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THERMOMECHANICAL ANALYSIS OF ELEMENTAL SULPHUR: THE EFFECTS OF THERMAL HISTORY AND AGEING

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ABSTRACT

The effect of thermal history on the ageing of elemental sulphur has been examined by thermomechanical analysis (TMA). Liquid sulphur at temperatures below (135°C), and above (180°C), the polymerization temperature of sulphur (159°C) was quick quenched to various lower temperatures. It has been demonstrated that TMA can be used to monitor the molecular and crystallographic transformations which occur in the subsequent ageing of sulphur.

INTRODUCTION

In view of the current interest and search for new large scale commercial uses for sulphur, an examination of the thermomechanical properties of sulphur is timely. Many of the sulphur-containing materials which have potential commercial value, contain large proportions of elemental sulphur. A knowledge of the mechanical properties of sulphur will serve as a basis for understanding how these properties are altered by various additives. It is perhaps not sufficiently appreciated that thermal history and ageing have profound effects on the mechanical properties of sulphur. This article will report some recent results of thermomechanical analysis (TMA) of elemental sulphur samples with different thermal histories.

PROPERTIES OF ELEMENTAL SULPHUR

Sulphur is perhaps unequalled among the elements for its number of allotropic modifications. The three most important forms are orthorhombic sulphur S_α, monoclinic sulphur S_β, and polymeric sulphur S_ω.

Orthorhombic sulphur S_α, is the thermodynamically stable form at room temperature and pressure. At 96.5°C, the phase transition of S_α to S_β occurs and above this temperature S_β is the thermodynamically stable allotrope until melting occurs. Polymeric sulphur S_ω is formed by the rapid cooling of liquid sulphur from above the equilibrium polymerization temperature at 159°C. Whereas, S_α and S_β are crystalline

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materials consisting of S_8 rings, S_ω is semi-crystalline and consists of linear chains of up to 10^6 sulphur atoms[1].

Widely varying values for the mechanical properties of sulphur have been reported[2–7]. The reported values for the properties of bulk sulphur are often unqualified in terms of purity, allotropic composition and thermal history. The work of Dale and Ludwig[2] demonstrated that these factors significantly affect the mechanical properties.

The factors in the thermal history of solid sulphur which primarily effect its mechanical properties are the upper temperature of liquid sulphur from which the solid formed, the rate of cooling to the lower temperature and the time and temperature of ageing. The species present in liquid sulphur have been the subject of several theoretical and experimental studies[8–12]. The S_8 ring species present in liquid sulphur above its melting point undergo polymerization abruptly at 159°C. Between 159 and 240°C the average number of S atoms in the polymer chain[12] varies between 10^5 and 2×10^4. The rate of cooling of liquid sulphur determines the extent to which the monomer–polymer equilibrium present at the upper temperature is "frozen". On ageing, reversion to the thermodynamically stable S_α form occurs and the variation of the relative amounts of S_α and other forms present undoubtedly determines the mechanical properties.

Only two investigations have been reported in which the effects of thermal history and ageing on mechanical properties were examined[2,6]. Dale and Ludwig[2] determined the tensile strength of various samples of solid sulphur including both pure orthorhombic S_α and pure monoclinic S_β sulphur. They showed that the tensile strength of sulphur increases as a function of the degree of polymerization and distribution of polymeric sulphur. Tensile strengths of up to ten times that for pure S_α were observed for S_α–S_β mixtures.

Rennie et al.[6], also examined the effect of temperature and thermal history on the break strength of solid sulphur bars. They showed that the break strength of sulphur quenched from the liquid at 130 to 22°C, increased with ageing at room temperature. The increase in strength which occurred in the first 24 h was attributed partly to the conversion of S_β to S_α. A subsequent slower increase in strength occurred. This paralleled the increase in CS_2 insoluble sulphur, i.e., S_ω. These authors also showed that the break strength of the sulphur is very temperature dependent, ranging from 200 psi at −80°C through a maximum of 1400–1600 psi at 35°C to near zero at 100°C.

