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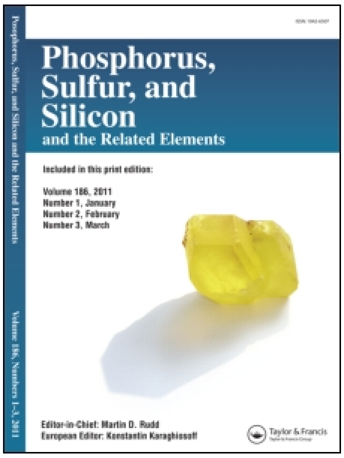

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SYNTHESIS AND CHARACTERIZATION OF POLY(KETO-SULPHIDE) RESINS

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Polycondensation of aliphatic and aromatic ketones with formaldehyde in the presence of sodium hydrogen sulphide affords the corresponding poly(keto-sulphide) resins. These resins have been characterized by elemental analyses, osmometry, conductometry, measurement of solution viscosity in DMF, IR spectra and thermal gravimetric analysis. Oxidation of poly(keto-sulphide) resins is also studied. Formation of the resin is explained. The results of preliminary tests for glass reinforcement of few produced poly(keto-sulphide) resins suggest that laminate sheets can be obtained.

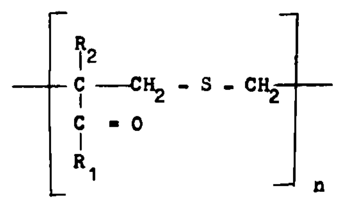
Key words: Ketones; formaldehyde; sodium hydrogen sulphide; poly(keto-sulphide); poly(keto-sulphone); nonaqueous conductometric titration.

INTRODUCTION

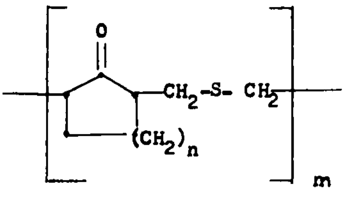
Hither to, the incorporation of sulphur into aliphatic chain of ketone resins has no systematic attention,[1,2] inspite of good-deal of properties of alkylketone-formaldehyde resins[3,4] and poly(alkylene-sulphide) resins.[5] Such ketone-formaldehyde resins are used in manufacturing of foam,[6] floor coating,[7] paint formulations,[8] etc. and alkylene-sulphide resins are used in the various applications like rubber lining and coating.[5] The incorporation of sulphur into aliphatic ketone-formaldehyde resin may alter the properties of (especially in view of application and processing) ketone-formaldehyde resins to a great extent. Hence it is thought interesting to explore the field of poly(keto-sulphide) resins. The present communication comprises the synthesis, characterization and formation of poly(keto-sulphide) resins prepared from aliphatic, alicyclic and aromatic ketones, formaldehyde and NaHS. The results of preliminary tests for glass reinforcement of these poly(keto-sulphide) are also discussed.

RESULTS AND DISCUSSION

All the poly(keto-sulphide) resins are white to dark brown solids, softening between 85°C and 200°C and formed in about 35 to 75% yield depending upon the nature of the ketone employed in the synthesis. All the resins except poly(cyclohexanone-sulphide), poly(cyclopentanone-sulphide) and poly(4-amino-acetophenone-sulphide) are soluble in organic solvents like dioxan and DMF. The elemental analyses of the resins agree with the expected values. The expected values are calculated on the basis of the proposed structure of the repeating unit. The repeating unit of the produced poly(keto-sulphide) resins were considered according to the results reported on the condensation of ketones and formaldehyde.[1,2] Masahiro ABO[9] and Tilichenko *et al.*[10] reported extensively that polycondensation between ketone and formaldehyde propagate through de-aldol condensation reaction and most depending on molar concentration of reactants and concentration of alkali catalyst. It was also reported[9,10] that the aldol condensation reaction exist via active methylene group. Hence, in the present study the ketones like methyl ethyl ketone (containing one active —CH_2— group), acetylacetone (containing one active —CH_2— group), cyclohexanone (containing two active —CH_2— groups), cyclopentanone (containing two active —CH_2— groups), propagate polycondensation through active —CH_2— group. Dronove *et al.*[1] have also reported that ketone, sodium hydrogen sulphide, formaldehyde condensation in their molar ratio of 1:1:2, afford linear poly(keto-sulphide) resin structures (as shown below) indicating that acetone under equimolar ratio partitipate only one —CH_3— group in such condensation.



