Bull. Chem. Soc. Jpn., 58, 1619—1625 (1985)

Effects of Uniaxial Pressure and Shear on the Electrical Conductivity of Solid. II. Electrical Conductivity in Some Amorphous Coordination Polymers[1]

Seiichi KANDA,* Kuwako OHKAWA,† Kenichi YAMASHITA,††
Nobuo ODA,††† and Hideaki CHIHARA☆
Department of Applied Chemistry, Faculty of Engineering, The University of Tokushima, Minamijosanjima, Tokushima 770
☆*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka 560*
(Received April 27, 1984)

Three amorphous coordination polymers, R_2dtoaCu, where R=CH_3, $C_6H_5CH_2$, or cyclohexyl and dtoa= (*N,N'*-disubstituted dithiooxamidato), were prepared and the effect of uniaxial pressure on their electrical resistivities in the direction of the external pressure was measured. Application of the pressure up to 6×10^8 Pa caused an increase in the resistivity but, before reaching the equilibrium state, the resistivity exhibited a complicated time variation, which was not completely reversible upon pressure release as far as the measurement could trace. The results were explained on the basis of a model in which at least two competing processes occur. One of the processes is assumed to be reorientation of the two-dimensional network of molecules perpendicular to the applied pressure, which is a slow process and takes as long as hundreds of hours to reach the equilibrium. Activation energies of various processes were derived.

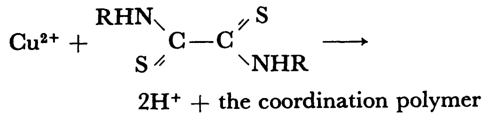
The three coordination polymers (R_2dtoaCu; R= CH_3, $C_6H_5CH_2$, and *cyclo*-C_6H_{11}) treated in this study are representatives of several *catena*-*μ*- (*N,N'*-disubstituted dithiooxamidato)-copper(II) coordination polymers, the resistivities of which range from 10^5 to 10^{10} Ωcm at 30°C.[2] Although the technique of X-ray structural analysis[4] is not applicable due to the amorphous structures, a two-dimensional network structure has been proposed on the basis of some evidence.[3] An example of such a network model (Fig. 1) will be discussed later.

While numerous studies have been reported on the electrical properties of semiconductive polymers, there have been a few that dealt with the effect of pressure on the electrical properties, *e.g.* resistivity,[5–8] dielectric constant,[5] activation energy for conduction,[6] electronic mobility,[7] and superconducting transition;[8] there have been no studies on the kinetic aspect of the pressure effect. Generally, the electrical resistivity of powder samples has been measured on compressed pellets or under pressure.[9] The resistivity of semiconductive organic crystals usually decreases reversibly by several orders of magnitude with an increase of pressure up to 10^{10} Pa. Beyond 10^{10} Pa, irreversible chemical changes occur in some compounds, which result in irreversible changes in their resistivity.[10] One exception was reported in the case of poly(phenylacetylene), where a large reversible increase in resistivity upon increasing the pressure was attributed to a large positive volume of activation.[11]

In contrast to these cases, application of a uniaxial pressure less than 10^9 Pa on R_2dtoaCu coordination polymers results in an increase in resistivity and complicated hysteresis.[1] Enhancement of this tendency with an application of shear stress substantiates the idea that the anomaly is attributed to the anisotropic structure of the macromolecule and its response to an external pressure.[12] In the last report[1] a semiquantitative study was presented on the hysteresis effect in the resistivity-pressure-temperature relationship. A model was then proposed which assumes molecular motions that depend on the temperature, the pressure, and the history of treatment. In this paper the phenomenon will be more quantitatively examined from standpoints of rate process and equilibrium properties.

Experimental

Materials. *N,N'*-dimethyldithiooxamide ((CH_3)$_2$dtoa-H_2), *N,N'*-dibenzyldithiooxamide (($C_6H_5CH_2$)$_2$dtoaH_2), and *N,N'*-dicyclohexyldithiooxamide ((C_6H_{11})$_2$dtoaH_2), were kindly donated by Mallinckrodt Chemical Works, and were recrystallized from ethanol. The copper coordination polymers were prepared by mixing an aqueous solution of copper sulfate and a water-ethanol solution of the equivalent amounts of the ligands according to the reaction of the type:



The structural model of the polymers is depicted in the Fig. 1. The amorphous precipitates were centrifuged and washed repeatedly with water and ethanol, successively.

Analyses of the Three Coordination Polymers. (CH_3)$_2$dtoa-Cu, Found: H, 2.83; C, 20.72; N, 11.22; Cu, 29.22%. Calcd for $C_4H_6N_2S_2Cu$: H, 2.89; C, 22.90; N, 13.35; Cu, 30.29%. ($C_6H_5CH_2$)$_2$dtoaCu, Found: H, 3.97; C, 53.27; N, 7.60; Cu, 16.70%. Calcd for $C_{16}H_{14}N_2S_2Cu$: H, 3.90; C, 53.10; N, 7.74; Cu, 17.47%. (C_6H_{11})$_2$dtoaCu, Found: H, 6.54; C, 48.4; N, 7.97; Cu, 18.41%. Calcd for $C_{14}H_{22}N_2S_2Cu$: H, 6.40; C, 48.6; N, 8.10; Cu, 18.36%. The slightly low values of nitrogen are frequently observed in coordination polymers containing copper(II) directly coordinated by nitrogen.[13] The atomic ratios of the elements in the polymers were calculated from the analytical values by fixing the number of carbon atoms at the limiting value for infinite degree of polymerization.