The correlation of mechanical properties with the allotropic composition has been restricted somewhat by the lack of a suitable quantitative method for determining the relative amounts of S_α and S_β present. Dale and Ludwig[2] reported the limitations of using X-ray diffraction (XRD) for distinguishing the crystalline allotropic modifications present in bulk samples. Recently, Currell and Williams[14] reported the use of differential scanning calorimetry (DSC) as a method for the quantitative estimation of S_α and S_β. However, the analysis for S_α and S_β in large test specimens using DSC may be limited by the ability to obtain a representative sample without alteration of the composition as a result of sampling. Thermal analysis of sulphur by differential thermal analysis, thermomechanical analysis and thermal depolarization analysis has been reported[14].

In the present study the effects of thermal history and ageing of sulphur were examined by thermomechanical analysis. This technique also has potential for the quantitative determination of the allotropic composition of sulphur samples. Relatively large samples (compared to those used in DSC) can be used and some of the limitations of XRD and DSC are eliminated.

EXPERIMENTAL

Thermomechanical analysis (TMA) involves the measurement of the expansion of a sample as a function of temperature. A Perkin-Elmer system consisting of an analyser unit, a control unit and a temperature programmer was used. The analyser unit (Perkin-Elmer TMA-1) includes a transducer and a Dewar-Furnace assembly in which the sample is placed. The temperature programmer (Perkin-Elmer UU-1) was used to control the temperature and heating rate of the furnace.

The recorded output from TMA is one of expansion versus time. The temperature of the sample was monitored by a thermocouple whose output was also recorded. The expansion and the thermocouple output were recorded on a two-pen Perkin-Elmer Model 56. In this manner any non-linearity of the heating rate and any temperature lag between the UU-1 programme temperature and the actual sample temperature could be determined precisely.

Elemental sulphur purified by the Bacon and Fanelli method[15] was used throughout. Samples for TMA were formed as cylinders of 0.25 in. diameter and about 0.38 in. in length. The length of each sample was measured precisely with a micrometer. The cylindrical sulphur samples were cast in an aluminum mold which consisted of two plates about 6 × 1 × 0.3 in. bolted together and into which six chambers were drilled centrally along the joint of the plates. Samples for TMA were quick quenched from 135 to 22°C (room temperature), 0°C (ice-water) and −80°C (dry ice-acetone). Samples quick quenched from 180°C to 0, −80° and −196°C (liquid nitrogen) were also prepared. Liquid sulphur which had been maintained at 135°C for at least 1 h was poured into the mold at the appropriate temperature. In the case of quick quenching from 180°C where the liquid sulphur is very viscous, the mold containing sulphur was heated in a vacuum oven for at least 1 h prior to being immersed in the appropriate coolant.

All samples were aged at room temperature (22±2°C). The TMA of samples quick quenched from 135°C were run over the range −80 to 120°C. Heating rates of 5°C min^{-1} up to 85°C and 1.25°C min^{-1}. from 85 to 120°C were employed. Samples quick quenched from 180°C were analysed in the range 30 to 115°C using a heating rate of 2.5°C min^{-1}.

RESULTS

General features of TMA thermograms

Curve A of Fig. 1 illustrates the principal features of the TMA behavior of samples quick quenched from 135°C. Three values of slope corresponding to three values for the coefficient of linear expansion, α, between −80 and 90°C are observed. A marked increase in length occurs at 96°C and contraction at 116–118°C indicates sample collapse on melting. The relative prominence of these TMA features varies with age. In some cases small expansion was observed prior to the collapse of the sample on melting (dotted portion on Curve A, Fig. 1).

