

# Polymerization of 2-dibutylamino-1,3,5-triazine-4,6-dithiol on Wire During Friction Process

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## SYNOPSIS

2-Dibutylamino-1,3,5-triazine-4,6-dithiol (DB) and a mixture of DB and triallylisocyanurate (TAIC) were used as a lubricant during steel wire drawing due to a dry process. DB gave a polymer film with 180 nm in thickness to wire surfaces during the wire drawing. The polymer film had a disulfide structure on the backbone and contained a small amount of DB monomer and oligomer. Molecular weight and polymer weight increased with the drawing rate. The mixture of DB and TAIC gave mainly a three-dimensional polymer film with 225 nm in thickness to wire surfaces during drawing. The polymer film insoluble in THF had mono and disulfide structures and contained a small amount of linear polymer, DB, and TAIC. Such tribological polymerizations are estimated as follows: DB produces dithiyl radicals on a nascent surface formed during drawing and in the presence of oxygen and heat. The dithiyl radicals were polymerized by coupling with each other to give disulfide bonds or added to allyl groups in TAIC to give monosulfide bonds. It is concluded that this technique should be possible to use for unifying metal processing and surface treatment.

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## INTRODUCTION

Tribological surface treatment makes possible the unification of processing and surface treatment of metal and lessens the requirements for metal processing. A few tribological reactions of organic compounds with solid substances have been already studied. Taubmann et al.<sup>1</sup> and Momose et al.<sup>2</sup> reported that mechanochemical polymerization occurs by milling inorganic substances in monomers. Tamai and Mori<sup>3</sup> found vibromilled aluminum and silica powders to be effective as anionic initiators for the polymerization of vinyl acetate, styrene, methyl methacrylate, and acrylonitrile. Mori et al.<sup>4</sup> described reactions of butylbromide with aluminum under vibromilling to give a polymerized material

on aluminum powders. Such treatment is actually not always effective for improving general metal surfaces such as plates, wires, and blocks with organic compounds since milling for long periods is required. The present authors directed attention to these studies to determine how exoelectrons are generated during and after substance processing.

In this study, 2-dibutylamino-1,3,5-triazine-4,6-dithiol was found to polymerize during wire drawing to give a linear polymer on wire surfaces and to react with double-bond compounds during wire drawing to give a network polymer on the surfaces.

## EXPERIMENTAL

### Reagents and Materials

2-Dibutylamino-1,3,5-triazine-4,6-dithiol (DB, mp 140°C) and triallyl isocyanurate (TAIC, mp 24°C)

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were obtained commercially. Steel wire (JIS-AWRH82: Fe, over 98.51%; C, 0.83%; Si, 0.25%; Mn, 0.45%; P, below 0.03%; S, below 0.03%) was also purchased. Each wire sample was immersed for 5 min at 20°C in 1% HCl aqueous solution and then in 1% NaOH aqueous solution and washed with methanol and dried in dry air (oxide film: about 10 nm).

### Steel Wire Drawing

The steel wire samples (1.43  $\phi$ m) pretreated above were drawn from a starting diameter of 1.43 mm to a final diameter of 1.30 mm in two passes by a dry drawing machine. Figure 1 shows the dies box and wire in the drawing machine. Drawing tests were conducted using DB and a mixture of DB and TAIC (1/1 molar ratio) as lubricants in normal production lines. The dies for drawing steel wire were standard tungsten carbide dies.

### Model Polymerization of DB on Iron Plates

Two types of iron plates were prepared as follows: An active Iron plate (0.2  $\times$  30  $\times$  60 mm) was initially polished with 8  $\mu$ m grain emery and degreased for 3 min at 20°C ultrasonically under methanol. The plate was immediately used for the thermal polymerization of DB. An inactive iron plate was prepared by heating the active iron plate for 24 h at 150°C in a dry-air oven after leaving the active iron plate for 24 h at room temperature in dry air. On two iron plates under different surface conditions, thin DB monomer film (20  $\mu$ m/cm<sup>2</sup>) was prepared by an air drier after immersing the iron plates in

methanol solution of DB ( $5 \times 10^{-3}$  mol/L) for 5 min at 30°C. DB monomer films were heated for 30 min at 80 or 120°C. The heated plates were immersed in THF (10 mL) for 30 min at room temperature. DB and formed linear polymers on the iron plates were dissolved in THF by this procedure. Molecular weight was determined from GPC data.

