Electrical Properties of Diphenyldiacetylene Annealed under Elevated Pressure

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SYNOPSIS

A unique class of conjugated compounds composed of the derivative of condensed polycyclic aromatic compound with the phenyl group and diphenyldiacetylene oligomer was synthesized by annealing of diphenyldiacetylene under elevated pressure. The effect of annealing pressure on the conductivity of the compounds was studied. The total conductivity of the compound decreased with a decrease of frequency, approaching a constant value (dc conductivity: C_{dc}). The dc conductivity of the compound increased from below 10^{-15} to 10 S cm^{-1} with increasing annealing pressure. The dc conductivity of the oligomer was below 10^{-15} S cm^{-1} and that of the derivative increased from 10^{-8} to 10 S cm^{-1} with decreasing H/C (H/C: 0.45–0.04). The conduction of the conjugated compound was electronic. The temperature coefficient of those dc conductivities was positive, with an approximately linear relation between $\ln(C_{dc}T^{0.5})$ and $(1/T)^{0.25}$, where T is the temperature. The ac conductivities C_{ac} were proportional to temperature and frequency f and had the following equation $C_{ac} = Tf^S$, $S = 0.67$–0.75. These results showed that the conduction mechanism can be explained by the hopping in a manifold of states at the Fermi level. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polydiacetylenes are conjugated polymers and can be obtained by the solid-state topochemical polymerization of substituted diacetylenes.[1] Polydiacetylenes are obtained in the solid state by heating or high-energy radiation and have attracted much attention as electrical and nonlinear optical materials.[2-4] In a previous article,[5] a conjugated compound composed of the derivative of a condensed polycyclic aromatic compound with a phenyl group and a diphenyldiacetylene oligomer was synthesized by annealing of diphenyldiacetylene under elevated pressure. The pressure decreased the H/C of the compound and the fraction of the oligomer.

The electrical conductivity of graphite and carbon black is attributed to their molecular structure of the aromatic compound, which is made of network plane of the conjugated double bonds of carbon atoms with π-electrons.[6] It is well known that the electrical conductivity of the aromatic compound increases with an increase of molecular size because of decreasing H/C.[7,8]

It is expected that the conductivity of the annealed diphenyldiacetylene under elevated pressure (pressure-annealed diphenyldiacetylene) increases with pressure. In this article, the objective was to study the annealing pressure dependence of the conductivity of the pressure-annealed diphenyldiacetylene.

EXPERIMENTAL

Commercially available diphenyldiacetylene (molecular weight: 202, Wako Pure Chemical Industries) was used for the reaction without further purification. The reaction of diphenyldiacetylene under pressures of 0.1–500 MPa was carried out using a piston and cylinder apparatus at a temperature of 210°C.[5] The electrical properties of the pressure-annealed diphenyldiacetylene were measured by two methods because they were widely varied with the annealing pressure. The DuPont Instruments Di-

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Journal of Applied Polymer Science, Vol. 54, 1567–1573 (1994)
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electric Analyzer (DEA 2970) was used for the low-pressure-annealed diphenyldiacetylene in 0.1–3.1 MPa. The measurements were carried out in the temperature range from room temperature to 200°C at a heating rate of 10°C/min. Specimens in powder form were used for measurement of electrical properties. After the powdered specimen was compressed between the single-surface module and sensor (pressure: 1.72 MPa), a sinusoidal voltage was applied to the specimen, creating an alternating electric field. The produced polarization in the specimen oscillated at the same frequency as did the electric field but had a phase angle shift, δ. This phase-angle shift was obtained by comparing the applied voltage, V, with the measured current, I. The conductivity, C (S/cm), was obtained by the following relationship:

$$C = I/V \cos \delta \tag{1}$$

The pressure-annealed diphenyldiacetylene in an annealing pressure of 50–500 MPa was placed between electrodes and compressed to 1.5 MPa with a hydraulic press. The conductivity of the specimen was measured with a digital multimeter (SOAR Co.).

