

The Stress Cracking of Polyamides by Metal Salts. Part III. Metal Thiocyanates

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Synopsis

The stress cracking of polyamide (nylon 6) by a number of metal thiocyanates in aqueous and nonaqueous solutions has been investigated. Lithium, zinc and cobalt_{II} thiocyanates were the most active and their activity was compared with that of the corresponding metal halides. Stress cracking parameters were determined and the mechanism of cracking studied by infrared techniques. The action of metal thiocyanates on nylon 6 is similar to that of the corresponding metal halides. Some metal cobaltothiocyanates were also found to be active stress cracking agents.

INTRODUCTION

The action of metal halides on polyamides (nylons) has previously been reported.¹⁻⁶ In our early work, Parts I² and II,³ we have described the action and mechanism, respectively of metal halides and certain other salts on polyamides.

On the basis of the observed stress rupture of polyamides by metal halides it was predicted that halide-like salts, especially the thiocyanates, should be effective stress cracking agents for nylons. In initial screening trials, it was noted that in concentrated aqueous solution, ammonium thiocyanate, barium thiocyanate, calcium thiocyanate, zinc thiocyanate, lithium thiocyanate, cobalt_{II} thiocyanate and ferric thiocyanate, all caused rupture of thin, stressed nylon films. This paper describes the stress cracking activity and behavior of metal thiocyanates on nylons.

EXPERIMENTAL

Nylon 6 (Trogamid B) extruded sheet, as described in Part I,² and 0.001 in. thick extruded, blown, unplasticized, nylon 6 film, as described in Part II,³ were used as specimens for the determination of stress cracking parameters. Lithium, barium, zinc, cobalt_{II}, ammonium and potassium thiocyanates were laboratory reagent grades, and were used, without further purification, in aqueous and methanolic solutions.

Calcium thiocyanate was obtained as a 50% w/w solution, and was used in this form for studies of activity in aqueous solution. Methanolic

solutions were prepared by evaporating a known amount of aqueous solution to dryness, under vacuum, and then adding the required amount of methanol.

Ferric thiocyanate was prepared by the addition of a saturated aqueous solution of ferric chloride to a saturated solution of ammonium thiocyanate in the stoichiometric ratio required. The aqueous solution containing the ferric thiocyanate was then extracted with diethyl ether and the ether extracts washed with distilled water. The ether extracts were then evaporated to dryness and the ferric thiocyanate recovered.

The cobalthiocyanates used in the work were prepared by addition of a saturated aqueous solution of the corresponding metal thiocyanate to a saturated aqueous solution of cobalt^{II} chloride in the stoichiometric ratio required. The cobalthiocyanates precipitated on standing and were filtered and recrystallized twice from distilled water. The ammonium, potassium, calcium, barium, zinc and mercuric cobalthiocyanates were prepared in this manner.

Insoluble mercuric cobalthiocyanate was prepared as a check on the method of preparation of the other cobalthiocyanates. The physical properties of the prepared compounds agreed with reported data.

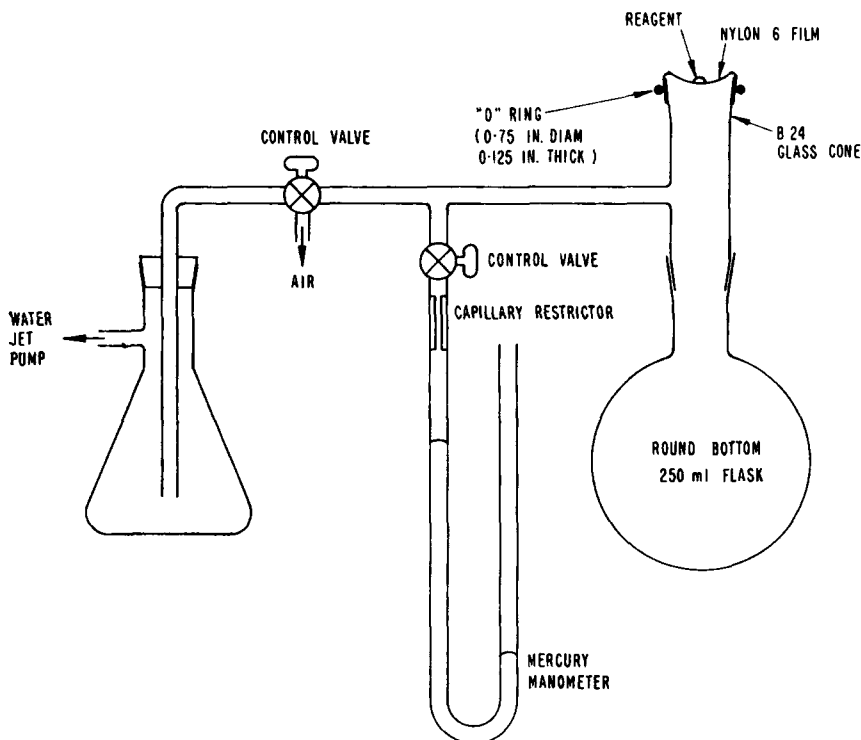


Fig. 1. Schematic diagram of apparatus used in the study of stressed nylon films (not to uniform scale).

