*Physical Properties and Structure of Polyacetonitrile**

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Although many kinds of polymeric semiconductors have been synthesized, most of them have consisted of carbon-carbon conjugated systems. When nitrogen, which has a free pair of electrons, is involved in a linear conjugated system, it may be expected that polymer will have different properties than when involved in a carbon-carbon conjugated system. Thus, the polymer of a linear alternate carbon-nitrogen conjugated sequence seems to be an interesting object for studies of physical and chemical properties.

As a polymer that has carbon-nitrogen conjugated double bonds, the polymer of cyanic acid is well known. This, however, is not a pure linear polymer of carbon-nitrogen conjugated double bonds; rather, it appears to have a ladder-like structure.(1) The same type of polymer was recently produced from cyanic acid under irradiation.(2) These polymers of cyanic acid have a low degree of polymerization, and their electric conductivity has not been measured. Other examples of polymerization by irradiation are the solid phase polymerization of nitriles at low temperatures(3) and the ring-opening polymerization of cyanuric chloride,(4) but the yield and the molecular weight of both polymers appear to be small.

Thermally-degraded polyacrylonitrile(5,6) and polycopperphthalocyanine(7) are of this type as well. The former has a considerably high electric conductivity when it is heated at a high temperature (e. g., 500°C) ; the latter also has good electric conductivity.

Recently Kargin et al. synthesized a linear polymer of carbon-nitrogen conjugated double bonds by heating the complex of acetonitrile with zinc chloride; they then examined the electrical properties of the polymer.(8) The same type of polymer has also been synthesized by high voltage discharge, although it has a low molecular weight.(9)

We have studied the polymerization of acetonitrile complexes with several kinds of metal chlorides and have reported the correlations of the infrared shifts of the nitrile-stretching frequency in the Lewis acid complexes with the polymerizability.(10) Moreover, we have obtained some information concerning the properties and structure of the polymer.

Experimental

Materials.—The metal chlorides used are titanium tetrachloride, zirconium tetrachloride, stannic chloride, aluminum chloride, gallium chloride, ferric chloride, and zinc chloride. Commercial reagents were used, including acetonitrile, but gallium chloride was prepared from gallium metal and hydrogen chloride(11) and was purified by sublimation.

Acetonitrile was used after distillation and drying over calcium hydride.

Titanium tetrachloride and stannic chloride were distilled just before the preparation of the complex.

Ferric chloride, zirconium tetrachloride and aluminum chloride were purified by sublimation.

For zinc chloride, a guaranteed reagent was used after drying it at an elevated temperature under reduced pressure.

The Preparation of Complexes.—The distillate or the solid mass of metal chloride was cooled with dry ice-methanol or liquid nitrogen in a flask, into which a little more than the calculated amount (molar ratio $RCN/MX_n=2/1$) of the acetonitrile was added drop by drop in an atmosphere of nitrogen. The excess nitrile was then distilled off under reduced pressure. The complexes were purified by sublimation. Since ferric chloride, zinc chloride and gallium chloride complexes could not be sublimed, these three chlorides were carefully purified before preparation. The complexes were handled afterwards in a dry box because they are easily decomposed, even by moisture in the air.

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The properties and analyses of the complexes have been given in a previous publication.[10)]

Polymerization.—After having been rinsed with nitrogen, a definite amount of complex was sealed into a thick-wall ampoule under the reduced pressure of 10^{-2} mmHg. The ampoule was then heated in a controlled electric furnace for the required time. The product prepared from the complex was powdered, and water was added. The product was filtered and washed repeatedly with distilled water or diluted hydrochloric acid, since water readily decomposes the complex and dissolves metal chlorides. When the heating time was shorter or the temperature was lower, the filtration was often difficult. Then a centrifuge was used. The infrared spectrum of the filtrate did not show the absorption due to the C=N conjugated double bond at about 1600 cm^{-1}. This suggests that the polymer is scarcely dissolved at all in the filtrate.

Most of the polymers obtained were dark brown to black and were insoluble in common organic solvents, although they were soluble in mineral acids.

The Addition of Silver Nitrate.—About 0.1 g. of a polymer was dispersed in an aqueous 1/10 N silver nitrate solution for 24 hr. at an ordinary temperature. The dispersed liquid was then filtered, and the residue was washed repeatedly with distilled water.

The Measurements of Physical Properties. — 1) The X-ray diffraction measurements were carried out using Cu$K\alpha$ of 30 kV., 20 mamp., and a scanning speed of $2\theta=2°$/min.

