

Synthesis and Electroconductivities of Poly(2-cyano-5-methoxy-1,4-phenylenevinylene) and Copolymers

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Poly(2-cyano-5-methoxy-1,4-phenylenevinylene), PCMPV and a series of PPV copolymers containing 2-cyano-5-methoxy-1,4-phenylenevinylene (CMPV) units were prepared *via* the water-soluble precursor method. They were obtained in films form and were easily doped with FeCl₃. Doping of undrawn and drawn films of PCMPV homopolymer with FeCl₃ led to conductivity of 10⁻⁵-10⁻⁴ Scm⁻¹. Conductivity of FeCl₃-doped copolymer films ranged from 10⁻³ 4.0 Scm⁻¹ depending on composition. As the content of CMPV units in the copolymer increased further, the electrical conductivity steadily decreased. Electronic effect by the CN substituent and morphological changes brought by copolymerization appear to interplay intricately resulting in the observation of a maximum conducting composition.

Introduction

Conducting polymer processibility has been achieved recently by the development of water-soluble precursor polymers for poly(1,4-phenylenevinylene) (PPV)¹, poly(2,5-thienylenevinylene) (PTV)² and their copolymers.³⁻⁵ The synthesis of high molecular weight PPV and its derivatives through this water-soluble precursor route is one of the most attractive methods to obtain the polymer films with extended π -conjugated structures, because these water-soluble precursor polymers can be cast into various types of films, making them easy to be processed homogeneously into shaped articles with mechanical integrity. The PPV derivatives are very important conductive materials after doping with various dopants and they also possess very good non-linear optical properties.^{6,7} Substitution on the phenylene ring of PPV with different types of electron-donating or electron-attracting groups imparts a significant influence on the electronic structure of the resulting polymers and thus affects the electrochemical properties.

The PPV films can be easily doped with strong oxidizing agents such as AsF₅ to produce highly conductive materials,^{8,9} while they can not be doped with weak oxidants like I₂. In contrast, poly(2,5-dimethoxy-1,4-phenylenevinylene)¹⁰, PDMPV, and poly(2-*n*-butoxy-5-methoxy-1,4-phenylenevinylene)¹¹, PBMPV, can be doped with weak oxidizing agents such as I₂ and FeCl₃ to give electrical conductivities of 10²-10³ Scm⁻¹. The presence of strong electron donors leads to a reduction in the band gap and ionization potential of the polymers, facilitating the oxidation with weak oxidants and thus contributes to high conductivities.^{12,13}

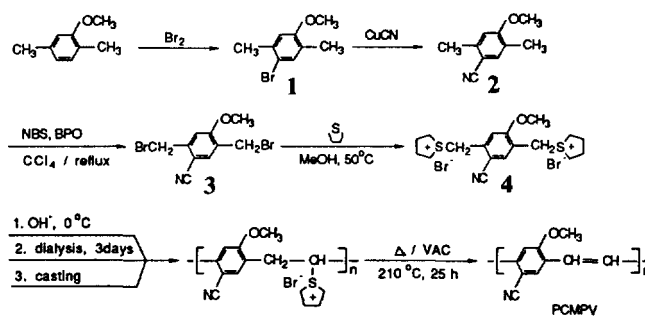
Recently, we prepared poly(2-bromo-5-methoxy-1,4-phenylenevinylene),⁴ PBrMPV, and its copolymers *via* water-soluble precursor polymers. The copolymer could be readily doped with I₂ to produce materials having a wide range of conductivities (10⁰-10⁻⁴ Scm⁻¹) depending on the copolymer composition. Conductivities of the films are lower than those of the copolymer films containing dialkoxy-substituted phenylene ring. The presence of electron-attracting bromine atom instead of electron-donating methoxy group lowered the conductivity values. It can be explained that conductivity depends upon how easily a conjugated polymer experiences oxi-

dizing attack by a dopant.