An infrared spectrophotometer (Japan Electron Optics Laboratory, JEOL, Model JIR-100) was used for infrared (IR) studies in the wavenumber from 4000 to 1800 cm^{-1}. Specimens in powder form were mixed with KBr (0.5 mg of specimen with 200 mg of KBr) and were formed into tablets by applying pressure. The transmittance of the IR spectrum in the absence of the absorption band was identified as the energy gap of the specimen.[9]

RESULTS AND DISCUSSION

Figure 1 shows a typical evolution of the total conductivity of the low-pressure-annealed diphenyldiacetylene in 0.1–3.1 MPa vs. frequency at 25°C. The conductivity decreases with a decrease of frequency, approaching a constant value. The conductivity is independent of the annealing pressure above 2.0 MPa. The conductivity, $C(f)$ (S/cm), is divided into a frequency f (Hz)-independent contribution and a frequency-dependent conductivity[10]:

$$C(f) = C_{dc} + C_{ac}(f) \tag{2}$$

where C_{dc} and C_{ac} are the dc conductivity and the ac conductivity, respectively. The dc conductivity increases with increase in the annealing pressure. The dc conductivity was 1–10 S cm^{-1} at a relatively high annealing pressure of 50–500 MPa. The annealing pressure dependence of the dc conductivity for the pressure-annealed diphenyldiacetylene is given in Figure 2. We find that the dc conductivity is varied in the range of below 10^{-15} to 10 S cm^{-1} through the annealing pressure.

In a previous article,[5] it was indicated that the pressure-annealed diphenyldiacetylene was a con-

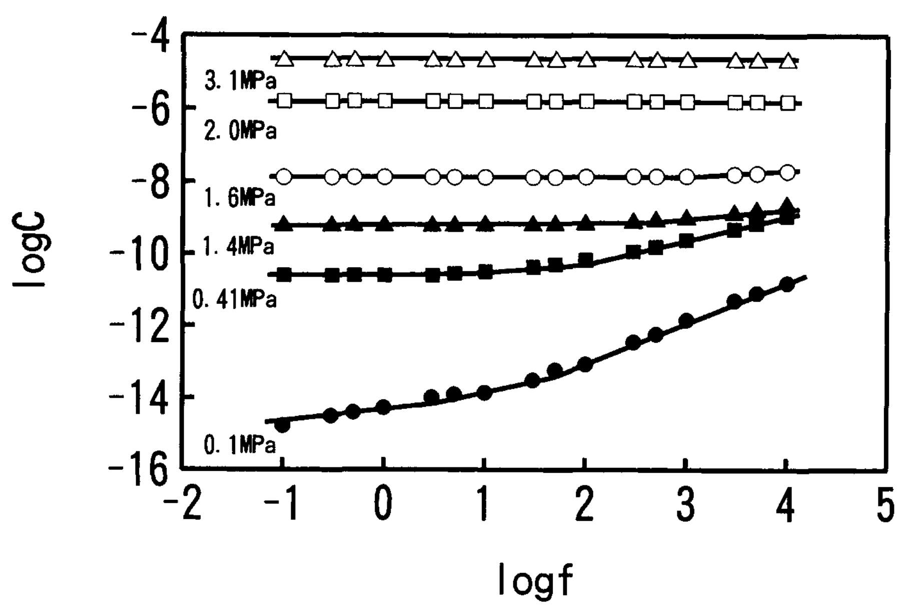

Figure 1 Plot of the log of total conductivity vs. the log of the frequency at 25°C (annealing pressure: 0.1–3.1 MPa).

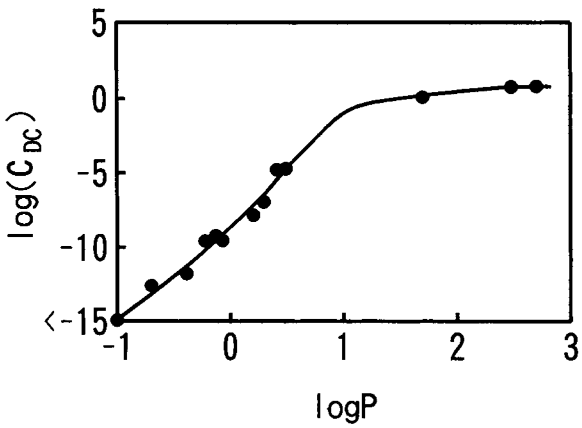

Figure 2 Dependence of the log of dc conductivity vs. the log of the annealing pressure at 25°C.

jugated compound composed of a derivative of a condensed polycyclic aromatic compound with a phenyl group and diphenyldiacetylene oligomer. The conjugated compound synthesized by annealing of diphenyldiacetylene at atmospheric pressure was mainly oligomer (oligomer content: 94 wt %).[5] Thus, the dc conductivity of the oligomer is below 10^{-15} S cm^{-1} at 25°C. The fraction of the derivative increased with increasing annealing pressure at pressure below 1.4 MPa, and the values of the H/C of the derivative in diphenyldiacetylene annealed at 0.1–1.4 MPa approximately agreed well (H/C $\sim$ 0.45).