2) The infrared absorption spectra were obtained by the usual KBr-pellet method.

3) The intrinsic viscosities of the polymers in sulfuric acid were measured at 40 ± 0.03°C using a modified Ubbelohde viscometer. Since the value of the intrinsic viscosily and the linear gradient of η_{sp}/c versus c did not vary when the same solution was measured again after a week, the polymer in sulfuric acid does not seem to be degraded.

4) The electric conductivity, σ, was measured under the pressure of 90 kg./cm². The current was measured with a vibration-reed electrometer. The temperature was raised by 0.5°C/min. from room temperature to about 100°C. The energy gap, ΔE_g, can be determined from the gradient of log σ versus $1/T$:

$$\sigma=\sigma_0\exp(-\Delta E_g/2\boldsymbol{k}T) \tag{1}$$

5) Stable unpaired electrons included in the polymers were observed with an ESR spectrometer at the Nissei Industry Co. Ltd.

Results and Discussion

Electric Conductivity.—The electric conductivity values of 10^{-10} to $10^{-5}\,\Omega^{-1}\text{cm}^{-1}$ summarized in Table I indicate that the polymer is a semiconductor. The electric conductivity increases and the activation energy decreases when the heat treatment of the complex is increased at a given temperature or at a given

TABLE I. ELECTRICAL PROPERTIES OF POLYACETONITRILE

No.	Temp. °C	Heating time, hr.	Elec. cond. σ $\Omega^{-1}\text{cm}^{-1}$ (20~22°C)	Energy gap ΔE_g, eV.	σ_0 $\Omega^{-1}\text{cm}^{-1}$
T 234	230	4	1.2×10^{-8}	0.73	2.5×10^{-2}
T 238		8	1.8×10^{-8}	0.70	1.9×10^{-2}
T 254	250	4	2.5×10^{-8}	0.66	1.9×10^{-2}
T 258		8	3.5×10^{-8}	0.68	2.2×10^{-2}
T 304	300	4	1.4×10^{-7}	0.64	3.0×10^{-2}
T 308		8	3.2×10^{-7}	0.6	4.1×10^{-2}
T 354	350	4	3.5×10^{-7}	0.57	2.6×10^{-2}
T 358		8	5.1×10^{-7}	0.53	1.7×10^{-2}
F 254	250	4	2.9×10^{-10}	—	—
F 258		8	3.6×10^{-10}	0.97	6.7×10^{-2}
F 304	300	4	1.2×10^{-8}	—	—
F 308		8	1.4×10^{-7}	—	—
F 354	350	4	5.1×10^{-6}	0.40	1.6×10^{-2}
A 354	350	4	1.3×10^{-9}	1.03	1.1
A 356		6	2.5×10^{-9}	—	—
A 358		8	2.8×10^{-9}	—	—
Z 254	250	4	4.2×10^{-10}	1.22	21
Z 304	300	4	3.9×10^{-10}	—	—
Z 308		8	1.1×10^{-9}	—	—
Z 354	350	4	3.0×10^{-9}	1.08	5.7
Z 358		8	6.6×10^{-8}	—	—
S 234	230	4	3.1×10^{-10}	—	—
S 254	250	4	1.4×10^{-9}	—	—
S 258		8	1.7×10^{-9}	0.86	5.6×10^{-2}

T : Product from titanium tetrachloride complex
F : Product from ferric chloride complex
A : Product from aluminum chloride complex
Z : Product from zinc chloride complex
S : Product from stannic chloride complex

heating time. This suggests that the formation of conjugated double bonds becomes more extensive in the polymer at a higher temperature and a longer heating time, while Eley et al. have shown that ΔE_g decreases to a limiting value as the number of conjugated double bonds increases.[12]

TABLE II. ADDITION OF SILVER NITRATE TO THE POLYMERS

No.	Wt. increase g./g. polymer
T 234	0.487
T 238	0.516
T 254	0.311
T 258	0.417
T 304	0.419
T 308	0.177
T 354	0.288
T 358	0.590

The number of conjugated π electrons in a polymer chain can be estimated from ΔE_g in Table I if Eley's calculation for a carbon-carbon conjugated system may be applied to a carbon-nitrogen conjugated system. The numbers obtained in this way were 17 for Z254 (ΔE_g=1.22) to 50 for F354 (ΔE_g=0.40). One-half of this value is the mean number of conjugated double bonds if the polymer is regarded as a completely linear carbon-nitrogen conjugated chain.

The products from the ferric chloride complex show the greatest change in σ at a given change in the heating temperature.