TECHNIQUES

Nylon films and tensile bar specimens were used to obtain infrared data and stress cracking parameters by the technique described in Parts I² and II³. All infrared spectra were obtained using a Beckman IR8 or a Perkin-Elmer 125 recording spectrometer.

A new technique using stressed nylon 6 film was used to determine stress cracking parameters of metal thiocyanates. Nylon 6 film, 0.001 in. thick, was supported over a glass annulus by a rubber "O" ring, as shown in Figure 1, and stressed by the application of a reduced pressure on one side of the film. The pressure differential was indicated by a mercury manometer and from this the stress at the centre of the film could be calculated. A single drop of stress cracking reagent was applied at the central surface of the stressed film, and time to failure measured with a stopwatch. Film rupture at failure was indicated by a sudden loss of pressure as recorded by the manometer.

This technique enabled very rapid screening of compounds to be carried out and also gave information on the cracking activity of dilute solutions which could not be obtained using bulkier specimens.

RESULTS

Stressed Film Results

In nylon 6 films stressed by the technique described above, the actual tensile stress at the center of the film was calculated using the relationship reported by Roark,⁷

$$S = 0.423 \left[\frac{Ew^2a^2}{t^2} \right]^{1/3}$$

where

S = tensile stress at the centre of the film, psi

w = instantaneous loading = $P \times \frac{14.96}{32.05}$ (P = pressure in inches of Hg)

a = radius of annulus = 0.5 in.

t = thickness of nylon 6 film = 0.001 in.

E = Young's modulus of nylon 6 film. A 1000 second value for this time dependent property of 1×10^5 psi for nylon 6, at 23°C, and water content of 4.75%, was used.

Substituting these values, the relationship between tensile stress (S) and differential pressure (P) becomes;

$$S = 744.3 P^{2/3}$$

This relationship is shown graphically in Figure 2 over the working range of pressures. Nylon 6 films stressed in this way yielded over the differential pressure range, 18.5–19.0 in. of mercury. From Figure 2, the

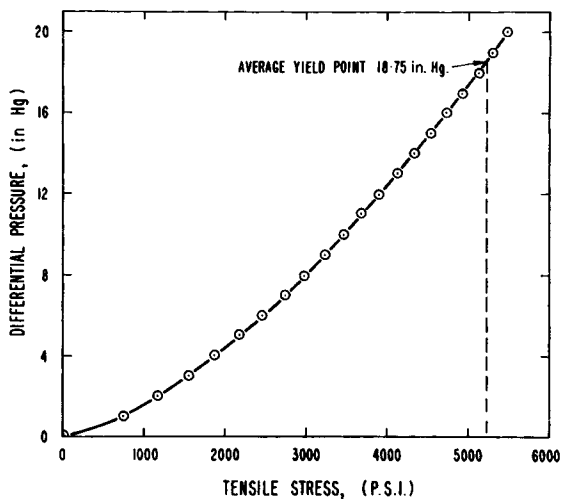


Fig. 2. The relationship between differential pressure and calculated stress at the center of stressed nylon 6 film.

average tensile yield stress from the above relationship, is 5250 psi. The tensile yield stress of the film, determined using a tensometer was found to be 5310 psi for specimens cut parallel to the direction of extrusion of the film and 5520 psi for specimens cut at right angles.

The lower value correlates well with the tensile yield stress calculated from the differential pressure, at yield, of the supported film.

The activity of aqueous solutions of metal thiocyanates and some halides was investigated using the stressed film technique. A measure of the activity of 1 *M* solutions is the critical stress (S_c) at which, or below which, stress rupture is slow and times to failure are greater than 300 sec. The critical stress for 1 *M* solutions of metal salts are given in Table I.

TABLE I
Activity of Aqueous Solutions on Stressed Nylon 6 Films

Solution in water (1 molar)	Concentration, % (w/v)	Critical pressure differential, in. of Hg	Approximate critical stress, psi
Zn(SCN) ₂	18.16	2-3	1360
Co(SCN) ₂ · 3H ₂ O	22.92	2-3	1360
HCl	3.65	12-13	4000
ZnCl ₂	13.63	12-13	4000
Ca(SCN) ₂ · 3H ₂ O	21.03	13-14	4220
Ba(SCN) ₂ · 2H ₂ O	28.96	13-14	4220
NH ₄ SCN	7.61	14-15	4420
LiSCN	6.50	16	4720
Fe(SCN) ₃	23.01	16-17	4820
KCl	9.72	16-17	4820
NH ₄ SCN (2 molar)	15.22	16-17	4820