The conductivity of the derivative of the condensed polycyclic aromatic compound with the phenyl group at a H/C of 0.45 was obtained by the method described below. For a two-phase system, the conductivity can be represented by the mixing law.[11] The relationship between the dc conductivity, C_{dc}, and the weight fraction of the derivative, W, is assumed as the following expression:

$$C_{dc}^n = C_{dcl}^n(1 - W) + C_{dch}^n W \qquad (3)$$

where C_{dcl} and C_{dch} are the dc conductivities of the oligomer and the derivative, respectively. The n is a morphology parameter and changes from -1 to 1. The product composed of the oligomer and the derivative in parallel has an n of 1. The n for the product consisting of the oligomer and the derivative in the series is -1. It is assumed that C_{dcl} is much smaller than is C_{dch}. Equation (3) approximately becomes eq. (4):

$$C_{dc}^n = C_{dch}^n W \qquad (4)$$

Equation (4) shows that the relation between $\log(C_{dc})$ and $\log W$ should be linear. Figure 3 shows the relation between $\log(C_{dc})$ and $\log W$. We find that the linear relation between the logarithm of C_{dc} and the logarithm of W is as shown in Figure 3. The values of C_{dch} and n are estimated to be 4.90×10^{-9} S cm^{-1} and 0.273, respectively. Thus, the conductivity of the conjugated compound is represented by the mixing low, and the value of dc conductivity of the derivative at a H/C of 0.45 is obtained.

Above 1.4 MPa, the pressure-annealed diphenyldiacetylene was a conjugated compound composed mainly of a derivative of the condensed polycyclic aromatic compound with the phenyl group and the annealing pressure decreased the H/C of the derivative. Figure 4 shows the dc conductivity of the derivative as a function of H/C. The dc conductivity

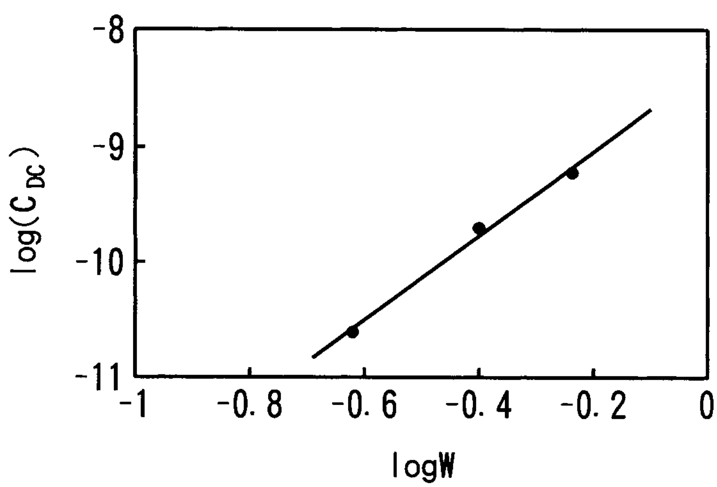

Figure 3 Relation between $\log(C_{dc})$ and $\log W$.

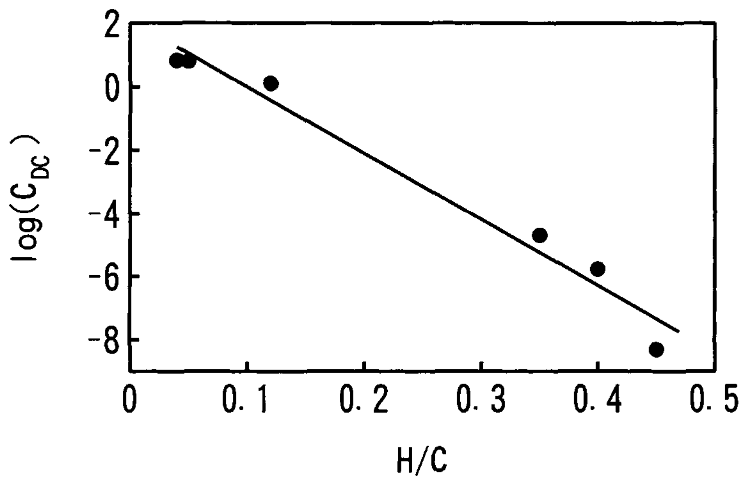

Figure 4 Relation between log(C_{dc}) and H/C (H: hydrogen; C: carbon).