The Addition of Silver Nitrate.—The weight increases in polymers upon the addition of silver nitrate are shown in Table II. They are sizable and seem to be due to chemisorption rather than to mere adsorption. Since the C=N bonds characteristically take up noble metal ions, these considerable weight increases support the idea that the polymer contains C=N bonds.[1] However, the values are not strictly reproducible because they depend on the surface area of the powdered samples.

X-Ray Diffraction. — In X-ray diffraction patterns no sharp peak could be seen, but the $2\theta=25°$ peak (d=3.56 Å) is comparable with that of phthalocyanine ($2\theta=26°$, d=3.38 Å),[13] consisting of a big circular carbon-nitrogen conjugated system. If parts of the resulting polymer are considered to form a band-like structure, the value of 3.56 Å would correspond to the distance between the bands.

It was found that polymers produced in a shorter heating time and at a lower temperature had a higher intensity of diffraction, probably indicating that these polymers have a relatively high regularity.

Electron Spin Resonance.—All the samples showed singlet spectra, as are seen in polyacetylene,[14] under the measuring conditions (Fig. 1). The g-factors were estimated to be from 2.0046 to 2.0003, but most of them have the value of nearly 2.0023, which is the value of a free electron. Hence, the unpaired electrons in polyacetonitrile are believed to be stabilized by resonance energy in a highly conjugated system and to be in a state similar to that of free electrons.

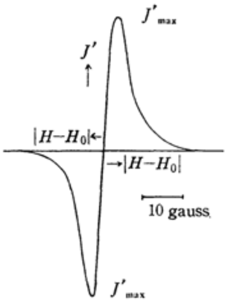

Fig. 1. ESR derivative curve of A352.

The relative spin concentrations in each group of metal chloride decreased with the temperature except for the Z-group and the G-group (products of the gallium chloride complex), in which the concentrations increased with the temperature; this has not yet been explained reasonably.

According to the method of analysis of the line shape proposed by Tikhomirova and Voevodskii,[15] the Gaussian (2) and Lorentzian (3) equations may be described, as respectively:

$$\log(y/J')=a^2y^2/2.3+\log(0.427/J'_{max}\ a) \qquad (2)$$

$$\sqrt{y/J'}=0.57/\sqrt{bJ'_{max}}+(0.57b\sqrt{b}/\sqrt{J'_{max}})y^2 \qquad (3)$$

where $a^2=1/1.45\,\Delta H_G{}^2$, $b^2=1/\Delta H_L{}^2$, $y=H-H_o$, and J' represents the ordinate (arbitrary unit) in a differential spectrum (Fig. 1).

ΔH_G and ΔH_L are obtained from the slope of the linear part in Eqs. 2 and 3 respectively. The value of ΔH corresponding to the transition region between 2 and 3 is ΔH_o. An example is illustrated for A352 in Figs. 1 and 2. Figure 2 suggests that the ESR line investigated is Lorentzian in the center, but Gaussian beyond ΔH=7.6 gauss.

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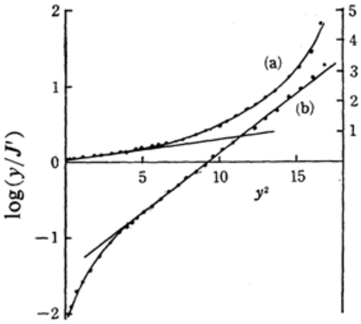


Fig. 2. Linearized form of A352 ESR curve.
Curve a: in coordinates corresponding to a Lorentzian relation
Curve b: in coordinates corresponding to a Gaussian relation
Abssissa: y^2 in arbitrary units ($y^2=10=1.46$ gauss)

The results of the analyses of line shape are summarized in Table III. The relatively small deviations of $\Delta H_G^2/\Delta H_L \Delta H_e$ from unity indicate that the analysis is valid. Table III shows a tendency for ΔH_G and ΔH_e to decrease simultaneously with the increase in the heating temperature. This is more clearly illustrated in Fig. 3. This decrease may not be clear between different complex groups at the same temperature, or at the difference of about fifty degrees, but when the temperature is raised from 230°C to 370°C, distinct decreases in ΔH_G and ΔH_e appear.