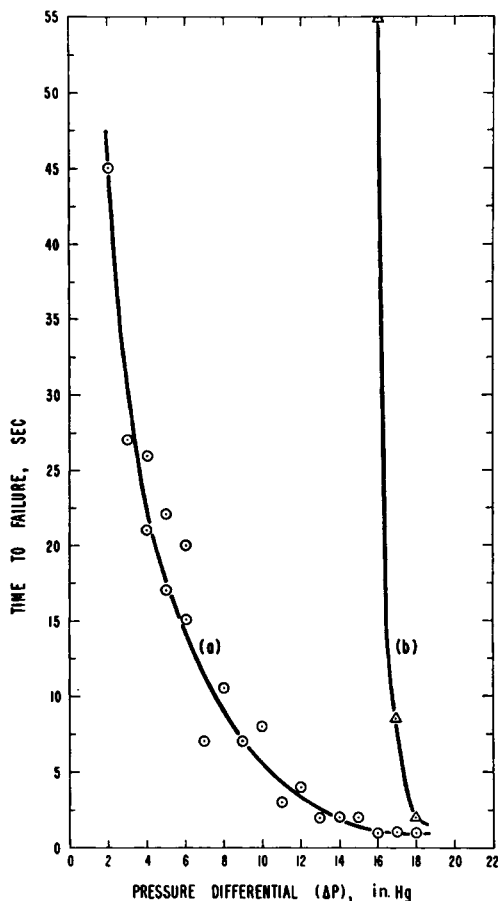


Fig. 3. The effect of stress on the time to failure of stressed nylon 6 films in contact with 1 *M* aqueous solutions of, (a), $Zn(SCN)_2$ and (b), $ZnCl_2$.

Using this technique, with dilute solutions it was shown that the activity of 1 *M* HCl and 1 *M* $ZnCl_2$ solutions were similar, and that even 1 *M* KCl would bring about rupture of films under high stress. This may appear to be in direct contrast to the results obtained with bulkier specimens and more concentrated solutions as described in Part I of this paper. However in dealing with more dilute solutions where extensive dissociation into ions has occurred, the rupture mechanism is believed to be one of simple ionic interference with hydrogen bonding between adjacent polymer chains and, as demonstrated, most salts are equally active at low concentrations. The stress dependence of time to failure for stressed films in contact with some 1 *M* solutions is shown in Figures 3 and 4.

With this technique film rupture was very rapid with concentrated solutions of metal salts, and generally dilute solutions were employed. The activity of zinc chloride solutions (25 and 50% w/v in water) has been

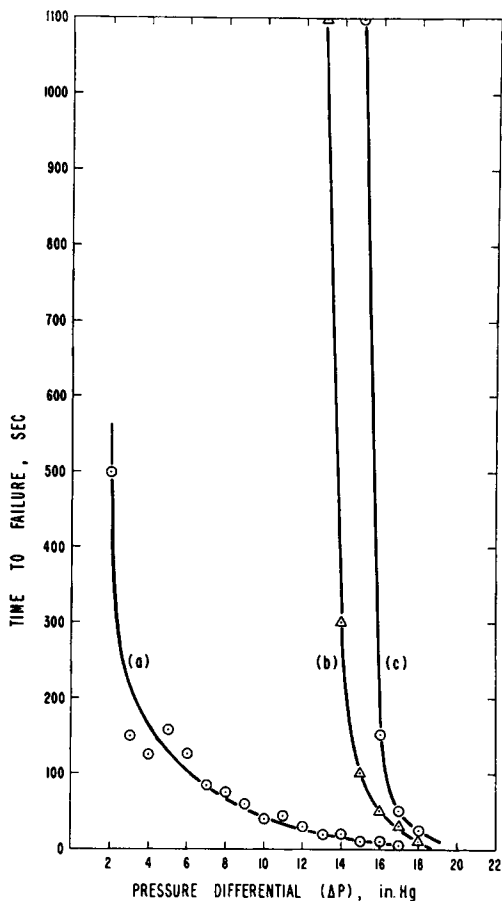


Fig. 4. The effect of stress on the time to failure of stressed nylon 6 film in contact with 1 *M* aqueous solutions of (a), $\text{Co}(\text{SCN})_2$, (b), $\text{Ca}(\text{SCN})_2$, and (c), Li SCN .

investigated using the stressed film technique and the results are shown in Figure 5.

Stress Cracking Parameters

The parameters, time to crack initiation, time to crack-through, time to rupture and the crack propagation rate were determined for solutions of thiocyanates in contact with stressed nylon 6 tensile bar specimens cut from extruded nylon 6 sheet using the techniques described in Part I.² Results are given in Tables II and III. The effect of stress on the time to crack-through and time to crack initiation of stressed nylon 6 tensile bar specimens in contact with aqueous zinc thiocyanate is shown in Figure 6. As indicated in Part I of this paper the crack propagation rates are a useful semi-quantitative measure of the activity of the cracking agents.

TABLE II
Stress Cracking Parameters for Metal Thiocyanates on Nylon 6 Tensile Bar Specimens

Compound	Concentration in aqueous solution, % (w/v)	Stressed at 2000 psi				Stressed at 4000 psi			
		Time to crack initiation (ΔT), min	Time to crack through (T_1), min	Time to rupture (T_R), min	Time to crack initiation (ΔT), min	Time to crack through (T_1), min	Time to rupture (T_R), min	Time to crack initiation (ΔT), min	Time to rupture (T_R), min
Zn(SCN) ₂	30	1.0	8.0	15	0.3	3.4	12		
	36 (saturated)	0.1	3.7	10	0.1	2.2	7		
Ba(SCN) ₂	30	18	>1500	No rupture	20	>1500	No rupture		
	92	0.7	50	230	0.02	0.7	10		
NH ₄ SCN	170 (saturated)	0.05	0.8	16	0.05	0.6	6		
	30	265	>1500	No rupture	6	>1000	No rupture		
LiSCN	160 (saturated)	120	>1000	No rupture	90	365	800 (approx)		
	30	>2000	>2000	>2000	>300	>1200	>1200		
Co(SCN) ₂	saturated	0.15	0.3	1	0.15	0.25	1		
	30	>360	>360	360	0.4	30	82		
Fe(SCN) ₃	saturated	60	90	130	0.2	1	7		
	30	76	87	170	36	100	180		
Ca(SCN) ₂	saturated	60	90	220 (approx)	0.4	80	185		
	50	No crack initiation	No crack initiation within 1500 min	1500 min					
100	No crack initiation	No crack initiation within 1500 min	1500 min						