### Measurements

Molecular weight and distribution were determined by gel permeation chromatography with Showadex GPC columns (KF-802, 804, and 805: exclusion limited molecular weight,  $5 \times 10^5$ ) and a UV detector (254 nm) (GPC, Shimadzu GPC SWRH82A) using THF as a solvent. Sample solutions were prepared by immersing drawn wires in the THF for 30 min at 30°C.

FTIR spectra were measured using a Nippon Denshi FTIR, IR-5500 (Nippon Denshi Co.) according to the ATR method. ESCA spectra were obtained at a base pressure of  $10^{-9}$  Torr on an X-ray photoelectrospectrometer (ESCA Lab-5, VG Scientific Co.). A take-off angle of 35° was used with a MgK $\alpha$  X-ray as the excitation source (23.500 eV). AES spectra were obtained at a base pressure of  $10^{-7}$  Torr on an auger electro-spectrometer (AES: JEOL, JAMP-10S). A take-off angle of 0° was used with the MgK $\alpha$  X-ray as the excitation source (23.500 eV). The etching rate by Ar<sup>+</sup> was 18 nm/min.

## RESULTS AND DISCUSSION

### Polymerization During Steel Wire Drawing

Metals assume activated surfaces during processing such as drawing, cutting, drilling, and rolling. This activity decreases rapidly in air. Active surfaces may cause organic compounds to change.<sup>5-7</sup> Steel wires were drawn through the dies box in the presence of DB and a mixture of DB and TAIC used as lubricants at various drawing rates (Fig. 1). After drawing, the wires were kept for 12 h at room temperature; thereafter, six cut wires (10 cm in length) were immersed in THF (20 mL) and the organic products adhering to the wire surfaces were dissolved in THF. The molecular weight and its distribution of the polymers in THF were measured by GPC.

Figure 2 shows the GPC patterns of THF solutions obtained by extraction of the treated wires,

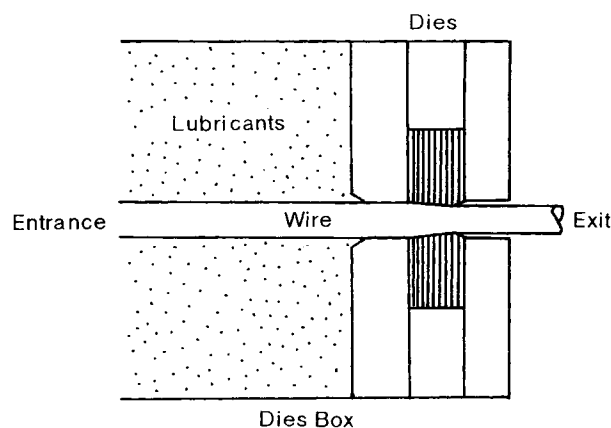
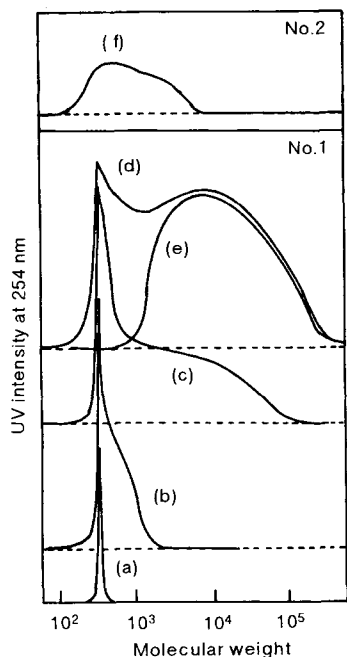
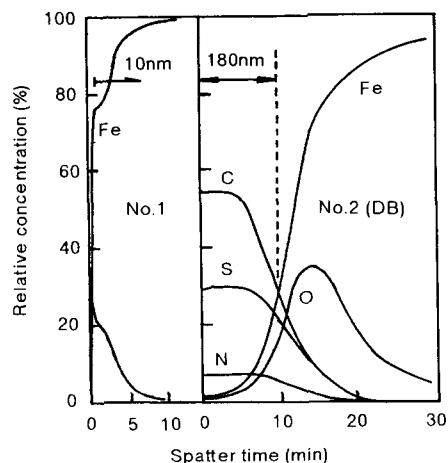