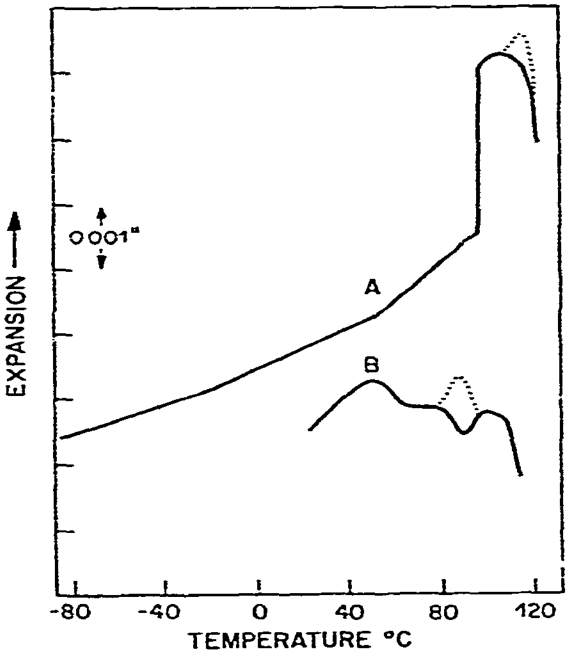

Fig. 1. Typical TMA curves for elemental sulphur. (A) = quenched from 135°C; (B) = quenched from 180°C.

In contrast, the features of the TMA thermograms for samples quick quenched from the higher temperature of 180°C are illustrated in Curve B, Fig. 1. The expansion in the 20 to 50°C temperature range is similar to that observed in the samples quenched from 135°C. However, the change in slope at approximately 55°C reflecting a contraction in at least young samples quenched from 180°C is to be compared with continuing expansion in samples quenched from 135°C. Beyond 70°C, the TMA behavior of the samples quenched from 180°C becomes very dependent on both the lower quench temperature (0, −80 and −196°C) and age. There appears to be a plateau followed in some cases by a maximum and in others a minimum. In all cases there is a final contraction around 106–110°C, accompanying melting.

Samples quenched from 135°C

Curves 2A, B and C contain TMA thermograms as a function of ageing time of samples quenched from 135°C to 22, 0 and −80°C, respectively. As can be seen, the variation of the lower quench temperature has relatively little effect on the form of the thermograms (cf., samples quenched from 180°C see below). Variations in slope of the plots between −80 and +80°C yield various values of α, the coefficient of linear thermal expansion. These are presented as a function of age of sample in Table 1. The transition temperatures T_{12}, T_{23} at which the slope, i.e., α changes are also noted.

TABLE 1

TMA DATA FOR THE AGEING OF SULPHUR QUICK QUENCHED FROM 135°C TO VARIOUS TEMPERATURES AS INDICATED

Age (h)	*Expansion coeff. $10^6\alpha_1$ (K^{-1})*	*Transition temp. T_{12} (°C)*	*Expansion coeff. $10^6\alpha_2$ (K^{-1})*	*Transition temp. T_{23} (°C)*	*Expansion coeff. $10^6\alpha_3$ (K^{-1})*	*10^3 Δl_{96} (in.)*
Quenched 135 to 22°C						
0.3			70	52	153	0.25
2.3	58	−24	71	68	110	0.65
6.0	56	−4	67			2.18
18.5	37	−20	45			3.15
24.0	45	+2	58			4.51
69	45	16	58			5.79
138	40	17	53			5.74
Quenched 135 to 0°C						
0.2	67		67	52	137	—
1.0	72		72	56	143	.46
4.5	66	27	87	77	157	1.70
6.5	58	−17	74	62	118	2.02
19	52	−22	66			4.06
27	26	−18	47			4.69
50	38	7	59			5.17
138	43	−7	54			5.78
337	33	2	61			6.14
Quenched 135 to −80°C						
0.3	64		64	59	162	0.12
1.1	57	−28	68	72	176	1.06
10.3	46	−13	83			4.99
19.5	40	−12	62			5.43
29.45	37	−5	61			5.74
46	40	10	70	—		6.40
69	32	11	64			6.34

It is immediately seen that precise control of the initial state and thus the thermal history of each individual sample is difficult to achieve. Numbers of nucleation sites etc. present in each sample will determine rate of interconversions. Generally speaking, however, on ageing, the temperature T_{12} at which the first change in α occurs, i.e., from α_1 to α_2, increases from −30 to +20°C, over about 60 h. The second change in slope which occurs at T_{23}, is evident only in samples less than 7 h old. The magnitude of the step change at 96°C, Δl_{96} increased from near zero initially to a limiting value (corresponding to a 1.5% increase in length) after about 60 h. Variation of the lower quench temperature has little effect on the TMA behavior of samples quenched from 135°C.