TABLE III. ANALYSES OF THE ESR LINE SHAPE

No.	ΔH_e	ΔH_G	ΔH_L	$\Delta H_G^2/$ $\Delta H_e \Delta H_L$
T234	13	7.1	3.9	1.0
T254	11	7.3	4.1	1.15
T258	13	7.6	3.6	1.2
Z304	9.0	5.8	4.1	0.91
Z308	7.6	5.0	3.7	0.91
Z354	8.0	5.4	4.5	0.81
F252	12	7.8	5.0	1.01
F256	11	6.8	4.6	0.91
A352	7.6	5.4	4.0	0.96
A353	7.6	5.1	4.1	0.84
A372	6.6	4.5	4.9	0.80
G303	9.4	6.5	5.3	0.85
G322	9.4	6.4	4.8	0.91
G323	8.9	6.1	5.2	0.81

The outstanding decreases of ΔH_G and ΔH_e in the pyrolysis of polyvinyl chloride have been explained as resulting from the increase of C=C conjugated double bonds in the process of dehydrochlorination, together with the formation of aromatic rings between polymer chains.[15] The extension of the conjugated system will bring about a delocalization of electrons and an exchange interaction between unpaired electrons, resulting in a gradual decrease of ΔH_G and ΔH_e. A similar explanation could be applied to polyacetonitrile. A higher heating temperature will bring about not only the extension of the C=N conjugated system, but also a cross-linking between polymer chains, which may decrease ΔH_G and ΔH_e. The cross-linking is expected from the experimental fact that ammonia was detected after polymerization, and from the results of a noncrystalline pattern of X-ray diffraction, infrared spectra, viscometric measurements (Fig. 5), and elementary analyses (Table IV).

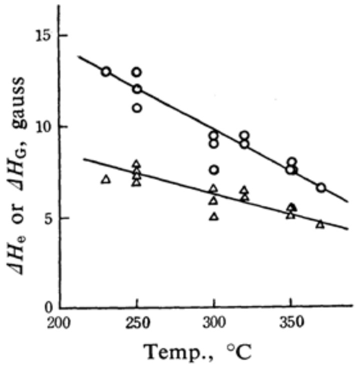


Fig. 3. Correlation of ΔH_e and ΔH_G with heating temperature.
○: ΔH_e, Δ: ΔH_G

Infrared Absorption. — An infrared spectrum of polyacetonitrile is shown in Fig. 4, where the absorption at 2247 cm^{-1} due to the nitrile groups completely disappears and a new strong absorption at 1600 cm^{-1} appears, one which is due to the sequence of C=N bonds, presumably also contributed by C=C double bonds resulting from the separation of ammonia. The existence of C=C double bonds is also supported by the decoloration of a neutral dilute potassium permanganate solution at an ordinary temperature. The oxidation of CH_3 and C=N groups needs more severe conditions. Moreover, a second new absorption, at 840 cm^{-1}, appears; this does not appear in the spectrum of acetonitrile. This absorpition may be due

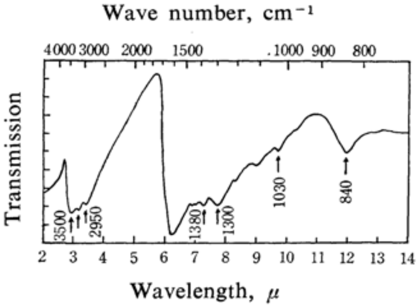


Fig. 4. Infrared spectrum of A304.

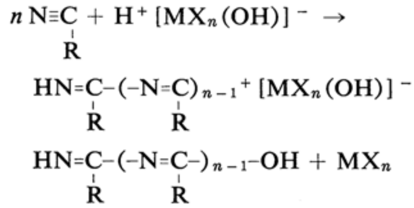
TABLE IV. ANALYSES OF THE POLYMERS

No.	C	H	N	Cl	O	Ash	Total	C/H	C/N
T234	58.3	4.2	21.5	—	10.1	0.3	94.4	14.0	2.7
T238	55.8	4.0	20.2	—	9.4	0.5	89.9	13.9	2.8
T254[a]	56.9	4.6	22.1	0.7	16.9	0.9	102.1	12.5	2.6
T258	58.4	4.4	20.2	—	10.2	1.0	94.2	13.4	2.9
T304[b]	57.3	4.2	18.7	—	10.3	4.2	94.7	13.8	3.1
T308	57.9	4.0	17.1	0.8	—	4.7	84.5	14.3	3.4
Calcd.[c]	58.6	7.3	34.1	0	0	0	100	8.0	1.7

a) Experimental formula: $C_9H_9N_3O_2$
b) Experimental formula: $C_{15}H_{13}N_4O_2$
c) Calculated value for CH_3CN

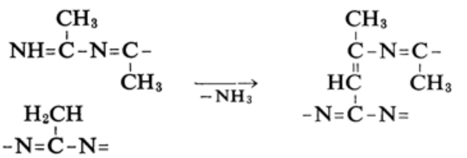
to the C–H in $>C{=}\underset{|}{\overset{}{C}}\!-$ (H), and probably $>N{-}H$. The absorptions at 2950, 1380, 1300 and 1030 cm^{-1} are weak, but they may be assigned to CH_3 groups. The absorptions at 3200 and 3500 cm^{-1} may be due to imine, amine or hydroxyl groups.