Figure 1 Dies box wire drawing.



**Figure 2** GPC patterns of polymers formed on steel wire during drawing: (a) DB, no drawing; (b) DB, drawing rate, 10 m/min; (c) DB, drawing rate, 30 m/min; (d) DB, drawing rate, 50 m/min; (e) washed sample; (d) with methanol; (f) DB + TAIC, drawing rate, 50 m/min.

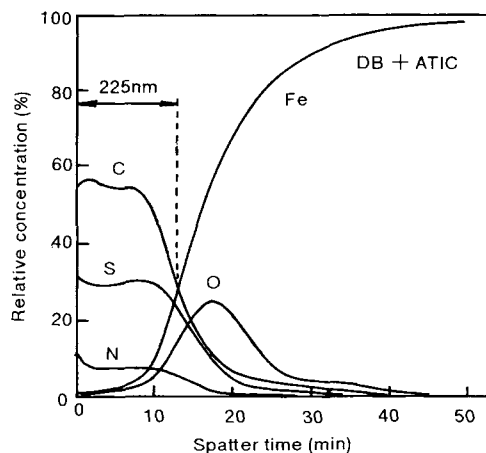
drawn using only DB and a mixture of DB and TAIC as lubricants; no stearic-type lubricants were used. It is evident as shown in Figure 2 (No. 1) that the DB monomer film was polymerized on the wire surfaces. The molecular weight and the polymer weight increased with increasing drawing rates. At a low drawing rate (10 m/min), these parameters were small but markedly increased at a high drawing rate (50 m/min) (d). The films contained DB and DB oligomers as well as the DB polymer. Sample (e) obtained by washing sample (d) with methanol does not contain DB and DB oligomer. The coefficients of the UV absorption of DB ( $\epsilon: 1.7 \times 10^3$  mol/L) and DB disulfide polymer ( $\epsilon: 1.9 \times 10^4$  mol/L) at 254 nm (Ref. 8) showed the amount of unreacted DB to be considerably less than that of a polymer. The treated wire surfaces after immersion in methanol had only DB polymer films with molecular weights of about 3000–200,000. An increased drawing rate caused the wire surface temperature to increase<sup>9-13</sup> as well as molecular weight and polymer weight. Tribological polymerization appears to run to completion instantly. No differences in molecular weight due to standing time, 10 min and 24 h, after the drawing could be detected.



**Figure 3** Changes in component atoms of wire surfaces before (No. 1) and after (No. 2) drawing at 50 m/min in the presence of the DB lubricant.

A mixture of DB and TAIC was also used as a lubricant in the drawing of iron wires at a drawing rate of 50 m/min, the maximum rate in the drawing test. The GPC patterns indicated the formed film to contain DB, TAIC, and their polymers as shown in Figure 2 (No 2). The intensity of UV adsorption of the polymer in the mixture was low, compared with that in DB. Thus, possibly, a polymer insoluble in THF may form as a result of the reaction of DB and TAIC on wires during drawing.