Repeating unit for aliphatic and aromatic ketones



Repeating unit for cyclic ketones.
where *n* = 2 for CHFS
and *n* = 1 for CPFS

where,

Poly(keto-sulphide)	R_1	R_2
AFS	—CH_3	—H
MFS	—CH_3	—CH_3
AAFS	—CH_3	—$COCH_3$
AMFS	4-aminophenyl	—H
ANFS	2-Naphthyl	—H
ACAFS	4-Acetanilide	—H
ACDFS	4-biphenyl	—H

The molecular weights of these resins estimated both by vapour pressure osmometry and nonaqueous conductometric titration are comparable and are low. The resins obtained from aliphatic ketones have higher molecular weight and those obtained from aromatic ketones have lower. As the molecular weights of these resins are low, the values of intrinsic viscosities $[\eta]$ of solutions of both aliphatic and aromatic type resins are low and agreed with their corresponding $\bar{M}_n$ values.

All the poly(keto-sulphide) resins yield the acid on vigorous oxidation listed in Table I. Their b.p./m.p. are agree with reported values. This is consistent with

TABLE I

Characterization of poly(keto-sulphide) resins

Poly(keto-sulphide) resin	% Yield	Softening range of poly(keto-sulphide) °C	Softening range of poly(keto-sulphone) °C	Acid formed on complete oxidation	m.p./b.p. of acid	Elemental analysis C% Calcd. (found)	H% Calcd. (found)	S% Calcd. (found)	N% Calcd. (found)
AFS	75	170–200	250<	Acetic acid	117 b.p.	51.72 (51.30)	6.90 (6.28)	27.59 (28.03)	—
MFS	40	95–110	143–148	Acetic acid	117	55.38 (55.98)	7.69 (7.25)	24.62 (24.16)	—
AAFS	35	140–155	170–178	Acetic acid	117	53.16 (53.82)	6.33 (6.92)	20.25 (20.30)	—
AMFS	51	250<	250<	4-amino benzoic acid	188 m.p.	62.18 (62.79)	5.70 (5.18)	16.58 (16.06)	7.25 (7.77)
ANFS	60	85–100	130–140	2-Naphthoic acid	186	73.68 (73.12)	5.26 (5.83)	14.04 (14.31)	—
ACAFS	40	160–175	180–188	4-Acetamido-benzoic acid	260 (dec.)	61.28 (61.68)	5.53 (5.22)	13.62 (13.33)	5.96 (6.15)
ACDFS	60	105–115	130–142	4-Biphenyl carboxylic acid	226	75.59 (75.90)	5.51 (5.03)	12.60 (13.13)	—
CHFS	65	250<	250<	Adipic acid	153	61.64 (61.70)	7.69 (7.89)	20.51 (21.08)	—
CPFS	70	250<	250<	Glutaric acid	97	59.15 (59.79)	7.04 (6.69)	22.54 (22.16)	—

The abbreviations show that the following are components of the polymer: A: Acetone; M: MEK; AA: Acetylacetone; AM: 4-aminoacetophenone; AN: 2-acetylnaphthalane; ACA: 4-acetylacetanilide; ACD: 4-Acetyldiphenyl; CH: Cyclohexanone; CP: Cyclopentanone; F: Formaldehyde; S: Sulphide.

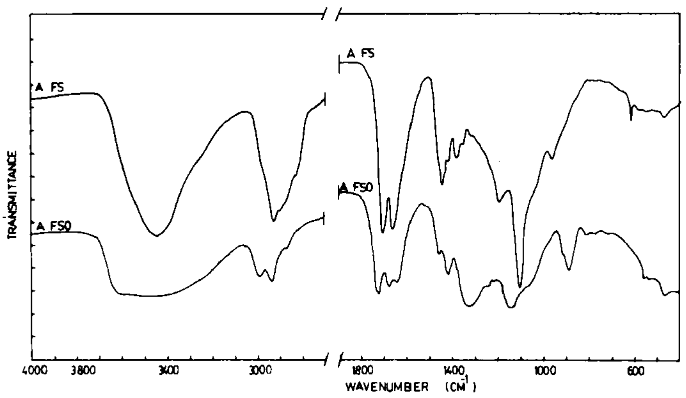


FIGURE 1 IR spectra of poly(acetone-sulphide) (AFS) and poly(acetone-sulphone) (AFSO).

the proposed structure of the resin. On controlled oxidation with aqueous H_2O_2 poly(keto-sulphide) afford corresponding poly(keto-sulphone) resins.