Samples quick quenched from 180°C

Figures 3A, B and C show TMA thermograms as a function of ageing time for samples quenched from 180°C to 0, −80 and −196°C. A comparison with Fig. 2

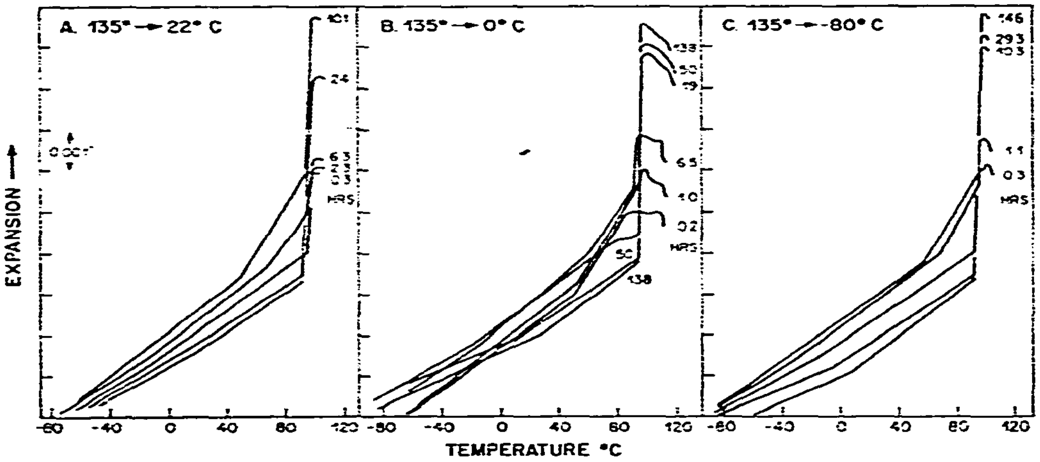

Fig. 2. TMA curves as a function of time (h) for sulphur quenched from (A) 135 to 22°C· (B) 135 to 0°C; (C) 135 to 80°C.

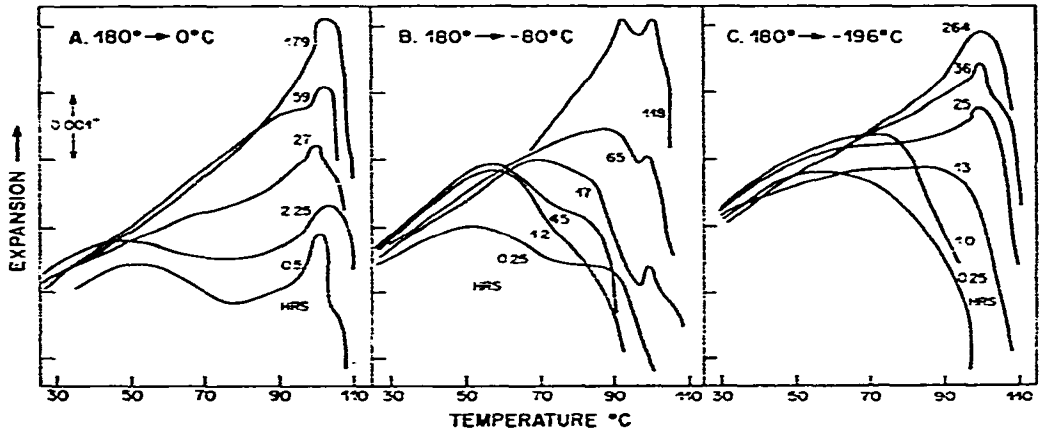

Fig. 3. TMA curves as a function of time (h) for sulphur quenched from (A) 180 to 0°C; (B) 180 to −80°C; (C) 180 to −196°C.

shows that samples quenched from the higher temperature do not show the same linear behavior patterns prior to the premelt stage. The thermograms are much more complex than in the 135°C cases and are much more dependent on the lower quench temperature. Because of this more complex behavior, it is not practical to analyse the data quantitatively as was done in Table 1 for the 135°C cases. Accordingly, discussion of the samples quenched from 180°C will be more qualitative.