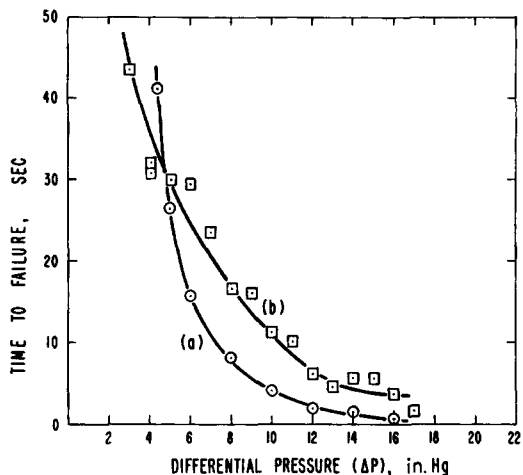


Fig. 5. The effect of stress on the time to failure of stressed nylon 6 films in contact with aqueous $ZnCl_2$, (a), 25% w/v and (b), 50% w/v.

Whilst numerical values are employed emphasis should only be placed on the order of magnitude.

Stress cracking data for metal thiocyanates indicates that in general these are more active than the corresponding metal halides. Crack prop-

TABLE III
Crack Propagation Rates (K) for Nylon 6 Stress-Cracked by Thiocyanate Solutions^a

Solvent	Salt	Concentration	Crack propagation rate (K), in./min	
			2000 psi stress	4000 psi stress
Water	$Zn(SCN)_2$	30%	6.4×10^{-3}	1.5×10^{-2}
Water	$Zn(SCN)_2$	36% (satd)	1.2×10^{-2}	2.0×10^{-2}
Water	$Ba(SCN)_2$	30%	$<3.0 \times 10^{-5}$	$<3.0 \times 10^{-5}$
Water	$Ba(SCN)_2$	92%	9.0×10^{-4}	6.2×10^{-2}
Water	$Ba(SCN)_2$	170% (satd)	5.6×10^{-2}	7.0×10^{-2}
Water	$NH_4(SCN)$	30%	$<3.0 \times 10^{-5}$	$<3.0 \times 10^{-5}$
Water	$NH_4(SCN)$	satd	$<4.0 \times 10^{-5}$	1.2×10^{-4}
Water	$Fe(SCN)_3$	30%	5.0×10^{-4}	4.5×10^{-4}
Water	$Fe(SCN)_3$	satd	5.0×10^{-4}	5.6×10^{-4}
Water	$Li(SCN)$	30%	^b	^b
Water	$Li(SCN)$	satd	2.4×10^{-1}	4.8×10^{-1}
Water	$Co(SCN)_2$	30%	^b	1.3×10^{-3}
Water	$Co(SCN)_2$	satd	1.3×10^{-3}	5.0×10^{-2}
Water	$Ca(SCN)_2$	100%	^c	^c
Methanol	$Ca(SCN)_2$	satd	—	1.5×10^{-4}
Methanol	$Li(SCN)$	satd	—	0.5

^a Conditions: Nylon 6 specimens, water content 3.5%, at 21°C.

^b Very slow crack propagation.

^c No crack initiation occurred.

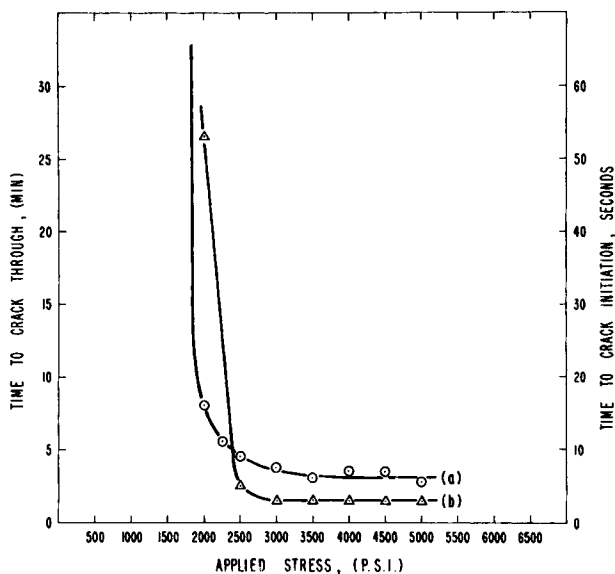


Fig. 6. The effect of stress on the time to crack-through, (a), and time to crack initiation (b), of stressed nylon 6 tensile bar specimens in contact with 30% w/v aqueous $Zn(SCN)_2$.

agation rate data (Table III) showed that saturated aqueous and methanolic solutions of lithium thiocyanate were extremely active stress cracking agents for nylon. The general activities of the thiocyanates and halides of some metals in both aqueous and methanolic solution are summarised in Table IV.