The trend in the IR spectra of these resins are explicable in terms of their proposed structure (Figure 1). They exhibit a carbonyl band at around 1700 cm^{-1}, the exact position depending upon the nature of the $R_1\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_2\text{—}R_2$ in the polymer chain. All of the spectra show a moderately strong band at 640 cm^{-1} assigned to the $\text{—}CH_2\text{—}S\text{—}CH_2\text{—}$ system. It is reported that[11] the band for this system occurs between 600 and 700 cm^{-1} for organic aliphatic sulphides. The spectra of poly(keto-sulphone) shows almost all characteristics of poly(keto-sulphide). The only apparent difference is that the bands due to $\text{—}CH_2\text{—}SO_2\text{—}CH_2\text{—}$ appeared at 1140 cm^{-1} and 1340 cm^{-1} and the bands due to $\text{—}CH_2\text{—}S\text{—}CH_2\text{—}$ vanished[12] (Figure 1).

The softening temperatures of poly(keto-sulphide) and poly(keto-sulphone) resins are shown in Table I. The data reveal that poly(keto-sulphone) resins soften at a considerably higher temperature than the corresponding poly(keto-sulphide) resin. This finding agrees with the relative melting behaviour of organic sulphur compounds such as phenacyl sulphide and phenacyl sulphone.[13,14]

Examination of thermogravimetric (TG) data of poly(keto-sulphide) resins (Table II) and the TG curves reveals that all of the resin samples undergo stepwise degradation. The first stage of slow degradation passes into a step of comparatively slower degradation. All the aliphatic and alicyclic poly(keto-sulphide) resins lost more than 65% of their weight when heated to 500°C. The aromatic poly(keto-sulphide)s are more stable than aliphatic and alicyclic poly(keto-sulphide)s. This behaviour is unlike that of aliphatic polysulphides, which are known to degrade rapidly due to cleavage of $\text{—}C\text{—}S\text{—}C\text{—}$ bonds into free radicals. In the present case, the unexpectedly high stability of the resin may be due to oxidation of the $\text{—}C\text{—}S\text{—}C\text{—}$ band to $\text{—}C\text{—}SO_2\text{—}C\text{—}$ during TGA in air. The thermal degradation of poly(keto-sulphone) starts around 225°C which is higher than corresponding poly(keto-sulphide) and all mass had disappeared by 625°C. The overall thermal stability of poly(keto-sulphone)s is considerably higher than poly(keto-sulphide)s.

TABLE II

Results of molecular weight determination, viscometric study and thermogravimetric analysis of poly(keto-sulphide) resins

Poly(keto-sulphide) resin	$\bar{M}_n$ values estimated by VPO ±50	$\bar{M}_n$ values estimated by Nonaqueous conductometric titration	$[\eta] \times 10^2$ $dl \times g^{-1}$ in DMF at 30 ± 0.1°C	% weight loss at temperature (°C)[a] 200	300	400	500	600
AFS	1100	1150	3.7	2	8	40	98	—
MFS	950	910	2.8	4	25	50	65	—
AAFS	900	950	4.2	5	12	33	58	96
AMFS	—	800	—	4.5	10	25	40	88
ANFS	1500	1450	3.5	3	11	45	53	65
ACAFS	950	940	3.4	3	10	37	48	75
ACDFS	800	775	3.2	5	15	50	60	80
CHFS	—	800	—	1.5	18	64	75	—
CPFS	—	800	—	3	12	68	95	—

[a] At 10°C/min heating rate.

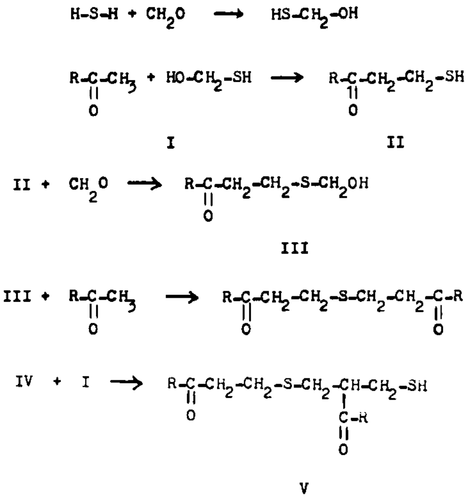
Qualitative observation were made on "in situ" glass reinforcement using a mixture of poly(keto-sulphide) resin and diisocyanate in an organic solvent. It was noted that laminate sheets could be made with good mechanical strength (Tensile strength: 60 MPa, Flexural strength = 100 MPa).