---

† Present address: Training Institute for Environmental pollution Control, 3-3 Namiki, Tokorozawa, Saitama 359.

†† Present address: Osaka Titanium Co., Ltd., Amagasaki, Hyogo 660.

††† Present address: Matsumura Oil Research Corp., Ashihara-cho, Nishinomiya, Hyogo 662.

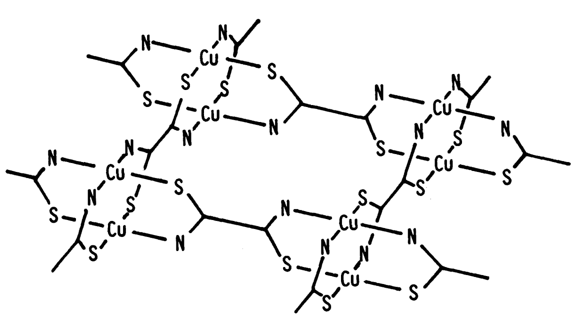


Fig. 1. The non-stereospecific two-dimensional network model with dimer structure of copper acetate type. For simplicity, substituents on nitrogen atoms are not shown.

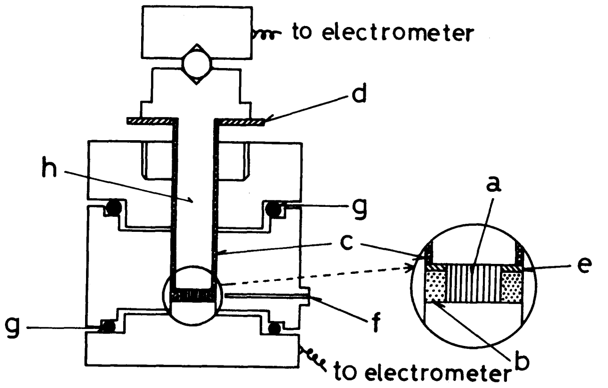


Fig. 2. High pressure cell remodeled from a pellet press.
a): Pellet of sample, b): pyrophyllite gasket, c): Teflon film for electrical insulation, d): polyethylene sheet, e): Teflon sheet, f): re-entrant well for thermocouple, g): O-ring for sealing, h): piston serving both as an electrode and a pressure transducer.

The reasonable agreements between the calculated and observed atomic ratios show that the polymers obtained have nearly stoichiometric composition, $(\mathrm{RNSC})_2\mathrm{Cu}^{\mathrm{II}}$. In fact, the polymers assume a two-dimensional network structure in which some vacancies of Cu sites are, in principle, possible. If it occurs, electroneutrality requires two additional hydrogen atoms to replace a copper atom. This is reflected in the low values of copper and the correspondingly high values of hydrogen in the elemental analyses.

Electrical Measurements. As a high pressure cell for the resistivity measurements, a pellet press was used with a steel piston having a diameter of 11.5 mm. The piston was used as an electrode with insulating Teflon film (0.2 mm thick) around it as shown in Fig. 2. By use of an oil pump and the above-mentioned cell, a maximum pressure of 9.0×10^8 Pa can be applied to the specimen. The temperature was controlled by a ribbon heater wound around the outside can, which is not shown in Fig. 2. A thermocouple for temperature measurements was inserted into the re-entrant well at the lower end. The vessel was not evacuated, but was sealed from the atmosphere with O-rings. The powder specimen was first premolded in 5 mm diameter at 1.8×10^8 Pa; the small pellet was mounted at the center of a pyrophyllite gasket which had been pretreated at 700 °C for 30 min; the assembly shown in Fig. 2 with a piece of thin Teflon ring, was pressed.

Electrical data under pressure were taken *in situ* a few minutes after the electrical field was applied. The electrical resistance was measured by means of a valve voltmeter with an applied electric field of 15 V cm^{-1}. The pellet assembly was replaced for each run at one temperature, which usually took as long as several hundred hours because of the long equilibration time under applied pressure. When, however, we measured the temperature dependence of the equilibrium resistivity values as shown later in Figs. 8 and 9, a single loading of the specimen was used. The effects of pressure were examined by using a uniaxial pressure of 6.0×10^8 Pa throughout this study. The same pressure value was used for determining the resistivity values of the specimens of the pellet form, which was applied only instantaneously and intermittently during the runs in which relaxation after pressure release was studied. Such instantaneous application of pressure would not affect the long-time response of the specimen. For the polymers under investigation there is a fast process which occurs upon compression or pressure release and which is followed by a very slow process as we will discuss in detail.