It may be reasonable to consider that the metal halide behaves as a cationic reagent with a trace of water and gives rise to cationic polymerization, nearly as in the case of the heating of polyacrylonitrile,[16] as follows:



$$n\,N{\equiv}\underset{R}{C} + H^+[MX_n(OH)]^- \rightarrow$$
$$HN{=}\underset{R}{C}{-}({-}N{=}\underset{R}{C})_{n-1}{}^+[MX_n(OH)]^- \rightarrow$$
$$HN{=}\underset{R}{C}{-}({-}N{=}\underset{R}{C}{-})_{n-1}{-}OH + MX_n \qquad (4)$$

The experimental fact of separation of ammonia may be brought about by pyrolysis when the complex is heated for a longer time; it gives, for example, the following change in the structure of the polymer:



(5)

This change is supported to some extent by the obscure absorptions due to CH_3 groups, and by the electric conductivities, the oxidation test and ESR analyses. It is also supported by the elementary analyses of the polymers given in Table IV.

It should be noted that the polymers of a highly conjugated system find it difficult to combust completely.

The simultaneous decreases in H and N contents corresponding to increases in the C/H and C/N ratios are attributed to the evolution of ammonia. These changes and the considerable oxygen content indicate that polyacetonitrile may consist of not completely conjugated double bonds of carbon-nitrogen, together with other groups containing oxygen. The followings will be most probable means of the introduction of oxygen into the polymer;

(a) The oxidation of the C=C bond which may be formed in the separation of ammonia. This oxidation is predominant in polyacetylenes.[14]

(b) Hydroxyl groups of polymer end as given in Eq. 4. This contribution to the introduction of oxygen will be small.

It can not be concluded from the infrared spectrum whether or not the polymers have carbonyl groups, because the band due to the carbonyl groups will overlap the band due to the C=N bonds.

Viscometric Measurements. — The intrinsic viscosities [η] of the polymers from the titanium terachloride complex versus polymer yields and t^2 (t=heating time, hr.) are shown in Fig. 5. If the polymer consists of a linear chain, then [η] versus t^2, as Kargin et at. indicated,[8] should be linear through the origin. However, the linear line greatly deviates from the origin. This fact and an unusual increase in [η] with the increase in yields support the structual change illustrated in Eq. 5.

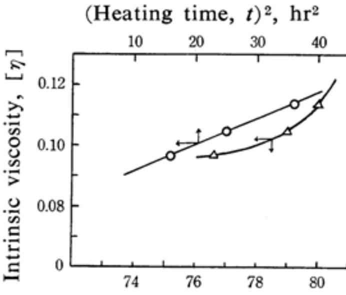


Fig. 5. [η] versus polymer yield.

Summary

The fact that a polymer containing C=N double bonds is formed from saturated nitrile

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[16] W. J. Burlant and J. L. Parsons, *J. Polymer Sci.*, **22**, 249 (1956).

complexes with metal chlorides is supported by the infrared absorption at about 1600 cm^{-1} and the characteristic addition of silver nitrate. The polyacetonitrile has an electric conductivity from 10^{-10} to 10^{-5} Ω^{-1} cm^{-1} and an energy gap from 0.4 to 1.2 eV., indicating that the polymer is an organic semiconductor.

The electric conductivity increases and the energy gap decreases with increases in the heating time and temperature, suggesting a more extensive formation of a conjugated system, including also C=C double bonds among polymer chains at a higher temperature. This theory is supported by the evolution of ammonia, resulting in simultaneous decreases of the H and N contents of the polymer, the appearance of the absorption at 840 cm^{-1}, by oxidation by potassium permanganate, by analyses of ESR line shapes, and by viscometric measurements. This structual change may bring about a noncrystalline pattern in X-ray diffraction. Therefore, it is indicated that polyacetonitrile does not have a complete C=N conjugated sequence because of some pyrolysis, accompanied by the extension of a conjugated sustem such as cross-linking at a higher temperature and a longer heating.

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