Polymer film thickness on treated wires was determined based on AES. The results are shown in Figures 3 and 4. Measurements were conducted after

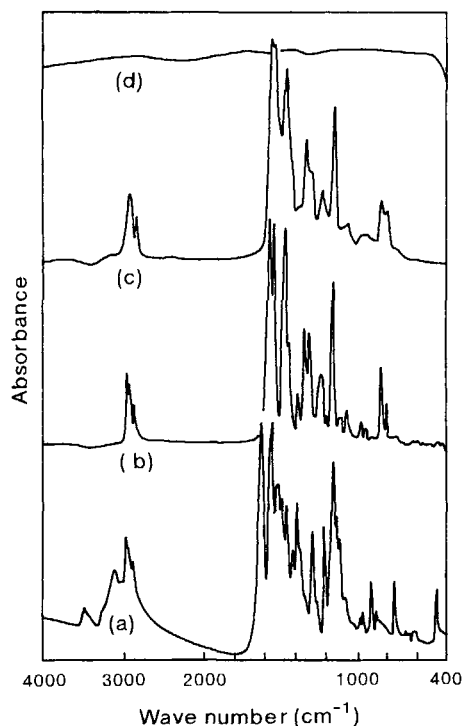


**Figure 4** Changes in component atoms of wire surfaces after drawing at 50 m/min in the presence of DB and TAIC lubricants.

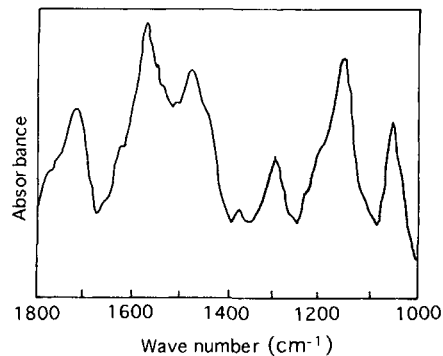
immersing the samples in methanol to remove the monomers and oligomers. They were dissolved in methanol, as shown in Figure 2 (No. 1e). The thickness was determined as the point of intersection on the curves of carbon and iron atom content. Oxide film thickness on the original wire surfaces was about 10 nm as shown in Figure 3 (No. 1). When DB was used as lubricant at a drawing rate of 50 m/min, the thickness of the polymer film on the wires was about 180 nm, as shown in Figure 3 (No. 2), and for the mixture of DB and TAIC, 225 nm, as shown in Figure 4. Thus, polymers were formed during drawing and organic film on the iron wires should generally be thick. These organic film thicknesses may improve the surface properties of wire for anticorrosion and adhesion.

### Chemical Structures of Polymer Films

To elucidate the chemical structures of polymer films, FTIR spectra were obtained for the treated wires. Figure 5 shows the IR spectra of DB-treated wire surfaces during drawing. Steel wire surfaces (c)

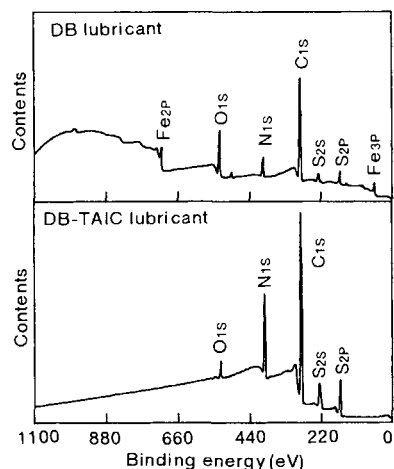


**Figure 5** IR spectra of wire surfaces after drawing at 50 m/min in the presence of DB lubricant: (a) DB lubricant; (b) authentic DB disulfide polymer; (c) wire surface after drawing in the presence of DB lubricant; (d) wire surface from which sample (c) was extracted with THF.