Results and Discussion

The Rate Process under a Uniaxial Pressure (6.0×10^8 Pa). Changes in the resistivity of $(\mathrm{CH_3})_2$dtoaCu, $(\mathrm{C_6H_5CH_2})_2$dtoaCu, and $(\mathrm{C_6H_{11}})_2$dtoaCu under a constant external pressure as the function of time are shown in Figs. 3, 4, and 5. The resistivities begin to change immediately after the external pressure was applied or released. These changes occur in a very short time and were not traced. However, such an initial stage of change was followed by a very gradual drift of the resistivity values extending up to several hundred hours. It is such a long-time behavior that we are interested in. In Figs. 3—5, $\rho_0^\pm$ is the initial resistivity value determined immediately after the fast process has been completed, the superscript ± meaning the compression or the pressure release operation.

The general feature of the time dependence as exemplified in Fig. 3a is that it is a kind of relaxation phenomenon. Ordinarily, such a relaxation process is characterized by a time constant which governs the first order rate process. In other words, the rate of change of resistivity, $\mathrm{d}\rho^\pm/\mathrm{d}t$, can be described by

$$\mathrm{d}\rho^\pm/\mathrm{d}t = -k^\pm(P, T)(\rho^\pm - \rho_{\mathrm{eq}}^\pm) \qquad (1)$$

Here, $\rho_{\mathrm{eq}}^\pm$ is the asymptotic (equilibrium) value of the resistivity, k is the rate constant and equal to the reciprocal of the relaxation time.

The experimental values of resistivity were fitted to Eq. 1 in the integrated form and it was found that the equations can reproduce the observed results in certain ranges of time. The values of k thus derived are listed in Table 1 together with the activation energies derived from the Arrhenius equation

$$k^\pm = k_0^\pm \exp(-\Delta H_\pm^\ddagger/RT). \qquad (2)$$

The plots of $k^\pm$ *vs.* T^{-1} are shown in Fig. 6.

The results of Figs. 3a and 3b fit Eq. 1 over the almost

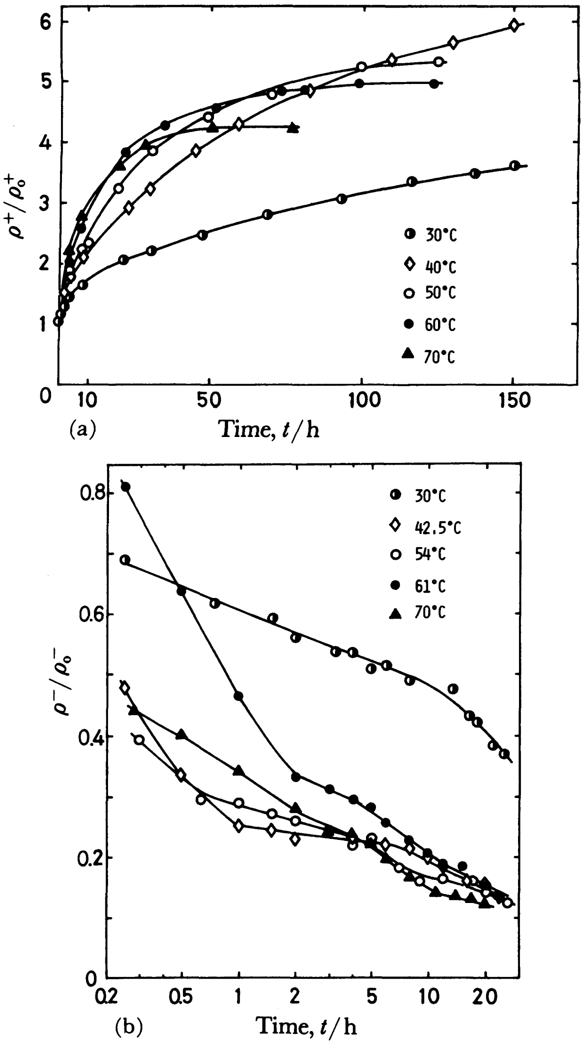


Fig. 3. Resistivity changes of $(CH_3)_2$dtoaCu.
a): Under uniaxial pressure, b): under ambient pressure after the operation of a).
For definition of ρ_0, see in the text.

entire range of time, whereas for the dibenzyl complex (Fig. 4b) and the dicyclohexyl complex (Fig. 5a), Eq. 1 can be applied only in the ranges in which dρ/dt<0 in Fig. 4b and dρ/dt>0 in Fig. 5a.

As shown by the insert of Fig. 4a, the resistivity of the dibenzyl complex does not show a monotonous change but has a small plateau. In the case of the dicyclohexyl complex (Fig. 5a), the initial change of the resistivity is opposite to the cases of the other two polymers, *i.e.* the resistivity decreases with time under a constant external pressure. After this initial process, the behavior (after 10 h. at 110°C) can be described by Eq. 1.

These additional features for which Eq. 1 does not apply strongly suggest that the time dependence of the resistivities, or the relaxation process, is not a simple process but there must be two or more mechanisms having different rate constants (or relaxation times) that proceed competitively.