TABLE IV
Activity of Metal Halides and Thiocyanates

Solvent	Metal ion	Activity ^a			
		Thiocyanate	Chloride	Bromide	Iodide
Water	Zinc	+++	+++	+++	+++
Water	Cobalt _{II}	+++	++	++	0
Water	Calcium	-	-	0	0
Water	Barium	++	-	-	-
Water	Lithium	+++	+	+++	-
Water	Iron _{III}	++	+	0	0
Water	Ammonium	++	-	-	-
Methanol	Zinc	-	+++	+++	+++
Methanol	Cobalt _{II}	-	++	0	0
Methanol	Calcium	++	++	0	0
Methanol	Barium	-	-	++	++
Methanol	Lithium	+++	++	+++	++
Methanol	Iron _{III}	-	++	0	0
Methanol	Ammonium	-	-	-	-

^a (+++) Highly active; (++) active; (+) weakly active; (-) inactive; (0) not tested.

The Action of Metal Thiocyanates on Nylon 6 Film

The action of metal thiocyanates on nylon 6 films was investigated by a study of the changes induced by the salts in the infrared spectrum of the polyamide.

Immersion of nylon 6 films in aqueous zinc thiocyanate solution for various periods of time produced progressive changes in the spectrum of the nylon, with the most obvious changes being in the amide I and amide II bands. These changes, shown in Figure 7, are similar to those produced by zinc chloride as reported in Part II.³ The close association between absorption of the zinc thiocyanate and the observed shifts of the amide I and amide II bands, and the appearance of a new characteristic band at

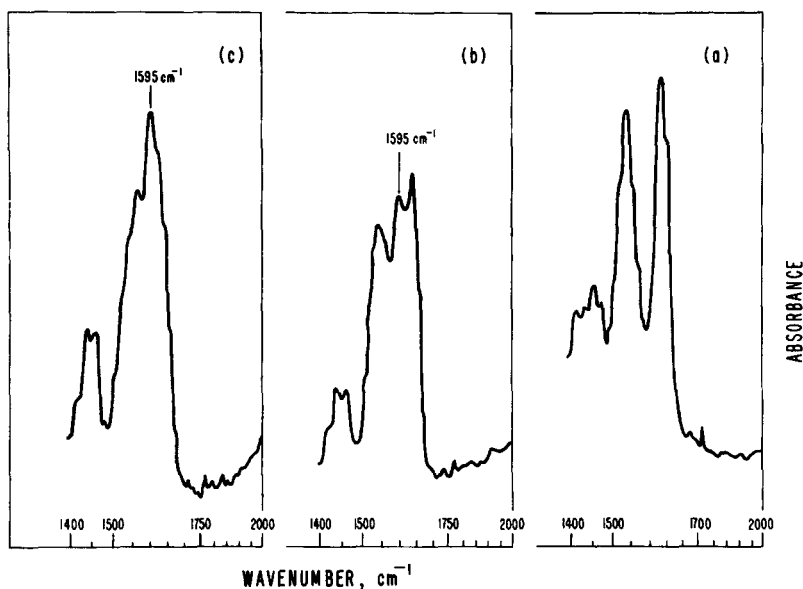


Fig. 7. Spectral changes in nylon 6 film treated with aqueous $\text{Zn}(\text{SCN})_2$, (30% w/v): amide I and amide II band region. (a) untreated; (b) treated 20 min; (c) treated 60 min.

1595 cm^{-1} , is indicated by the simultaneous appearance of a strong $-\text{SCN}$ band in the spectra. Cobalt_{II} thiocyanate similarly caused shifts of the amide I and amide II bands, together with the appearance of a strong $-\text{SCN}$ band. These are shown in Figure 8.

Other thiocyanates did not cause shifts in the amide I and amide II bands and gave weaker $-\text{SCN}$ bands. With calcium thiocyanate, the $-\text{SCN}$ band was extremely weak. The spectra of nylon 6 films treated with calcium and barium thiocyanates are shown in Figure 9. Lithium thiocyanate treated films rapidly became soft and rubbery and eventually dissolved completely in the reagent. The spectra of lithium thiocyanate treated films showed evidence of the film being highly amorphous in a

