpha} \quad (19)$$

Remembering that

$$\bar{x} = \frac{8[S_8]_0 - 8[S_8]_{eq}}{[P]_0} + 1 \quad (20)$$

We finally obtain

$$K_{\bar{x}} = \left( \frac{\bar{x} - 2}{\bar{x} - 1} \right) 8 \frac{1}{[S_8]_{eq}} \quad (21)$$

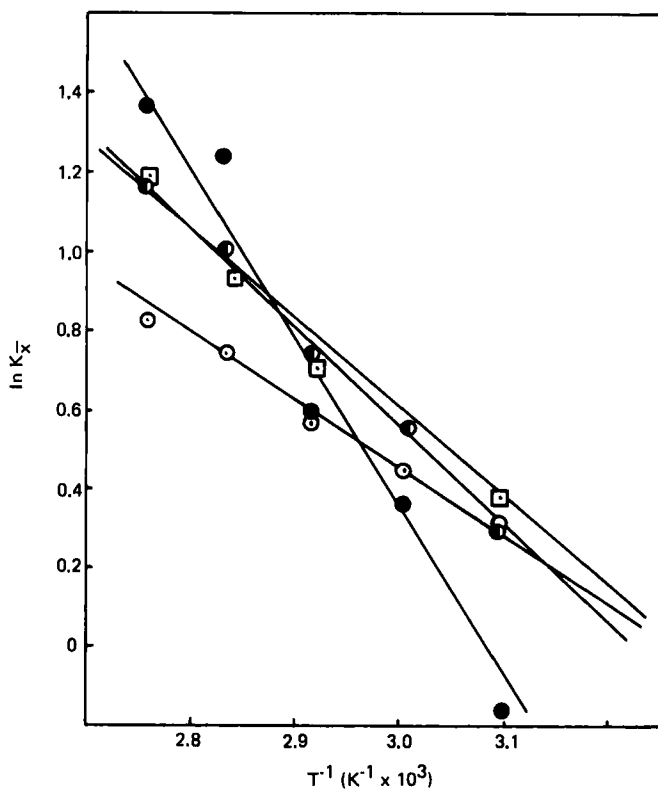


FIG. 4. Dependence of  $\ln K_{\bar{x}}$  on the reciprocal of the absolute temperature. Conditions: cf. Fig. 4.

After evaluation of the  $K_{\bar{x}}$  values from Eq. (21) for a given feed and temperature ( $\bar{x}$  known from  $[P]_0$ ,  $[S_g]_0$ , and  $[S_g]_{eq}$ ), the dependence of  $K_{\bar{x}}$  on temperature was plotted:

$$-\ln K_{\bar{x}} = \frac{\Delta \bar{H}_{\bar{x}}}{RT} - \frac{\Delta \bar{S}_{\bar{x}}}{R} \quad (22)$$

where  $\Delta \bar{H}_{\bar{x}}$  and  $\Delta \bar{S}_{\bar{x}}$  are not unique thermodynamic functions, but the average enthalpy and entropy depending on the value of  $\bar{x}$ .

In Fig. 4 the dependence of  $\ln K_{\bar{x}}$  on the reciprocal of the absolute

TABLE 1. Dependence of the Average Enthalpy and Entropy Values of Reaction (7) on the Feed Ratio of Comonomers

$y_0 = \frac{[P]_0}{8[S_8]_0}$	0.3	0.2	0.15	0.10
$\Delta\bar{H}_x^-$ (kcal/mol)	9 ± 0.9	5.20 ± 0.25	4.30 ± 0.60	3.30 ± 0.30
$\Delta\bar{S}_x^-$ (cal/mol·deg)	22.8 ± 2.5	16.7 ± 0.8	14.2 ± 1.5	11.0 ± 1.0