of the derivative is larger than that of the oligomer and increases with decreasing H/C. It is considered that the electrical conductivity of the pressure-annealed diphenyldiacetylene is attributed to the molecular structure, which is composed of the condensed polycyclic aromatic structure of the conjugated double bond of carbon atoms with π-electrons.

It is expected that the conductivity of the conjugated compound is electronic and decreases with an increase in the energy gap.[12] The energy gap was estimated by the IR absorption spectra.[9] The spectra of the pressure-annealed diphenyldiacetylene revealed two main features: One was a band of complete absorption. The limit of this band was seen to move progressively toward a longer wavelength as the annealing pressure increases. The other feature is the presence of characteristic bands corresponding to different types of bands present in the specimen. The transparency of the pressure-annealed diphenyldiacetylene in the absence of characteristic bands decreased with an increase in pressure. This corresponded to motion of electrons in the aromatic lattice. The relation between the energy gap obtained from the midpoint of the transparency expressed in electron volts and the dc conductivity is shown in Figure 5. The dc conductivity decreases with an increase in the energy gap. This supports that the conductance of the conjugated compound is electronic.

dc and ac conductivity measurements have proven to be valuable in giving rich information on the electronic conduction mechanism. The temperature dependence of ac and dc conductivities and the frequency dependence of dc conductivity are considered

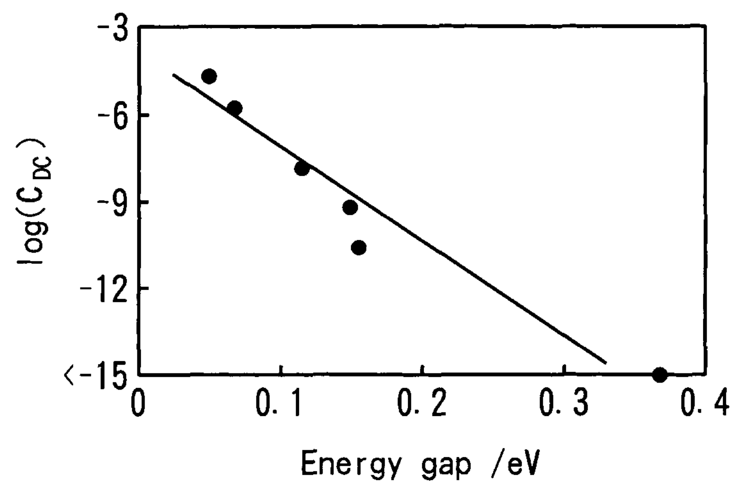

Figure 5 Relation between log(C_{dc}) and the energy gap obtained by infrared absorption.