A Structural Model. Application of uniaxial pressure usually decreases the resistivity of polycrystalline semiconductors parallel to the external stress. It is interpreted as due to improved contact between grains and decreased intermolecular distances. All the three substances examined in the present study, on the contrary, showed an increase in the resistivity under uniaxial pressure. However, the conditions of time and/or temperature were different from substance to substance, under which such an anomalous behavior was observed. This means that there must be some special cause that operates in these substances and opposes the ordinary compaction effects mentioned above. The special cause, which we will try to identify, will give rise to a complex overall behavior as seen in Fig. 5a in the case of the cyclohexyl complex.

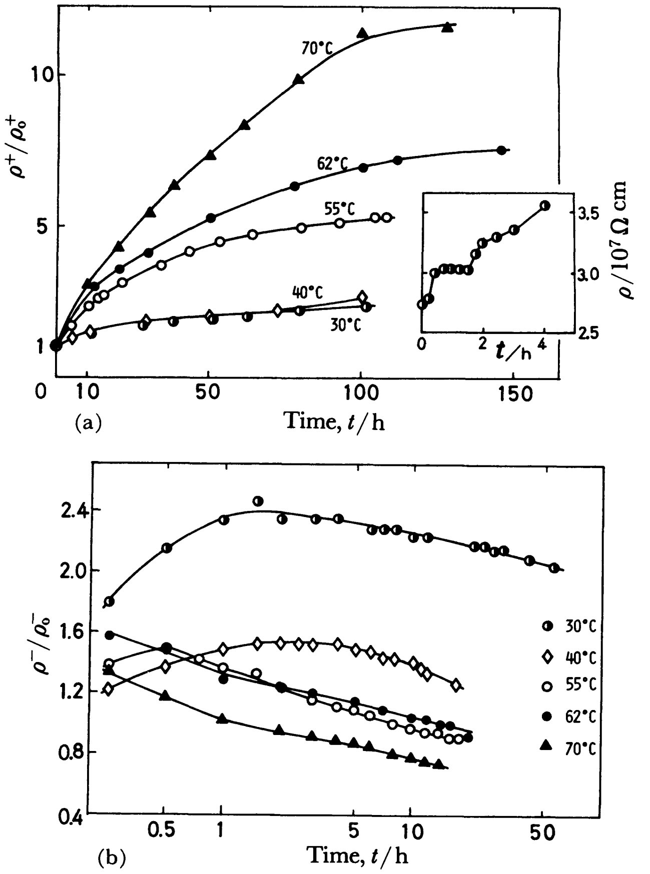


Fig. 4. Resistivity changes of $(C_6H_5CH_2)_2$dtoaCu.
a): Under uniaxial pressure, b): under ambient pressure after the operation of a).

Similarly, the release of the uniaxial pressure results in a decrease in the resistivity although here again there are differences in the overall behavior among the coordination polymers.

In order to find a mechanism by which such anomalous pressure dependence occurs, let us first consider about the structure of these polymers. The model of Fig. 1 is based on some evidence obtained from the composition, the X-ray diffraction pattern, and the magnetic data.[3] In this model, the polymer complex forms a two-dimensional network with the substituent, methyl, benzyl, or cyclohexyl group, attached at every N atom. The substituents will therefore protrude above and below the network plane but it is not easy to

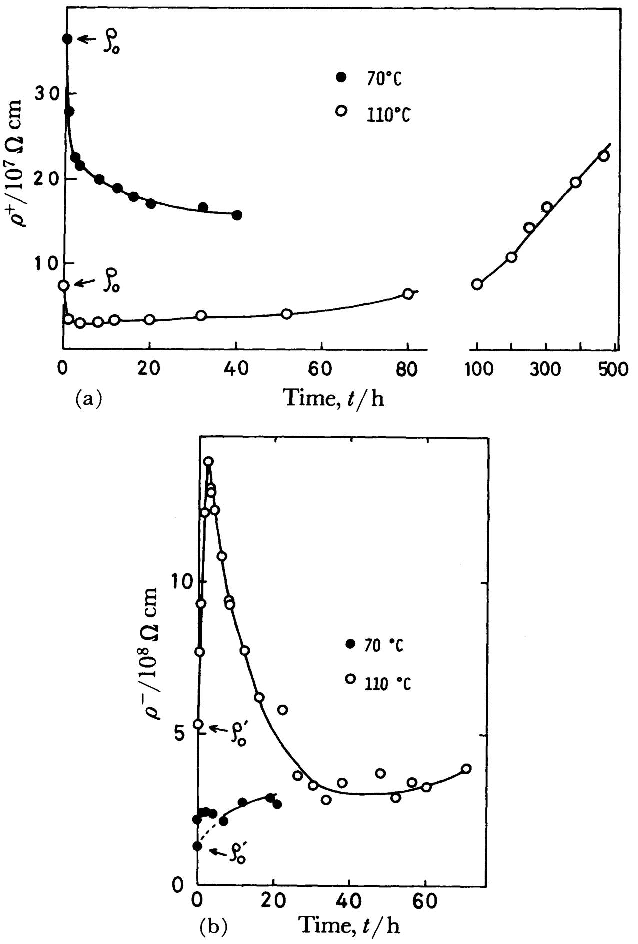


Fig. 5. Resistivity change of $(C_6H_{11})_2$dtoaCu. a): Under uniaxial pressure, b): under ambient pressure after the operation of a).