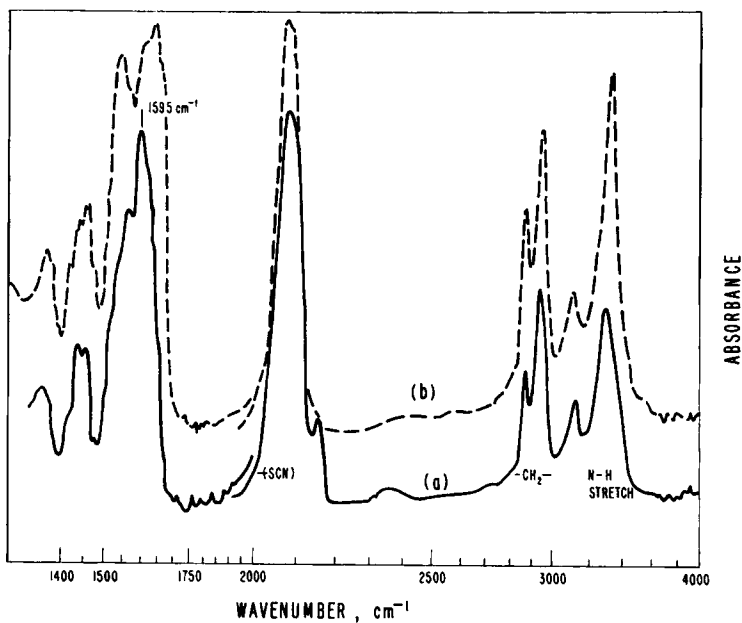


Fig. 8. Spectra of nylon 6 films treated with 30% w/v aqueous solutions of (a) $\text{Zn}(\text{SCN})_2$ for 60 min; (b) $\text{Co}(\text{SCN})_2$ for 120 min.

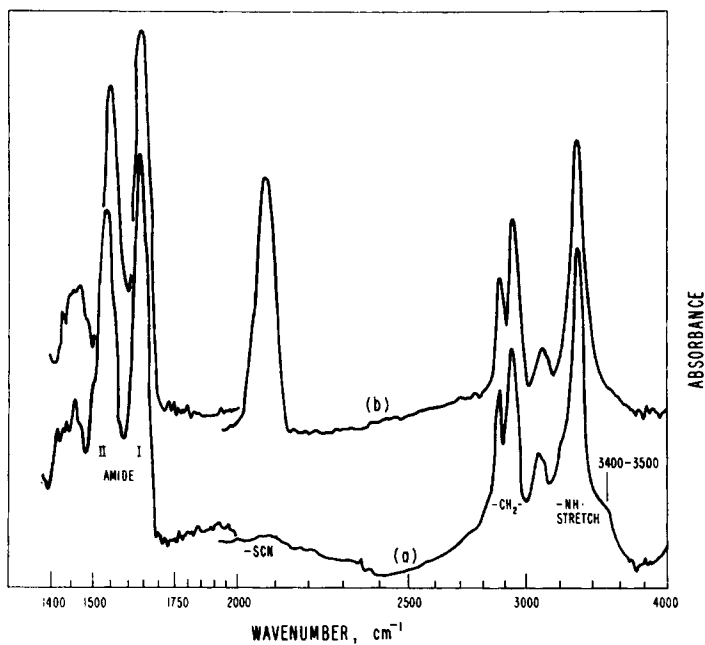


Fig. 9. Spectra of nylon 6 films treated with 30% w/v aqueous solutions of (a) $\text{Ca}(\text{SCN})_2$ for 120 min; (b) $\text{Ba}(\text{SCN})_2$ for 82 min.

manner similar to cast films containing lithium halides, as reported in Part II.³

The rate of absorption of the thiocyanates by nylon 6 was determined by measuring the optical density of the $-\text{SCN}$ absorption at 2050 cm^{-1} ($D_{-\text{SCN}}$) and the optical density of the $-\text{CH}$ absorption at 2940 cm^{-1}