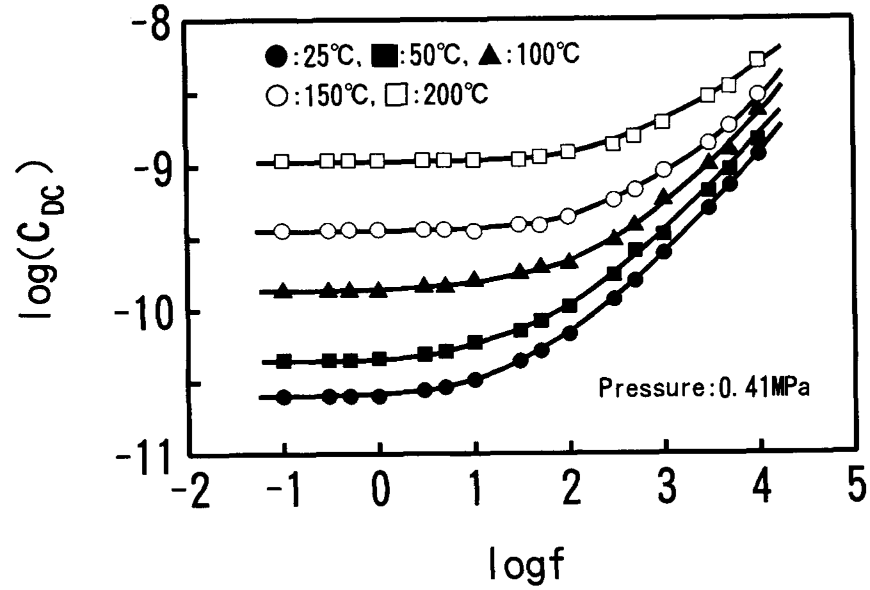

Figure 6 Frequency dependence of total conductivity in the temperature range of 25–200°C (annealing pressure: 0.41 MPa).

in relation to the electronic transport mechanism. Figure 6 shows, e.g., the temperature dependence of the total conductivity for the pressure-annealed diphenyldiacetylene at an annealing pressure of 0.41 MPa. The conductivity decreases with a decrease of frequency, approaching a dc conductivity. The dc conductivity increases with an increase of temperature. The evolution of the dc conductivity vs. temperature, T (K), is used to characterize the transport type inside the specimen. Hopping in a manifold of states at the Fermi level[10] was applied to analyze our data. A classic example is the Mott variable range hopping model. This hopping model in three dimensions gives

$$C_{dc}T^{0.5} \propto \exp[(T_0/T)^{0.25}] \quad (5)$$

where T_0 (K) is the constant and the formula is written intentionally analogous to that for semiconductors. According to the hopping mechanism, the

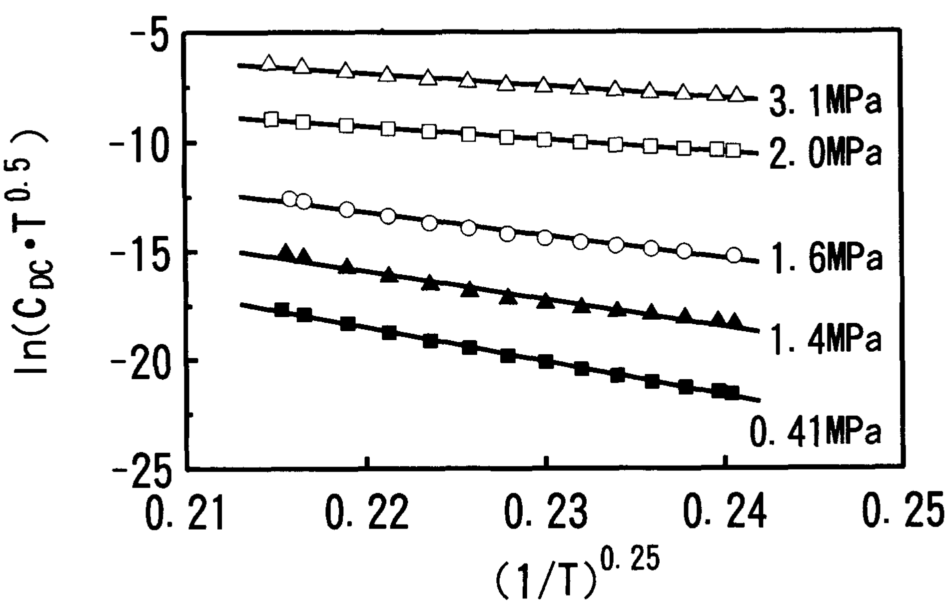

Figure 7 Plot of $\ln(C_{dc}T^{0.5})$ vs. $(1/T)^{0.25}$.