**Figure 6** IR spectrum of wire surfaces after drawing at 50 m/min in the presence of DB and TAIC lubricants.

treated by DB during drawing showed essentially the same FTIR spectrum patterns as those of the authentic DB disulfide polymer prepared separately (b), although the spectrum was different from that of DB. Sample (d) after immersion in THF showed no absorption in the FTIR spectrum. DB-treated wires thus shed all organic films by THF immersion. Before immersion, they were covered with a linear polymer. Steel wires treated with a mixture of DB and TAIC during drawing showed clear IR spectrum patterns even though the samples had been extracted with THF, as shown in Figure 6. This shows that the formed film consists of a network polymer. An absorption peak due to a CO stretching vibration at  $1715\text{ cm}^{-1}$  (TAIC), a C=C bond at  $1635\text{ cm}^{-1}$  (TAIC), and a C=N bond at  $1559$  and  $1525\text{ cm}^{-1}$  (DB) was seen. The decrease in absorption due to



**Figure 7** ESCA wide scan of wire surfaces after drawing at 50 m/min in the presence of DB and DB-TAIC lubricants.

**Table I** Assignment of Bonding Energy for  $C_{1s}$ ,  $N_{1s}$ , and  $S_{2p}$  on a Narrow Scan in ESCA Spectra

Lubricant	Electron Spectrum	Bonding Energy (eV)	Bond Groups	Component (%)
DB	$C_{1s}$	286.61	$-\text{CH}_2-$ , $-\text{CH}_3$	63
		286.00	$\text{C}=\text{N}-$	22
		287.57	$\text{C}-\text{N}$	15
	$N_{1s}$	398.66	$-\text{N}-\text{C}$	58
		399.98	$\text{C}-\text{N}$	42
	$S_{2p}$	162.0, 163.1	$-\text{SS}-$	46
		163.4, 165.2	$\text{C}-\text{S}-$	47
		168.1, 169.5	$\text{C}-\text{SO}_n-$	7
	DB/TAIC	$C_{1s}$	286.61	$-\text{CH}_2-$ , $-\text{CH}_3$ $-\text{CH}=\text{CH}_2$
287.02			$\text{C}-\text{N}$ , $\text{C}=\text{N}-$ $\text{C}=\text{O}$	34
$N_{1s}$		398.62	$-\text{N}=\text{C}$	23
		400.03	$\text{C}-\text{N}$	77
$S_{2p}$		162.0, 163.1	$-\text{SS}-$ , $-\text{S}-$	40
		163.4, 165.2	$\text{C}-\text{S}-$	57
		168.1, 169.5	$\text{C}-\text{SO}_n-$	3

$\text{C}=\text{C}$  bonds in TAIC and the  $-\text{NHCS}$  group ( $1601\text{ cm}^{-1}$ ) in DB suggests the formation of monosulfide groups.<sup>8</sup> Only TAIC-treated wire showed no adsorption peaks in the FTIR spectra following THF immersion. TAIC and DB in combination gave an

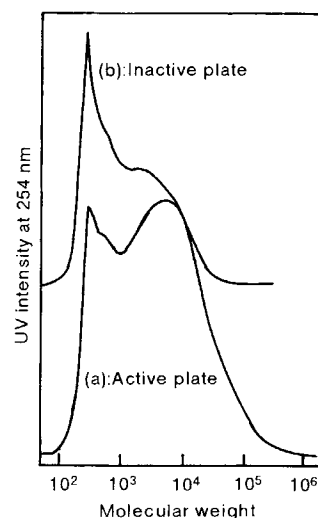
insoluble network polymer film by reaction of  $\text{C}=\text{C}$  bonds in TAIC with the  $-\text{NHCS}$ -group in DB.

To further elucidate the chemical structure of a polymer on treated wire, ESCA was measured for samples extracted with methanol to remove un-