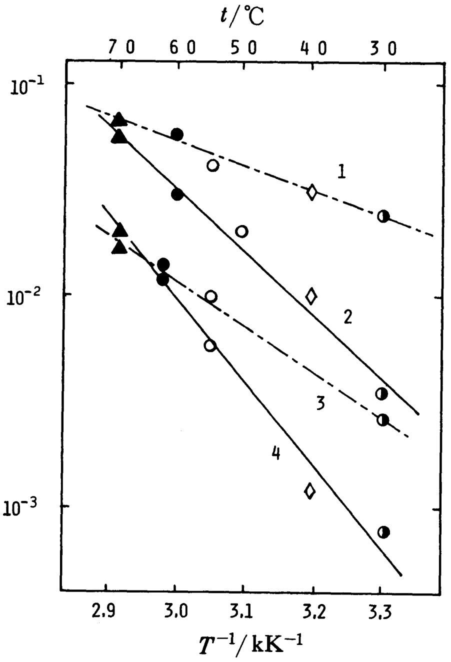


Fig. 6. Arrehnius plots of the rate constants for R_2dtoaCu.
(1): CH_3, $k^-(P=0)$, (2): CH_3, $k^+(P=6.0\times10^8$ Pa), (3): $C_6H_5CH_2$, $k^-(P=0)$, (4): $C_6H_5CH_2$, $k^+(P=6.0\times10^8$ Pa).

speculate about the conformation of the substituents. It is interesting in this connection to note that the measured bulk densities of the complexes under ordinary pressures were 1.55, 1.659, 1.76 g cm^{-3} for the methyl, benzyl, and cyclohexyl complexes, respectively; *i.e.* the methyl complex has the largest void space fraction and the cyclohexyl complex the smallest. In other words, the bulky substituents may lie more or less flat in parallel to the network plane. The electronic conduction will be very anisotropic because the electrons are likely to be delocalized whithin a network plane and only van der Waals interaction exists between the planes.

Now, the plausible explanation for the anomalous positive pressure coefficient of the electrical resistivity seems to be that there occurs some rearrangement of molecules as a result of compression. The increase in the resistivity in the direction of applied pressure will mean an increased contribution of the resistivity component perpendicular to the molecular plane. The polymer specimens as prepared have little preferred orientation but, as the uniaxial pressure is applied, the molecular plane will be gradually reoriented so that the plane tends to become perpendicular to the stress, thus increasing the resistivity in the direction of the stress. Such reorientation effect will, of course, be accompanied by deformation of grains. In quite general terms, the uniaxial stress causes randomly oriented molecular planes to be more or less ordered.

Change of Resistance with Time–An Interpretation. It should be noted that the pressure effects are not completely reversible. After a cycle of compression and pressure release, the resistivity does not completely return to its original value. This indicates that there are plastic parts in the deformation as well as elastic parts. Furthermore, if one compares Fig. 4a with Fig. 4b, the benzyl complex shows a smooth change of the resistivity upon compression, but, when the pressure is released, it shows a maximum in the resistance below 55 °C. Therefore, there are at least two competitive processes which give rise to a maximum in the resistivity; one is faster than the other. The faster process is not seen at or above 62 °C in Fig. 4b because the process becomes too rapid at higher temperature in the case of the benzyl complex. The fast process is the process by which the resistivity increases upon pressure release; this is the normal behavior in semiconductors and will be called the process N hereafter. The second process will be called the process A which shows an anomalous effect of decreasing resistivity upon pressure release (we assume that the processes N and A occur upon compression as well as upon pressure release).

The case of the cyclohexyl complex may be interpreted in an analogous way. Upon pressure release (Fig. 5b), there is a maximum in the resistivity which is seen at 110 °C. It is again the competitive effect of the processes N and A, only the process N being observed at 70 °C in a short time (less than 20 h). Upon

Table 1. Parameters for the rate processes upon compression and release

Under uniaxial pressure of 6.0×10^8 Pa

$(CH_3)_2$dtoaCu			$(C_6H_5CH_2)_2$dtoaCu			$(C_6H_{11})_2$dtoaCu	
t	k^+	$\Delta H^{\ddagger}_{+}$	t	k^+	$\Delta H^{\ddagger}_{+}$	t	k^+
°C	10^{-3} h^{-1}	kJ mol^{-1}	°C	10^{-3} h^{-1}	kJ mol^{-1}	°C	10^{-4} h^{-1}
30	3.5		30	0.7		90	3.6
40	10.1		40	1.2		110	3.8
50	20	57.2	55	5.6	75.5	(time>10 h)	
60	$30._8$	±3.2	62	12	±3.6		
70	55		70	20			

Under ambient pressure

t	k^-	$\Delta H^{\ddagger}_{-}$	t	k^-	$\Delta H^{\ddagger}_{-}$	t	k^-
°C	10^{-2} h^{-1}	kJ mol^{-1}	°C	10^{-2} h^{-1}	kJ mol^{-1}	°C	10^{-3} h^{-1}
30	2.4		30	0.2_7		110	$11._8$
$42._5$	3.0		40	$1.4^{a)}$		(20>time>4 h)	
54	4.1	23.0	55	1.0	40.8		
61	5.8	±1.7	62	1.4	±1.6		
70	6.6		70	1.7			

a) Omitted for the calculation of $\Delta H^{\ddagger}_{-}$.

compression (Fig. 5a), only the process N is seen in a short time particularly at a lower temperature. For this complex, the change of the resistivity was measured to 500 h (Fig. 5a) and the process A is seen to proceed slowly.