The dominant feature in samples less than 10 h old is the maximum in the 45–65°C range irrespective of the lower quench temperature (see Fig. 3). This maximum occurs because of the subsequent contraction observed in the 50–75°C range. In older samples, this contraction disappears and an increase in slope in the 70–80°C range becomes the prominent feature continuing up to 96°C where the characterisitic $S_\alpha \rightarrow S_\beta$ expansion is again observed. In general the samples quenched from 180°C differ most markedly in TMA behavior from those quenched from 135°C only in the early stages of the ageing process. As the 180°C samples age the TMA thermograms approach the more regular linear form typical of the 135°C samples.

DISCUSSION

The striking differences in the TMA of samples quick quenched from 135°C as compared with 180°C are no doubt a consequence of the partial "freezing out" of the S_ω present in the liquid sulphur at temperatures above 159°C.

The most prominant feature of the TMA of samples quick quenched from 135°C, is the increase in the magnitude of the step change at 96°C as the sample ages.

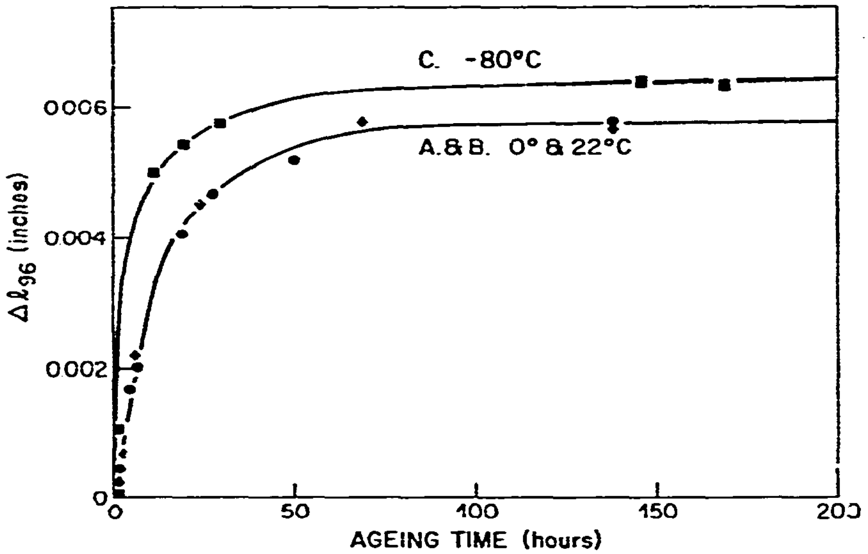

Fig. 4. Δl_{96}—the expansion for S_α to S_β conversion—as a function of age for sulphur samples quenched from 135°C to (A) 22°C, (B) 0° and (C) −80°C.

This step change or discontinuity in length is characteristic of a first order transition which in this case must be the S_α to S_β transition which is known[17] to occur at 96°C. This transition is accompanied by an increase in volume and hence length. The specific volumes of S_α and S_β at 25°C are 0.484 and 0.515, respectively[17]. The magnitude of the step change at 96°C (Δl_{96}) is indicative of the amount of S_α formed during ageing. Plots of Δl_{96} as a function of age are shown in Fig. 4 for samples quenched from 135°C to 22, 0 and −80°C. As can be seen from Fig. 4, the magnitude of Δl_{96} increases most rapidly for samples quick quenched to −80°C as compared with quenching to 22 or 0°C. The rate of the S_β to S_α transformation on ageing is therefore dependent on the rate of quenching of the melt and this conversion occurs more rapidly the greater the quench rate, i.e., the lower the quench temperature.

The other principal features of the TMA of samples quenched from 135°C are the changes in coefficient of linear expansion summarized in Table 1. Such changes are usually associated with second order transitions or glass transitions. One of the two changes in α exhibited by samples quenched from 135°C is transient. The T_{23} change in α in the 50–70°C range occurs only for samples less than 7 h old. This feature is probably due to the conversion of small amounts of relatively unstable cyclic sulphur species (i.e., other than S_8) into the more stable S_ω (polymer) or orthorhombic S_α cyclooctasulphur. These ring units have been isolated from sulphur melts cooled from 120°C and have been claimed to be the precursors of the small amounts of polymeric sulphur which are present in solid sulphur formed from melts quenched from below 159°C (ref. 18).