reacted monomers and oligomers. Figure 7 and Table I show an ESCA wide scan of the wire surface of the drawing at 50 m/min in the presence of DB and a mixture of lubricants and assignments of functional groups based on  $C_{1S}$ ,  $N_{1S}$ , and  $S_{2P}$ . DB and a mixture of DB and TAIC-treated wires showed clear peaks for  $C_{1S}$ ,  $N_{1S}$ , and  $S_{2P}$ . In the former, peaks for  $Fe_{2P}$  and  $Fe_{3P}$  were observed. In the latter, none could be detected, thus indicating the latter to be thus more homogeneous because of the lack of detection of  $Fe_{2P}$  and  $Fe_{3P}$  peaks, although both thicknesses are roughly same. Assignments of peaks in the  $C_{1S}$ ,  $N_{1S}$ , and  $S_{2P}$  narrow spectra of DB-treated wires showed the formation of the DB disulfide polymer. Assignments of peaks in the  $C_{1S}$ ,  $N_{1S}$ , and  $S_{2P}$  narrow spectra of DB- and TAIC-treated wires indicated formation of a three-dimensional polymer containing monosulfide and disulfide groups. The monosulfide group is formed by the addition of  $C=C$  bonds to TAIC and  $-NHCS-$  groups in DB.<sup>14</sup> The disulfide group is formed by an oxidative reaction between NHCS groups in DB in air.

#### Mechanism for Tribological Polymerization

The activity of mechanically processed metal surfaces may be due to (1) high temperature and pressure at the point of working contact,<sup>15</sup> (2) newly formed nascent surfaces,<sup>16</sup> (3) lattice disorders,<sup>17</sup> or (4) exoelectrons.<sup>3</sup> Surface temperatures of steel wires during drawing have been examined by Mid-diemiss.<sup>9</sup> For an areal reduction of 9.8% and drawing rate of 50 m/min, surface temperature reaches about 120–140°C.<sup>18,19</sup> At 80°C, DB was not polymerized at all on an ordinary iron plate, but at 120°C in air, DB with a melting point of 140°C gave a polymer on the plate. DB was polymerized in the solid state. At 120°C in a nitrogen atmosphere, DB, however, was polymerized in very low yield on the ordinary iron plate. The polymerization of DB on iron requires the presence of oxygen and high temperature. Figure 8 shows the effects of an iron plate on the polymerization of DB for 30 min at 120°C. An active iron plate was prepared for clarification of the effects of surface activity toward DB. The used iron plate was made as a model of an ordinary inactive surface. The surface activity of the iron plate was a major determining factor of the polymerization activity of DB in air. The ordinary iron plate gave low polymerization activity to DB since it is chemically inactive. The active iron plate immediately after polishing imparted high polymerization activity to DB under the same conditions. The contribution of a nascent surface or exoelectrons to the polymeriza-



**Figure 8** GPC patterns in the thermal polymerization of DB on inactive and active iron plates.

tion of DB may be the reason for these differences, i.e., polymerization is strongly influenced by surface activity.

It thus follows that the polymerization of DB on steel wires during drawing requires oxygen, heat, and a nascent surface or exoelectrons. Figure 9 illustrates the polymerization equation of DB and a mixture of DB and TAIC on steel wires during drawing. By drawing of wire, ferrous and ferric ions are formed as a result of the generation of exoelectrons, as shown in eq. (1). Thiol compounds are generally oxidized by oxygen in air in the presence of  $Fe^{3+}$  to give disulfides,<sup>16,17</sup> i.e., DB changes to the biradical cations of DB in the presence of  $Fe^{3+}$  as shown in eq. (2). The biradical cations of DB are oxidized in the presence of oxygen to give a disulfide polymer as shown in eq. (3). The mechanism is substantiated from the experimental results that the polymerization of DB did not give a polymer on a glass plate and inactive iron plates in air for 60 min at 120°C and further that the polymerization did not occur in the absence of air for 60 min at 120°C.