The case of the methyl complex looks simple, but it is probably because the process N finishes in a very short time. With regard to the process A, the value of $k^{\pm}$ (Table 1) is generally much larger for the methyl complex than for the other two complexes. This suggests a quicker response of the methyl complex with regard to the process N. The rate of the two processes depends strongly on temperature; at lower temperatures the process N can be so slow (as slow as the process A) that the two processes are not separable, causing a maximum in the resistivity to appear at a certain time as in the case of the dibenzyl and the dicyclohexyl complexes.

To rationalize the relationship between experimental observations on the processes N and A and the usual dynamics of the viscoelastic body, let us consider the Voigt model.[14)]

Strain γ of polymer solids due to an external load is analyzed by use of a spring for elasticity and a dash-pot for plasticity. The two elements, the spring and the dash-pot, can be combined in parallel to build the Voigt element, which represents anelasticity *i.e.* time-dependent elastic deformation. The three macroscopic deformations (elastic, plastic and relaxationally elastic), γ_e, γ_p, and γ_r, are expressed schematically as a function of time in Fig. 7a. The elastic after-effect of anelasticity is given by

$$\gamma_r = \gamma_\infty[1 - \exp(-t/\tau)]. \qquad (3)$$

The reciprocal of the relaxation time τ corresponds to $k^{\pm}$ in Eq. 1. The change in time of the resistivity of the three coordination polymers, $\Delta\rho$, generally have components, $(\Delta\rho)_e$, $(\Delta\rho)_p$, and $(\Delta\rho)_r$, in a manner similar to the case of the macroscopic deformation. While the sign of all the components of γ is the same, the sign of the $(\Delta\rho)_e$ is opposite to the sign of $(\Delta\rho)_r$ or $(\Delta\rho)_p$ in the compound studied (Fig. 7b). Typical examples of combination of these components are shown in Fig. 7c. It should be noticed that the apparent τ's (*i.e.* $1/k$) can be different during the compression and during release because of the relaxational components in the Voigt model.

If we associate the $(\Delta\rho)_e$ components mainly with the process N and $(\Delta\rho)_r$ and $(\Delta\rho)_p$ mainly with the process A, we obtain good correspondence between the behavior of the Voigt model and the time-dependence of the resistivities. Thus the elastic portion or the process N has a very fast response to external stimulations, whereas the process A is slower and causes an apparent hysteresis even if the molecular processes involved are the same upon compression and upon release.

What happens when the specimen is compressed will be viewed in the following way. The initial process will be deformation or collapse of grains to fill the void space between the grains (improved contact between grains), which is followed by a simple compression (time-dependent elastic deformation) which changes the intermolecular distances. This corresponds to the process N. The instantaneous elastic deformation will bring the molecular arrangement into an energetically unstable configuration which will then be relaxed by the time dependent elastic process and by the slow plastic deformation process (the process A). If we pursue our picture a little further, this relaxation will occur in such a way as to reorient the network planes so that the planes will become perpendicular to the direction of the stress. As the molecular arrangement is gradually relaxed, further elastic deformation will become possible at successively new molecular configuration and such secondary elastic deformation