Course of the poly(keto-sulphide) resin formation

The possible steps involved in the poly(keto-sulphide) resin formation from aliphatic, alicyclic and aromatic ketones are shown in the following charts as Equations 1–13.

These are consistent with the molar proportions of ketone, formaldehyde and sodium hydrogen sulphide (1:2:1) required for the synthesis.[1]

(For aliphatic ketones)



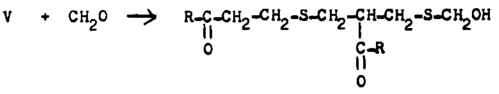
$$H\text{-}S\text{-}H + CH_2O \longrightarrow HS\text{-}CH_2\text{-}OH \qquad (1)$$

$$\underset{\text{I}}{R\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3} + HO\text{-}CH_2\text{-}SH \longrightarrow \underset{\text{II}}{R\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}SH} \qquad (2)$$

$$\text{II} + CH_2O \longrightarrow \underset{\text{III}}{R\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2OH} \qquad (3)$$

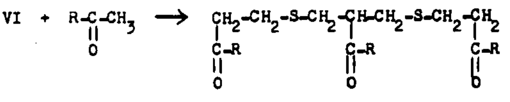
$$\text{III} + R\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 \longrightarrow R\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}R \qquad (4)$$

$$\text{IV} + \text{I} \longrightarrow \underset{\text{V}}{R\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}\underset{\substack{|\\ C\text{-}R\\ \|\\ O}}{C}H\text{-}CH_2\text{-}SH} \qquad (5)$$



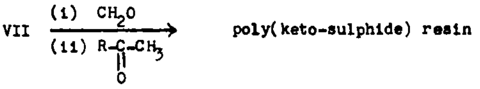
$$V + CH_2O \longrightarrow R\text{-}\underset{\substack{\|\\O}}{C}\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}\underset{\substack{|\\C\text{-}R\\\|\\O}}{CH}\text{-}CH_2\text{-}S\text{-}CH_2OH \qquad (6)$$

VI



$$VI + R\text{-}\underset{\substack{\|\\O}}{C}\text{-}CH_3 \longrightarrow \underset{\substack{|\\C\text{-}R\\\|\\O}}{CH_2}\text{-}CH_2\text{-}S\text{-}CH_2\text{-}\underset{\substack{|\\C\text{-}R\\\|\\O}}{CH}\text{-}CH_2\text{-}S\text{-}CH_2\text{-}\underset{\substack{|\\C\text{-}R\\\|\\O}}{CH_2} \qquad (7)$$

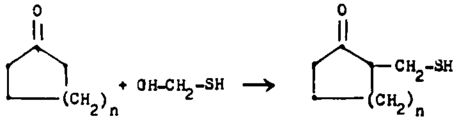
VII



$$VII \xrightarrow[\text{(ii) } R\text{-}\underset{\substack{\|\\O}}{C}\text{-}CH_3]{\text{(i) } CH_2O} \text{poly(keto-sulphide) resin}$$

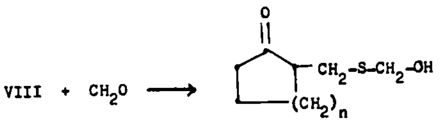
(For alicyclic ketones)

$H\text{-}S\text{-}H + CH_2O \longrightarrow HS\text{-}CH_2\text{-}OH$ (1)



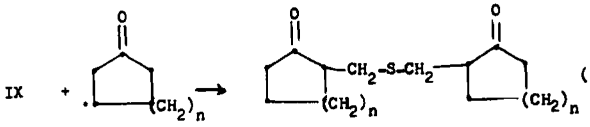
(8)

VIII



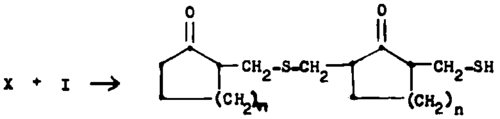
(9)