The polymerization of DB and TAIC on wires during drawing occurs by the formation of monosulfide and disulfide bonds. In this case, the disulfide bond is formed by the reactions in eqs. (1)–(3). After the radical cations of DB make an addition to double bonds in TAIC to give the sulfonium cation, the monosulfide bond is formed by the reduction of sulfonium cations with ferrous ions as shown in eqs. (4). As a result of these two reactions for the formation of mono- and disulfides, a three-dimensional network polymer is formed on wire surfaces during

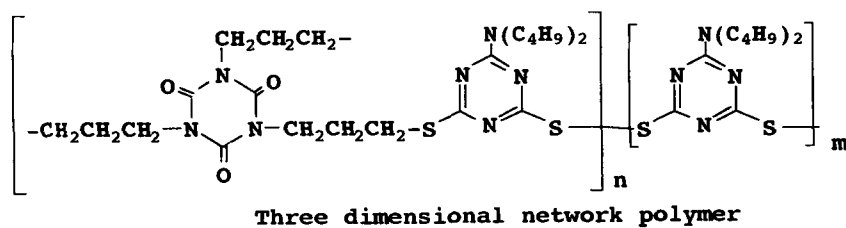
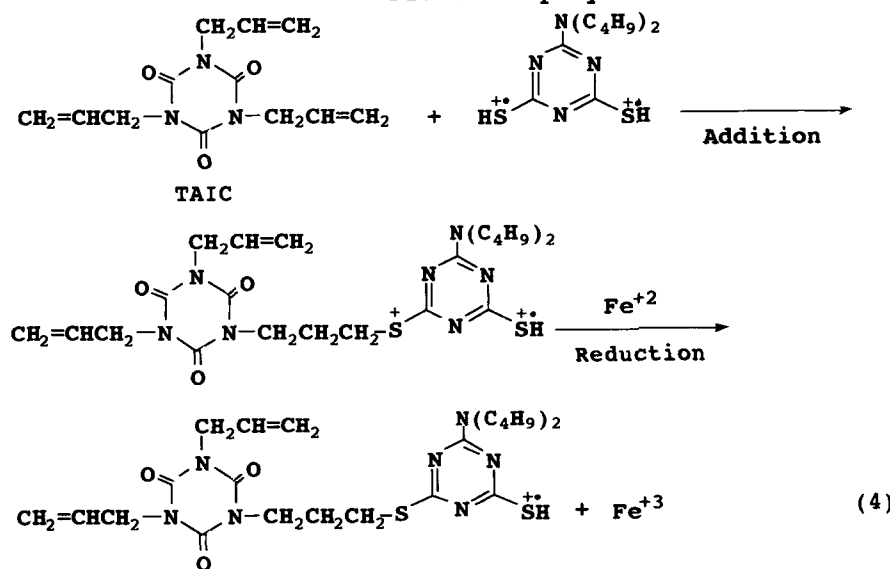
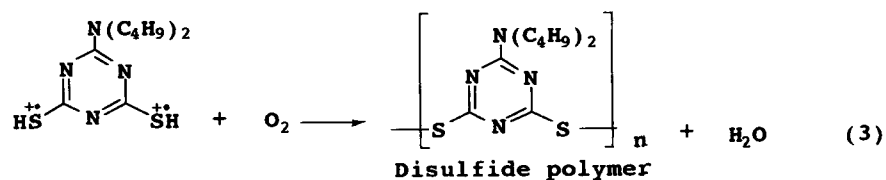
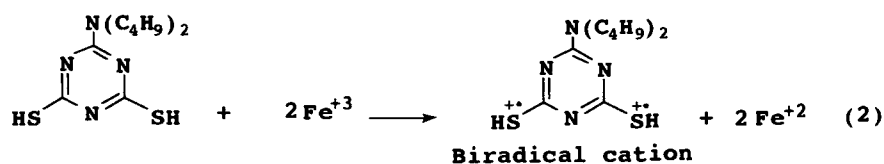
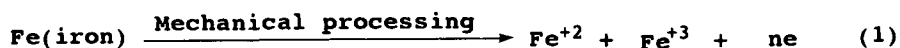


Figure 9 Polymerization of DB and a mixture of DB and TAIC on steel wire drawing.

drawing. The addition of DB to TAIC on glass and inactive iron plates left for a long time in air failed to occur for 60 min at 120°C. This would imply the formation of radical cations on a nascent surface during drawing.

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