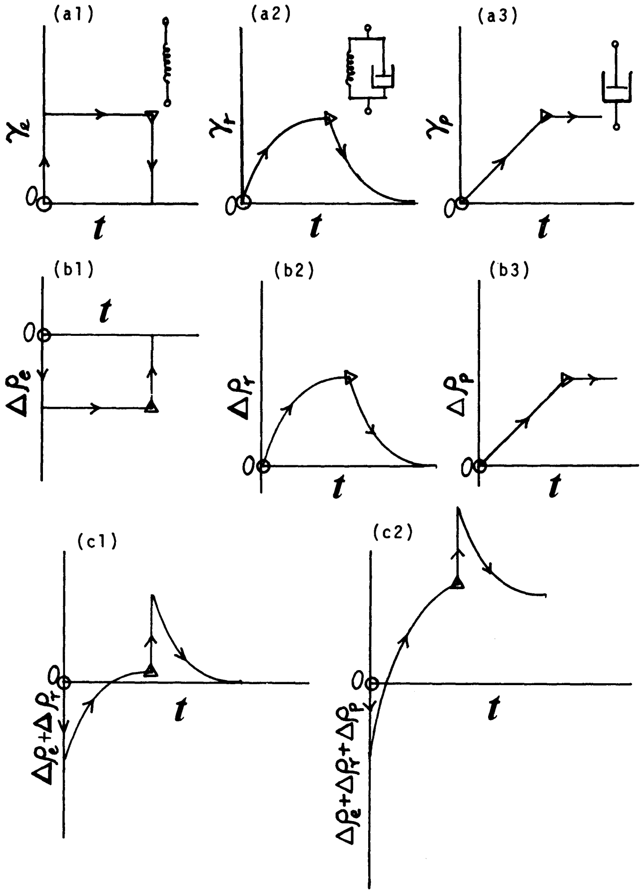


Fig. 7. Schematic representation of time evolution of the strain γ, and the electrical resistivity $\Delta\rho$ for elastic, Voigt, and plastic models: a1—a3 for the three models of γ respectively, b1—b3 for the three models of $\Delta\rho$, c1—c2 for combinations of the models of $\Delta\rho$.
See in the text.
O: Starting-point of stress application, ▷: starting-point of stress release.

will cause further relaxation due to plastic deformation. Therefore, the elastic and plastic processes mutually affect each other and so do the processes N and A. The values of $k^{\pm}$ in Table 1, in this vein, should be considered to correspond not to a well-defined single process but to a composite process.

Activation Energies for The Mechanical Process. From the plots of Fig. 6, the apparent activation energies of the relaxation process (the process A) were derived for the methyl and benzyl complexes as listed in Table 1. In both substances, the activation energy is larger upon compression than upon pressure release. The differences between the values for the two directions are almost the same in the two substances, 34 kJ mol^{-1} (57.2—23.0) and 35 kJ mol^{-1} (75.5—40.8) for the methyl and the benzyl complex, respectively. If the same activated state can be assumed in the two directions, the equality shows that the difference in energy between the initial state (random molecular arrangement) and the final state (oriented molecular arrangement) does not depend on whether the substituent is methyl or benzyl; the difference between the two substances lies in the height of the potential barrier hindering the relaxation.

Temperature Dependence of Equilibrium Resistivity. Because the long-time behavior was an extremely slow process, it was not easy to obtain the reliable equilibrium values of resistivity $\rho_{\rm eq}^{\pm}(P,T)$ at a given temperature. The criterion for equilibrium and the method for determining the equilibrium values were as follows: (1) An attempt was first made to wait until a steady value was obtained under a constant external pressure at a temperature. (2) The temperature was then lowered under the same pressure and the specimen was brought to a state of equilibrium at that temperature. After a certain length of time, usually a few hours, the specimen was heated back to the original temperature where the resistivity approached the equilibrium value from the opposite side to the case (1). If the final value agreed with the value obtained in (1), it was taken as the equilibrium value. If it did not, the average value was adopted. This procedure was employed only at 70 °C.

Figures 8 and 9 will illustrate such sequence of changes. In Fig. 8, the point on the line 1 corresponds to the equilibrium state at the ambient pressure, which we call the random state. Suppose that the specimen (the dimethyl complex) which had been brought to equilibrium at 70 °C under the ambient pressure was pressed for 77 h; the final steady value was assumed to be the equilibrium state. The specimen was then cooled under pressure to a lower temperature where a new equilibrium was waited. Such a cooling was done usually in a short time and the change in the resistivity that occurred in this time is indicated by the broken lines in Figs. 8 and 9. After the equilibrium at 40 °C was obtained for the dimethyl complex (Fig. 8), it was heated back to 70 °C. This heating was done also in a short time and the change in resistivity followed the broken line. At 70 °C, the equilibrium state was approached from the opposite side this time, as explained in (2). Figure 9 shows similar results for the dibenzyl complex. It is interesting to note that the broken lines are more nearly parallel to the line 1 in Figs. 8 and 9 in comparison with the line 2 which connects the equilibrium values under pressure and has a larger slope than the line 1.

Now let us examine the activation energy for electronic conduction in the same direction as that of the external stress as obtained from Figs. 8 and 9. Under no uniaxial stress it was 0.34 eV (33 kJ mol^{-1}) and 0.29 eV (28 kJ mol^{-1}) for the methyl and benzyl complex, respectively. Under the stress of 6.0×10^{8} Pa, the values are 0.45 eV (44 kJ mol^{-1}) and 0.43 eV (41 kJ mol^{-1}) corresponding to the state of oriented molecular arrangement. On the other hand, the non-equilibrium resistivity under the pressure gave the same activation energy as the equilibrium resistivity at the ambient pressure (dashed line and line 1 of Fig. 8). This fact

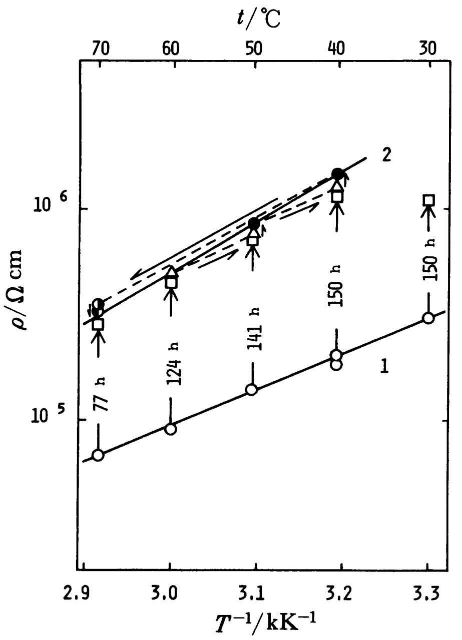


Fig. 8. Resistivity-temperature relation in the transient and the equilibrium states of $(CH_3)_2$dtoaCu. 1 and ○ correspond to the initial random state; 2 and ● the oriented equilibrium state, △ is the cooled state where a new equilibrium state ● is waited, ◑ is the heated-back state where the equilibrium is approached through ◐. □ is the values after the indicated elapse of time. See in the text.