The T_{12} change in slope which occurs in the −30 to +20°C range may merely be a reflection of a non-linear temperature variation of the coefficient of linear expansion. However, the temperature T_{12} (Table 1) at which the slope changes does increase from −30°C in young samples approaching a limiting value of about 20°C after about 60 h. The variation of T_{12} does not parallel the increase of Δl_{96} exactly, although T_{12} reaches a maximum value after about the same ageing period as Δl_{96} reaches a maximum. This suggests that the T_{12} change in α is not related in a simple manner to the relative amounts of S_α and S_β as a function of age.

Liquid sulphur at temperatures above 159°C is predominantly an equilibrium mixture of polycatena species of varying chain-length. Mathematical models for the molecular composition of the equilibrium mixture existing throughout the entire liquid range of sulphur have been constructed[13]. There is satisfactory agreement between experimental results and predictions of the models. On quenching liquid sulphur from temperatures above 159°C, the equilibria between the polymeric species is partially frozen. Several studies have been carried out on material obtained when sulphur is quick quenched from temperatures above the polymerization temperature to room[22–24], dry ice[25,26] and liquid nitrogen[15,27] temperatures. The amount of semicrystalline polymer obtained on quenching has been determined as the CS_2 insoluble fraction and X-ray defraction has been utilised to determine crystallographic data. Koh and Klement[21] showed that on quenching molten sulphur to room temperature the weight fraction of polymeric species increases monotonically with temperature from <0.01 at 135 °C to a limiting value of ~ 0.56 at 250 °C with a very rapid increase at ~ 159 °C. The experimental values of the S_ω content of solid sulphur obtained by quenching the melt from various temperatures to room temperature agree very well with the calculated values for the polymeric content of the parent liquid sulphur. It thus appears that in the quenching experiments of Koh and Klement[21] the equilibrium at the higher temperature was virtually completely frozen during quenching.

The ageing of quenched sulphur has not been extensively studied but Tobolsky et al.[24] concluded that sulphur quick quenched from 200 to −80 °C consisted initially of a solution of polymeric and ring species both in the amorphous state. This material, termed elastic sulphur S_ψ, has a glass transition at −30 °C as determined by density measurements. It remains amorphous if maintained below −30 °C. At temperatures above −10 °C crystallization occurs rapidly on ageing. Some of this crystallization was observed in our molds as they were allowed to attain room temperature after being quenched to −80 and −196 °C.

The data of Tobolsky et al., show that the specific volume of quick quenched sulphur S_ψ is greater than that of the semi-crystalline polymeric species Crystex. The crystallization process is therefore expected to be accompanied by a decrease in volume. During the TMA of samples quenched from 180 °C, the contraction in the 50–60 °C range showed by younger samples (see Fig. 3) is probably due to the completion of the crystallization process which occurs more rapidly at this temperature. This contraction becomes less pronounced as the samples age.

The next feature of note in the TMA plots of samples quenched from 180 °C is the flattening of the TMA curve which occurs in the 70–80 °C range in the young samples. This corresponds to an increase in the coefficient of linear expansion, compared with the decrease observed in the 50–60 °C range. Semicrystalline polymeric sulphur, Crystex of S_ω, has a well-characterised glass transition[24] at 75 °C. The increase in the positive slope in the 70–80 °C range exhibited in the TMA and seen particularly as a shoulder in Fig. 3B is assigned to this glass transition.

As the samples age the TMA thermograms in the 70–95 °C range become progressively more similar to those characteristics of sulphur quenched from 135 °C. In all Fig. 3 cases the oldest samples examined had TMA thermograms essentially the same as those of Fig. 2. This behavior must be a reflection of the increasing amount of S_α formed with ageing and the conversion of the less stable forms (Crystex, S_ω) to the more stable orthorhombic form.

The variation of the lower quench temperature in those samples quenched from 180 °C might be expected to determine how efficiently the equilibrium existing in the liquid at the higher temperature is frozen. Samples quenched to 0 °C as compared with −80 and −196 °C might then contain less of the polymeric species. They therefore exhibit at a much earlier age (59 h) behavior similar to samples quenched from 135 °C. Samples quenched to −80 and −196 °C contain initially larger amounts of polymeric species. The reversion to the thermodynamically stable S_α occurs very slowly hence these samples do not behave like samples quenched from 135°C until they have aged for a considerably longer period (118 h plus).