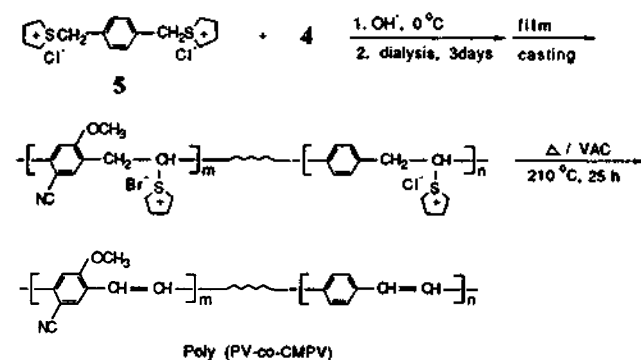
In this paper, we prepared poly(2-cyano-5-methoxy-1,4-phenylenevinylene), PCMPV, and its copolymers by the water-soluble precursor method. These polyconjugated polymers contain strong electron-donating methoxy (OCH₃) group together with strong electron-withdrawing nitrile group (CN) on a phenylene ring. It is our purpose to learn more about the effect of substituents on the electrical-properties of PPV derivatives and their copolymers. The synthetic route and the structures of PCMPV and copolymers prepared and characterized in this study are shown below:

Experimental

Syntheses of Monomers. 4-Bromo-2,5-dimethylanisole,



Scheme 1



Scheme 2

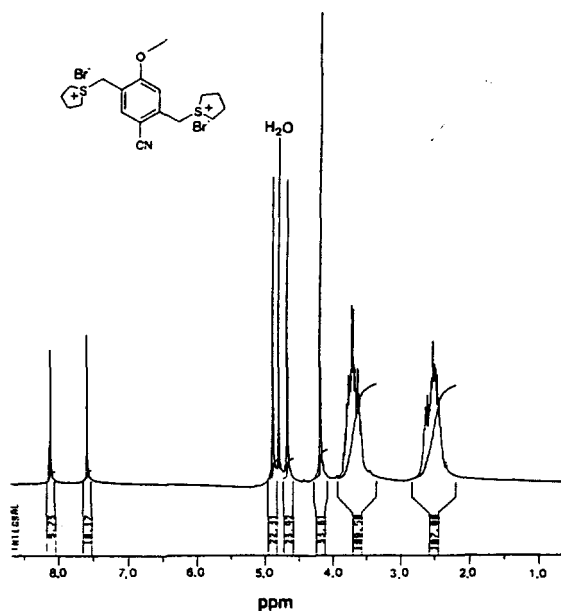


Figure 1. NMR spectrum of 2-cyano-5-methoxy-1,4-phenylenedimethylene bis (tetrahydrothiophenium bromide).

1, was prepared by reacting 2,5-dimethylanisole (44.0 g, 0.32 mol) with bromine (51.1 g, 0.32 mol) in CCl_4 at -5°C . A vigorous reaction soon occurred and hydrogen bromide was evolved. When the reaction slackened, the reaction mixture was warmed in a bath at $25-30^\circ\text{C}$ for 5 hrs, and then the bath temperature was raised to $65-70^\circ\text{C}$ for further 5 hrs. The reddish reaction product was washed with 10% sodium hydroxide and with water several times. After drying with anhydrous MgSO_4 and filtering, the resulting filtrate was evaporated, and the liquid product was vacuum distilled. The resulting product was colorless liquid. The yield was 96% $^1\text{H-NMR}$ (300 MHz, CDCl_3); δ 7.4 (s, 1H), 6.8 (s, 1H), 3.9 (s, 3H), 2.5 (s, 3H), and 2.3 (s, 3H).

4-Bromo-2,5-dimethylanisole (57.6 g, 0.27 mol) and CuCN (25.0 g, 0.28 mol) were reacted for 4 hrs at 160°C in 70 ml of DMF. The mixture containing 80 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 23 ml of conc. HCl and 120 ml of H_2O was poured into the reaction mixture and vigorously stirred. The resulting mixture was poured into excess cold water and then filtered. The obtained solid product was dissolved in diethylether and dried with anhydrous MgSO_4 . The resulting filtrate was evaporated in a rotary evaporator. The residue was vacuum distilled. White solid product, **2**, 4-cyano-2,5-dimethylanisole was obtained (yield, 85%). $^1\text{H-NMR}$ (CDCl_3); δ 7.3 (s, 1H),

6.7 (s, 1H), 3.8 (s, 3H), 2.5 (s, 3H), and 2.2 (s, 3H).