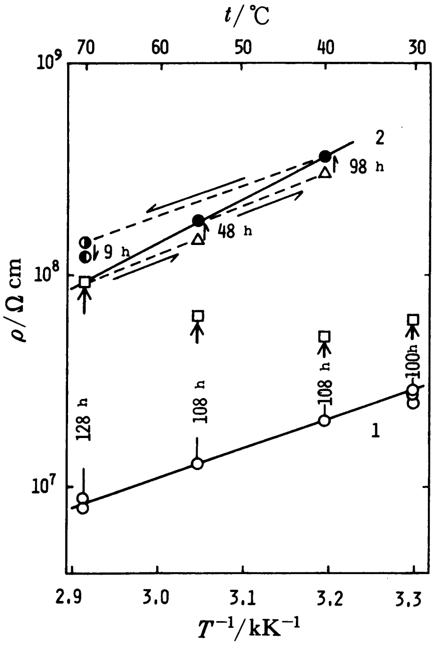


Fig. 9. Resistivity-temperature relation in the transient and the equilibrium states of $(C_6H_5CH_2)_2$dtoaCu. △, ●, ◑, ◐, and □ are essentially the same as in Fig. 8.

justifies our interpretation that the initial process that occurs when the specimen is compressed is the process N involving the improved contact between grains and the elastic deformation. The process A which follows brings the specimens to a state (the oriented state corresponding to the line 2) which requires higher activation energy of conduction (0.45 eV and 0.43 eV). The fact that the difference in the activation energy with or without the external stress is small indicates that reorientation of network planes is not complete under the stress of 6.0×10^8 Pa; the solid would become almost an insulator if the molecular reorientation were complete. Nevertheless the activation energy does increase rather than decrease upon compression and such an effect is also consistent with our picture about the nature of the process A by which the resistivity component increases in the direction perpendicular to the network plane.

Finally, it is very interesting to note that despite the close similarity in the response to uniaxial stress, the methyl and the benzyl complexes show very different equilibrium resistivity values, by a factor of about 10^2 both in the random and the oriented state. The methyl and benzyl complexes have very similar activation energy in their oriented state. Bulkiness and steric hindrance of the substituents are probably related to such a large difference in the resistivity through the deformation of the network structure.

The authors wish to express their thanks to Mr. Satoru Morinishi and Mr. Hideo Minami for their assistance in the measurment and the instrumentation. The present work was partially supported by Grant-in-Aid for Scientific Research No. 754123 from the Ministry of Education, Science and Culture.

References

1) Part I of this study was published in S. Kanda, *Kogyo Kagaku Zasshi*, **71**, 1426 (1968); Part of this study was presented at the 14th High Pressure Conference of Japan, Osaka, October 1972, Abstr., No. 23A12, and at the 29th National Meeting of the Chemical Society of Japan, Hiroshima, October 1973, Abstr., No. 4S09.

2) S. Kanda, *Nippon Kagaku Zasshi*, **83**, 560 (1962).

3) S. Kanda, A. Suzuki, and K. Ohkawa, *Ind. Eng. Chem., Prod. Res. Dev.*, **12**, 88 (1973).

4) R. Hasegawa, Y. Tanabe, M. Kobayashi, and H. Tadokoro, *J. Polym. Sci., A-2*, **8**, 1073 (1970).

5) V. A. Zhorin, S. I. Beshenko, Yu. A. Berlin, and N. S. Enikolopyan, *J. Appl. Polym. Sci.*, **28**. 2467 (1983).

6) J. P. Crine, *Phys. Status Solidi A*, **72**, 789 (1982).

7) H. A. Phol and J. R. Wyhof, *J. Polym. Sci., A1*, **10**, 387 (1972).

8) K. J. Dunn, F. P. Bundy, and L. V. Interrante, *Condens. Matter*, **23**, 106 (1981).

9) One of the earliest examples: H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **28**, 570 (1955).

10) W. H. Bentley and H. G. Drickamer, *J. Chem. Phys.*, **42**, 1573 (1965).

11) G. M. Holob and P. Ehrlich, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 627 (1977).

12) H. A. Pohl and D. A. Opp, *J. Phys. Chem.*, **66**, 2121 (1962).

13) S. Kanda, K. Yamashita, and K. Ohkawa, *Bull. Chem. Soc. Jpn.*, **52**, 3296 (1979).

14) T. Alfrey, "Mechanical Behavior of High Polymers," Interscience, N. Y. (1948).