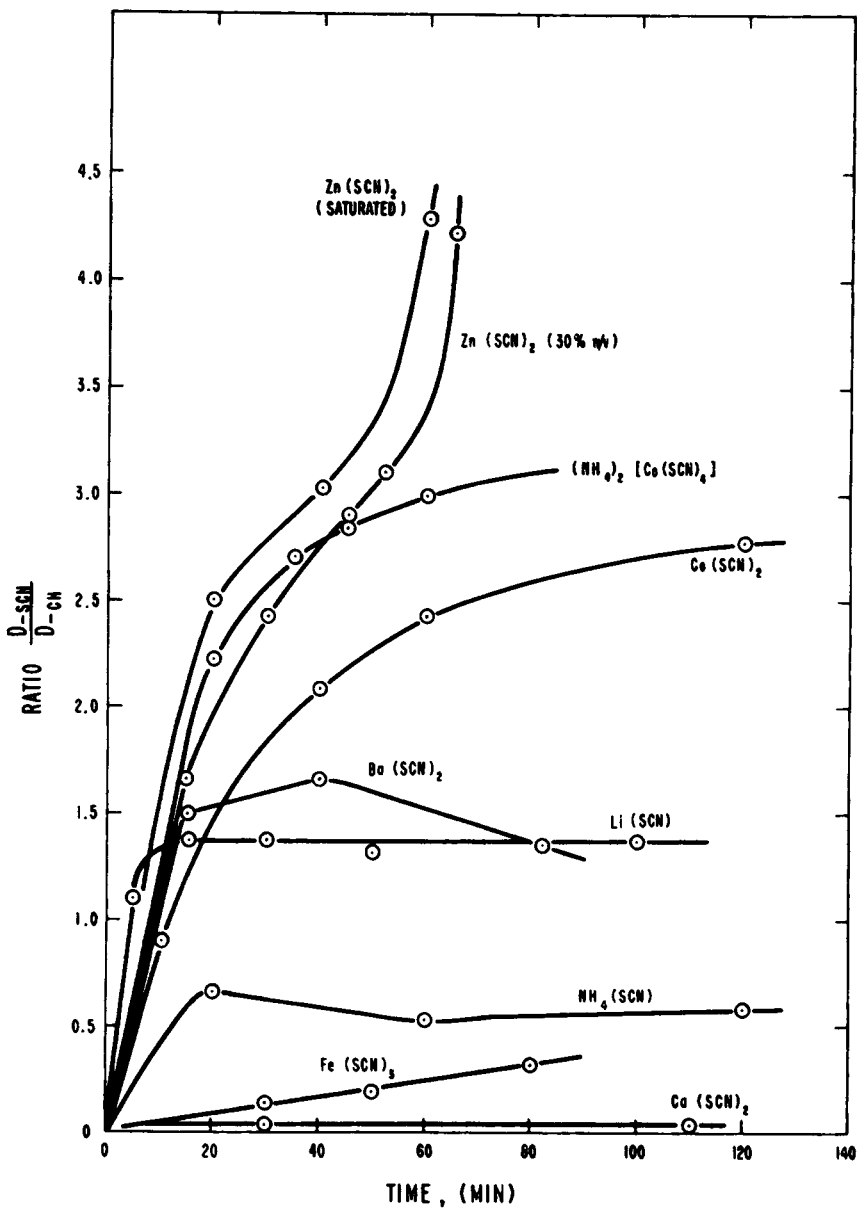


Fig. 10. The sorption of metal thiocyanates by nylon 6 film.

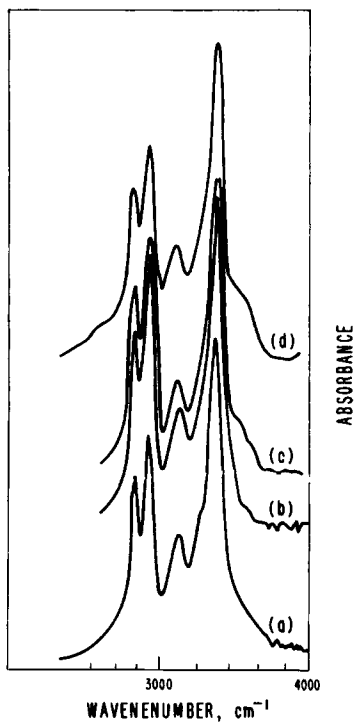


Fig. 11. Spectral changes in nylon 6 films treated with metal salts: N—H stretching band region (a), untreated; (b), treated with $\text{Co}(\text{SCN})_2$; (c) treated with $\text{Ca}(\text{SCN})_2$; (d), treated with LiBr.

($^{\text{D}}\text{—CH}$), in films treated for various periods. The ratio, $^{\text{D}}\text{—SCN}/^{\text{D}}\text{—CH}$, was used to indicate the quantity of thiocyanate absorbed per unit thickness of nylon.

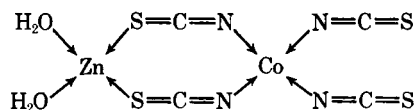
In Figure 10 values of $^{\text{D}}\text{—SCN}/^{\text{D}}\text{—CH}$ are plotted against time of treatment for a number of thiocyanates. Equilibrium values of $^{\text{D}}\text{—SCN}/^{\text{D}}\text{—CH}$ were obtained, at 21°C , within 140 min for most thiocyanates. Zinc thiocyanate was unusual and showed continued rapid absorption into nylon 6 film.

Changes in the —NH stretching band and amide II overtone band at $3060\text{—}3080\text{ cm}^{-1}$ were also noted in the infrared spectra of treated films, these are shown in Figure 11, for films treated with cobalt_{II} thiocyanate, calcium thiocyanate and lithium bromide.

The Behavior of Cobalthiocyanates

Ammonium cobalthiocyanate was found to be a highly active cracking agent giving instantaneous crack initiation with nylon 6 tensile bar specimens under an applied tensile stress of 2000 psi. Crack propagation rates were also rapid being approximately 9.0×10^{-2} in./min, and total rupture

of the specimens occurred within 5 to 10 min. Potassium cobalthiocyanate was found to be equally active. Barium cobalthiocyanate was also an active cracking agent but crack initiation was slower and times to rupture longer. Calcium cobalthiocyanate, like calcium thiocyanate and calcium chloride, was not active in aqueous solution but was a weak cracking agent in methanolic solution. Zinc cobalthiocyanate was inactive in both aqueous and methanolic solution. This was an unexpected result and it is believed that in this compound the complex anion is coordinately linked to the zinc thus:



Jeffery⁸ has already shown the existence of similar $\text{S} \rightarrow \text{Hg}$ bonding in mercuric cobalthiocyanate. Coordination of this type would prevent formation of a complex with nylon. Nylon 6 films treated with ammonium and potassium cobalthiocyanate solutions rapidly developed an intense blue colour and became soft and rubbery. The infrared spectra of these films showed no shifting of the amide I and amide II bands. Uptake of these cobalthiocyanates by nylon 6 was rapid and the equilibrium value of $\text{D}-\text{SCN}/\text{D}-\text{CH}$ was high. In addition marked changes occurred in the