4-cyano-2,5-di (bromomethyl) anisole, **3**, was prepared by reacting 4-cyano-2,5-dimethylanisole (28.8 g, 0.18 mol) with N-bromosuccinimide (65.5 g, 0.36 mol) in 150 ml of CCl_4 . A small amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 80°C for 2 hrs under nitrogen atmosphere. A slightly yellow colored solution was obtained after filtration. The solution was concentrated and poured into a mixed solvent of diethyl ether and petroleum ether. The white solid, 4-cyano-2,5-di (bromomethyl) anisole, was obtained by recrystallizing the resulting precipitate from methanol. Yield was 45%, $^1\text{H-NMR}$ (CDCl_3); δ 7.6 (s, 1H), 7.0 (s, 1H), 4.6 (s, 2H), 4.5 (s, 2H), and 4.0 (s, 3H).

The compound **3** (15.9 g, 0.05 mol) and excess tetrahydrothiophene were reacted for 20 hrs at 55°C in 70 ml of methanol. The final salt monomer, **4**, 2-cyano-5-methoxy-1,4-phenylenedimethylene bis (tetrahydrothiophenium bromide), was obtained by concentration of the reaction solution, precipitation in cold acetone, filtration, and vacuum drying. The product yield was 85% and it was very hygroscopic. $^1\text{H-NMR}$ (D_2O); δ 8.1 (s, 1H), 7.6 (s, 1H), 4.9 (s, 2H), 4.7 (s, 2H), 4.2 (s, 3H), 3.9-3.5 (m, 8H), 2.7-2.4 (m, 8H) and 4.8 (s, HDO); Figure 1.

The compound, **5**, was prepared similarly from 1,4-bis (chloromethyl)-benzene and tetrahydrothiophene following the literature method.^{1,14}

Polymerization. Synthetic methods for the homopolymer and copolymers were the same as reported by us^{3,4} and others.^{8,10} The polymerization was carried out in a deoxygenated sulfonium monomer solution (1.04 M) with an equimolar sodium hydroxide solution at 0°C . A homogeneous viscous solution was obtained. For the copolymers, the total moles of the two monomers, **4** and **5**, were kept constant, but their mole ratio was varied. The reaction was quenched by neutralization with 0.5 N HCl, and the neutralized precursor polymer solutions were dialyzed against deionized water for 3 days using a Spectropor membrane tubing (M.W. cut-off at 12,000) to remove the low molecular weight reactants and products. The films cast from these aqueous precursor polymer solution were subjected to thermal elimination (~ 1 torr) at 210°C for 25 hrs to transform into the final polyconjugated polymer films.

Doping. The polymer films were placed in contact with a saturated solution of anhydrous ferric chloride in nitromethane. FeCl_3 -doped films were washed with fresh nitromethane before drying. The degree of doping was calculated from the weight uptake.

Characterization. Elemental analyses were performed by the Analytical Department of the Korea Research Institute

Table 1. Composition, Monomer Conversions and Polymers Yields

Polymers ^a	Molar Ratio in Feed 5 : 4	PV : CMPV Actual	Monomer Conversion mole %	Polymer Yield ^b , wt. %
PCMPV	0 : 100	0 : 100	95	60
76-poly(PV-co-CMPV)	17 : 83	24 : 76	90	38
31-poly(PV-co-CMPV)	50 : 50	69 : 31	74	25
10-poly(PV-co-CMPV)	83 : 17	90 : 10	47	20
5-poly(PV-co-CMPV)	91 : 9	95 : 5	40	18

^aThe numbers stand for the mole % of CMPV units incorporated in the copolymers. ^bThe values were estimated from the weight of precursor polymer film.