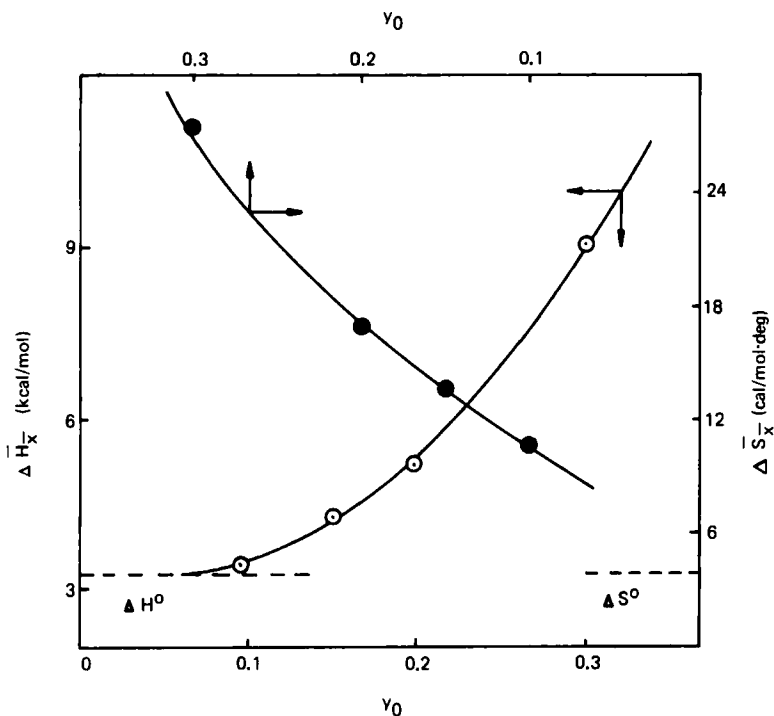


FIG. 5. Dependence of the average enthalpy ( $\Delta\bar{H}_x^-$ ) and entropy ( $\Delta\bar{S}_x^-$ ) of the equilibrium  $\dots -S_x^- + S_8 \rightleftharpoons \dots -S_{x+8}^-$  on the feed composition,  $y_0 = [P]_0/8[S_8]_0$ .  $\Delta H^0$  and  $\Delta S^0$  indicate values determined for the radical homopolymerization of elemental sulfur.

temperature is given for four different feed ratios  $[P]_0/8[S_8]_0$ . The corresponding sets of  $\Delta\bar{H}_{\bar{x}}$  and  $\Delta\bar{S}_{\bar{x}}$  are given in this order, following the related  $y_0$  ratios (Table 1).

By plotting these  $\Delta\bar{H}_{\bar{x}}$  and  $\Delta\bar{S}_{\bar{x}}$  values as a function of  $[P]_0/8[S_8]_0$ , we obtain the experimental dependence of the average thermodynamic functions on  $y_0$  (or  $\bar{x}$ , since  $y_0$  and  $\bar{x}$  are interrelated, as shown in

Fig. 2). This plot is shown in Fig. 5;  $\Delta H^0$  and  $\Delta S^0$  of the radical homopolymerization of elemental sulfur are indicated by broken lines (values taken from Ref. 6).

$\Delta S^0$  (this work)  $\neq \Delta S^0$  (in the Tobolsky-Eisenberg treatment) because of different standard states. Omitting the differences resulting from the density changes with temperature caused by the monomer - polymer transition,  $\Delta H_3^0$  (this work) =  $\Delta H_3^0$  (Tobolsky-Eisenberg), but  $\Delta S^0$  (this work) =  $\Delta S^0$  (Tobolsky-Eisenberg) +  $R \ln \frac{\text{mol/kg}}{\text{mol/L}} \approx 3.63 \text{ cal/mol}\cdot\text{deg}$ .

It could be assumed that  $\Delta\bar{H}_{\bar{x}} - \Delta H^0$  and  $\Delta\bar{S}_{\bar{x}} - \Delta S^0$  with  $y_0 \rightarrow 0$ , i.e., when the excess of sulfur bridges ( $\bar{x}$ ) becomes large enough that the influence of the remote carbon atoms disappears. This is why the thermodynamics of sulfur copolymerization and homopolymerization tend to merge for higher  $\bar{x}$ .

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