CONCLUSION

This study has demonstrated the applicability of thermomechanical analysis to the study of some of the molecular and crystallographic transformations which occur on ageing elemental sulphur. The ageing behavior is determined principally by the upper temperature of the melt and to a lesser extent by the temperature to which the melt is quenched. More particularly, for samples quenched from below the equilibrium polymerization temperature, the lower quench temperature has little effect on the subsequent ageing behavior. For these samples, however, the rate at which the thermodynamically stable S_α species is formed appears to be greater for samples quenched to −80°C as compared with 22 or 0°C.

Samples quenched from above the equilibrium polymerization temperature show more complex behavior. The major changes which occur on ageing are the formation of semicrystalline polymeric and S_8 species from initially amorphous materials followed by the slower formation of the thermodynamically stable S_α species. The temperature to which the melt at 180°C is quenched determines the relative amounts of amorphous S_8 and polymeric species formed. The lower the temperature to which the melt is quenched, the more polymeric species are formed. This is consistent with more efficient freezing of the equilibrium in the melt as the quenching is performed more rapidly.

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REFERENCES

1 B. Meyer (Ed.), *Elemental Sulphur, Chemistry and Physics*, Interscience, 1965.
2 J. M. Dale and A. C. Ludwig in ref. 1.
3 R. B. Seymour, W. Pascoe, W. J. Energy, A. C. Loewer, R. H. Steiner and R. D. Stout, *J. Am. Water Works Ass.*, 43 (1951) 1001.
4 W. A. Cunningham, *J. Chem. Educ.*, 12 (1935) 120.
5 G. Bruni, *Chemica*, 13 (1937) 119.
6 W. J. Rennie, B. Andreassen, D. Dunay and J. B. Hyne, Alberta Sulphur Research Ltd., *Quarterly Bulletin*, Vol. VII, No. 3, 1970.
7 M. Von Wobst, Wiss. Z. der Hochsch. fur Maschinenbau Karl-Marx-Stadt, Vol. 1, No. 1, 1958/59.
8 R. Powell and H. Eyring, *J. Am. Chem. Soc.*, 65 (1943) 648.
9 G. Gee, *Trans. Faraday Soc.*, 48 (1952) 515.
10 F. Fairbrother, G. Gee and G. Merrall, *J. Polym. Sci.*, 61 (1955) 459.
11 F. S. Dainton and Irvin, Quart. Rev., 12 (1958) 67.
12 A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.*, 81 (1959) 780.
13 R. E. Harris, *J. Phys. Chem.*, 74 (1970) 3102.
14 B. R. Currell and A. J. Williams, *Thermochim. Acta*, 9 (1974) 733.

15 G. W. Miller, *J. Appl. Polym. Sci.*, 15 (1971) 1995.
16 R. F. Bacon and R. Fannelli, *Ind. Eng. Chem.*, 34 (1942) 1043.
17 Robert C. Weast (Ed.), *Handbook of Chemistry and Physics*, 54th ed., 1973–1974.
18 M. Schmidt and H. D. Block, *Angew. Chem.*, 79 (1967) 944; *Angew. Chem.* Int. Ed., 6 (1967) 955.
19 A. V. Tobolsky, *J. Chem. Phys.*, 12 (1944) 402.
20 P. J. Flory, *J. Chem. Phys.*, 12 (1944) 435.
21 J. C. Koh and W. Klement Jr., *J. Phys. Chem.*, 74 (1970) 4280.
22 P. W. Schenk, *Z. Anorg. Allg. Chem.*, 280 (1955) 1.
23 P. W. Schenk and V. Thummlar, *Z. Electrochem.*, 63 (1959) 1002.
24 A. V. Tobolsky, W. J. McKnight, R. B. Beevers and V. D. Gupta, *Polymer*, 4 (1963) 423.
25 S. R. Das and K. Ghosh, *Ind. J. Phys.*, 13 (1939) 91.
26 J. Chin, *Anal. Chem.*, 35 (1963) 933.