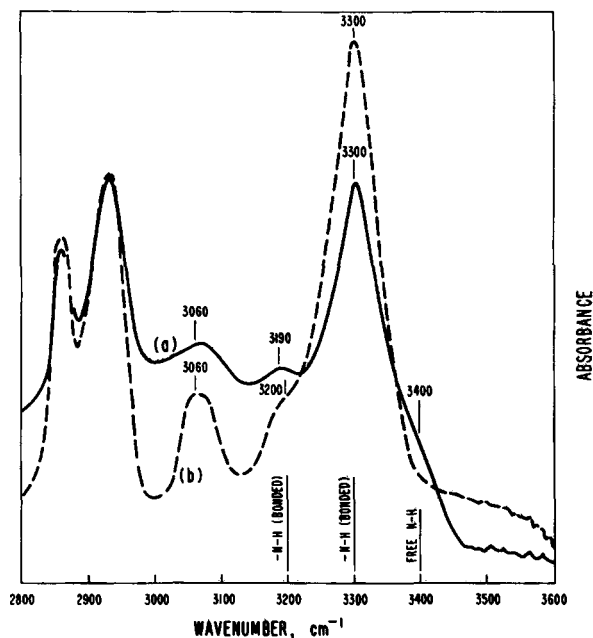


Fig. 12. Spectral changes in nylon 6 film; (a) treated with aqueous ammonium cobalthiocyanate solution for 30 min; (b), after "reversion" on washing with hot water and drying.

N—H stretching region, similar in some respects to those previously observed in nylon 6 films treated with hydrochloric acid.³ These changes are shown in Figure 12.

DISCUSSION

The metal thiocyanates, like the metal halides described in Part II,³ show no uniform action on nylons.

Zinc thiocyanate and cobalt_{II} thiocyanate appear to be Type I cracking agents, and act in a similar manner to the Type I halides described earlier.³ These agents are believed to form complexes with the amide groups of the nylon. In the complex the metal ion is coordinately linked to the carbonyl oxygen atom of the nylon and inter-amide group hydrogen bonding is no longer possible. These agents are characterised by their very rapid absorption by the nylon, their rapid rupture of nylon 6 films at low stresses and their rapid crack initiation and rupture of stressed nylon 6 tensile bar specimens.

Calcium, lithium and barium thiocyanates appear to act as Type II cracking agents similarly to the Type II halides previously described.³ With these agents hydrogen bonding between the solvated metal ion and the carbonyl oxygen atom of the amide group appears to occur, effectively destroying interchain hydrogen bonding in the polyamide. These agents can be effective solvents for nylons, their solvent power being determined by the acid strength of the solvated metal ion. Lithium thiocyanate in aqueous solution is a very powerful solvent for nylon 6, similar to lithium bromide, and causes very rapid crack propagation in stressed nylon 6 by simple solvent cracking. Ammonium, potassium and ferric thiocyanates are weak cracking agents for nylon 6 giving slow crack initiation and very slow absorption of the metal salt with low equilibrium values for $\frac{D-SCN}{D-CH}$. These agents are believed to bring about stress cracking by simple ionic interference with the interchain hydrogen bonding in the polyamide.

The equilibrium values of $\frac{D-SCN}{D-CH}$ are of interest as they may indicate the ability of the thiocyanates to be absorbed by rendering the nylon 6 more amorphous. Wood and King⁹ have shown, by deuteration studies, that only a limited quantity of nylon 6 is accessible to deuterium oxide, and is capable of being deuterated. This proportion has been identified with amorphous regions in the polymer. These same regions are also believed to be accessible to water, while the crystalline regions are not. The low equilibrium thiocyanate absorption values observed with calcium, ammonium and ferric thiocyanate ($\frac{D-SCN}{D-CH}$; 0.04, 0.55 and 0.35, respectively) may reflect the absorption of these solutions by the normal amorphous regions in the polymer. The higher equilibrium values observed with the Type II thiocyanates, such as lithium thiocyanate, $\frac{D-SCN}{D-CH}$ 1.35 and barium thiocyanate, $\frac{D-SCN}{D-CH}$, 1.5 are believed to be due to increased absorption of the solutions, as a result of the reagent rendering the polymer more amorphous. The very high values for the

Type I reagents, such as zinc thiocyanate, $D-SCN/D-CH$, 4.0+ and cobalt_{II} thiocyanate, $D-SCN/D-CH$, 3.0+ represent the very high absorption of solution, resulting from amorphous polymer regions being created as a result of complex formation.

Some cobaltothiocyanates are active cracking agents but do not appear to act as Type I agents. This is not unexpected since in these compounds the cobalt_{II} atom is fully coordinated in the anion. These agents are believed to interfere with hydrogen bonding between polymer chains by simple ionic charge effects.

The spectra of nylon 6 films treated with calcium and barium thiocyanate and ammonium cobaltothiocyanate show only minor absorbance above 3300 cm^{-1} (Fig. 11 and 12). This is probably due to a very low contribution from free N—H stretching in the presence of the solvent.

We believe, from the stress cracking parameters and infrared data, that metal thiocyanates and corresponding metal halides promote stress cracking in polyamides by similar mechanisms.

The assistance of Dr. A. G. Moritz of these Laboratories in determining the NMR spectra and helping with the interpretation of the NMR and infrared spectra is gratefully acknowledged.

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Received January 31, 1969