IX



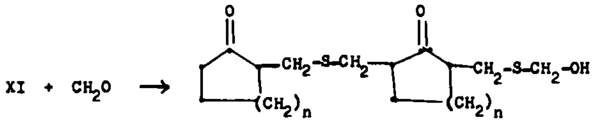
(10)

X



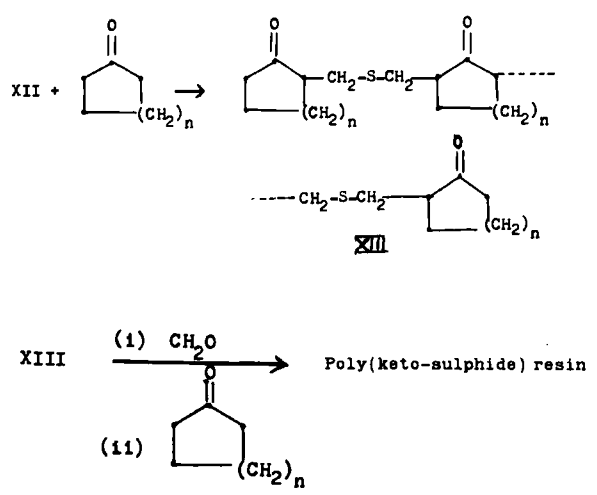
(11)

XI



(12)

XII



where $n = 1$ and 2.

The first step involved in the formation of a mercaptomethanol I is well established.[15,16] The reactivity of I in steps 2 and 8 is also very well known.[1] The type of reaction involved in I is repeated in steps 3, 5, etc. In the case of alicyclic ketones both of the carbons to the $-\overset{\overset{\text{O}}{\|}}{\text{C}}-$ groups are equally active and react as shown in steps 10 and 11. The product VII and XIII may be repeated or terminated with monomers, thus affording a polymeric material.

EXPERIMENTAL

The IR spectra of all the poly(keto-sulphide) and poly(keto-sulphone) resins were recorded in KBr on a Perkin Elmer 983 spectrophotometer. Viscometric measurements of solutions of the resin samples in DMF were carried out at $30 + 0.1$°C using an Ubbelohde viscometer. Thermogravimetry of the resins was carried out on a Du Pont thermobalance at a heating rate of 10°C min^{-1}. C and H contents were estimated on a C, H, N, O, S Carlo Erba analyser (Italy). The number-average molecular weights ($\bar{M}_n$) of all the resin samples soluble in DMF were measured on a Hewlett-Packard Vapour Pressure Osmometer using DMF as solvent at 70°C and benzil as calibrant. $\bar{M}_n$ estimation of resins was also carried out by using nonaqueous conductometric titration as reported earlier.[17,18] Nonaqueous conductometric titration was carried out in pyridine against sodium methoxide (NaOMe) in pyridine as standard. A Digital conductivity meter, Toshniwal, India was used for this purpose.

Acetone, methyl ethyl ketone, cyclohexanone and acetyl acetone were of laboratory grade. Cyclopentanone,[19] 4-acetylbiphenyl,[20] 4-acetylacetanilide[21] and 4-aminoacetophenone[22] were synthesized by methods reported in literature. 2-Acetylnaphthalene (Fluka AG.) was used without purification. Sodium hydrogen sulphide was prepared by passing the required amount of dry H_2S through conc. methanolic NaOH.

The polycondensation of all the ketones listed in Table I and their oxidations were carried out following the procedures described by Patel *et al.*[2] On complete oxidation by excess alkaline $KMnO_4$ at 100°C, poly(keto-sulphide)s of ketones, viz, acetone, methyl ethyl ketone and acetylacetone yielded acetic acid and ketones viz, 4-aminoacetophenone, 2-acetylnaphthalene, 4-acetylacetanilide, 4-acetyldiphenyl, cyclohexanone and cyclopentanone yielded 4-aminobenzoic acid, 2-naphthoic acid, 4-acetamidobenzoic acid, 4-biphenylcarboxylic acid adipic acid and glutaric acid respectively. The acids were separated and m.p./b.p. were checked which agree with reported values (Table 1). The molecular weights of acids were determined by nonaqueous conductometric titrations.[17,18]

Controlled oxidation[2] of poly(keto-sulphide) gives poly(keto-sulphone). The m.p.s of the corresponding poly(keto-sulphide)s are furnished in Table I.

ACKNOWLEDGEMENTS

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