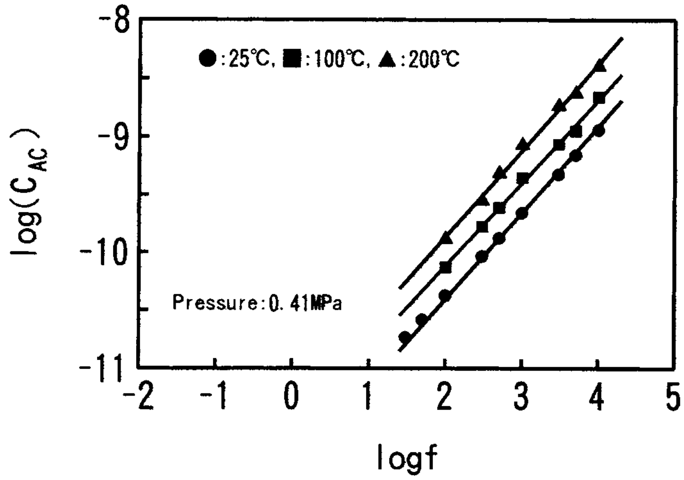

Figure 8 Plot of log(C_{ac}) vs. frequency in the temperature range of 25–200°C (annealing pressure: 0.41 MPa).

dc conductivity data are replotted as ln($C_{dc}T^{0.5}$) vs. $(1/T)^{0.25}$ in Figure 7. This figure shows an approximately linear relation between ln($C_{dc}T^{0.5}$) and $(1/T)^{0.25}$. This indicates that the hopping in a manifold of states at the Fermi level as the conduction mechanism seems to be certainly independent of pressure. If the hopping in a manifold of states at the Fermi level is appropriate, then C_{ac} should be proportional to temperature, T, and frequency, f, [eq. (6)]:

$$C_{ac} \propto Tf^{s} \tag{6}$$

where s is a constant. The ac conductivity data of the pressure-annealed diphenyldiacetylene at 0.41 MPa is plotted as log(C_{ac}) vs. log f in the temperature range of 25–200°C in Figure 8. As log f increases, log(C_{ac}) increases linearly. The value of s is 0.67–0.71 and the s variation with annealing pressure is very small for the specimens. Furthermore, log(C_{ac}) of the pressure-annealed diphenyldiacetylene in various annealing pressures of 0.4–1.6 MPa increased linearly with log f at 25°C. The value of s was independent of pressure (s: 0.71–0.75). Figure 9 shows the temperature dependence of the ac conductivity, C_{ac}, according to eq. (6) (pressure: 0.41–1.6 MPa; frequency: 10^4 Hz). The ac conductivity increases linearly with temperature. It is noticed that we obtain the linear relation between C_{ac} and temperature at various frequencies. Therefore, it is considered that the conduction mechanism can be ex-

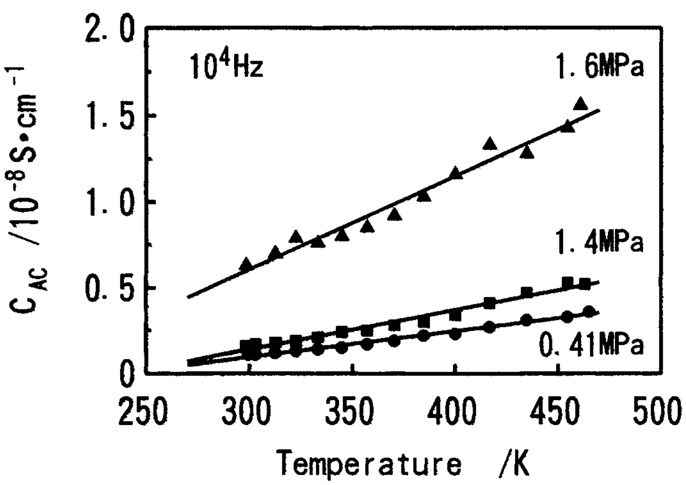

Figure 9 Plot of ac conductivity vs. temperature at 10^4 Hz (annealing pressure: 0.41–1.6 MPa).

plained by the hopping in a manifold of states at the Fermi level.

CONCLUSION

Pressure-annealed diphenyldiacetylene was a conjugated compound composed of the derivative of the condensed polycyclic aromatic compound with the phenyl group and the diphenyldiacetylene oligomer. The conductivity of the conjugated compound increased from below 10^{-15} to $10\ S\ cm^{-1}$ with increasing of the annealing pressure. The temperature and frequency dependence of the dc and ac conductivities revealed that the hopping in a manifold of states at the Fermi level explained the conduction mechanism in the conjugated compound.

We are greatly indebted to Mr. Y. Esaki and Ms. K. Nakai of the Toyota Central Research & Development Labs, Inc., for helping with the FTIR measurement.

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Received November 24, 1993
Accepted June 6, 1994