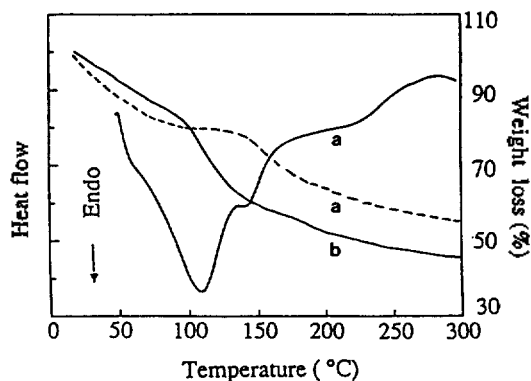


Figure 2. DSC and TGA thermograms of the precursor polymers: a) PCMPV, b) 10-poly (PV-co-CMPV).

of Chemical Technology. $^1\text{H-NMR}$ spectra were recorded on a Bruker AM 300 spectrometer. FT-IR spectra were obtained on a Bomem Michelson series FT-IR spectrometer. UV-visible spectra were obtained on a Perkin-Elmer spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ with DuPont 9900 analyzer. Electrical conductivities were measured using a four-in-line probe configuration with evacuating the doping chamber at room temperature. Four-probe resistance measurements were made using a Keithley 197 digital multimeter. Carbon paste was used for sample-electrode contact.

Results and Discussion

Table 1 summarizes the data for monomer conversions to precursor polymers, polymer yield, and the compositions of the final copolymers as calculated from nitrogen contents. Data for conversions were obtained by titration of the precursor polymer solution with 0.5 N HCl. Polymer yield were estimated gravimetrically from the weight of cast films. The degree of monomer conversions (40-95%) to precursor polymers and polymer yields (18-60%) are comparable to or slightly higher than those reported for other similar polymerization systems,^{3,4} and both of the monomer conversions and polymer yields are increased by increasing 2-cyano-5-methoxy-1,4-phenylenevinylene (CMPV) monomer ratio. Molecular weights of these polymers are reasonably high because they were obtained after dialysis using a dialysis tube whose molecular weight cut-off was at 12,000. All of the precursor polymer films cast from aqueous precursor polymer solutions after dialysis appeared homogeneous and transparent. They could be drawn up to 5 times their initial length at the temperature range of $110\text{-}120^\circ\text{C}$ using a zone-heating apparatus. The content of CMPV units incorporated in the copolymers was significantly lower than that in the monomer mixture, suggesting that the reactivity of the CMPV-monomer, **4**, is less than the PV-monomer, **5**.

Thermal analysis of the elimination reaction of the precursor polymer by DSC indicates that major weight losses occurred at between about 110°C and 140°C as shown in Figure 2. The low temperature endotherm corresponds to the loss of water absorbed in precursor polymer films and the higher temperature one to the chemical elimination of tetrahydro-

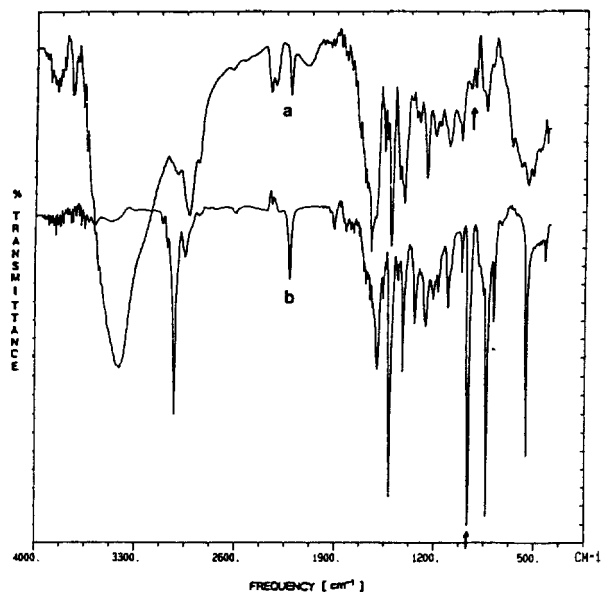


Figure 3. FT-IR spectra of a) precursor and b) final 10-poly (PV-co MPV).

thiophene and HCl. TGA thermograms of the precursor polymers in Figure 2 show that two major weight losses occurred at the temperature ranges of $27\text{-}110^\circ\text{C}$ and $150\text{-}180^\circ\text{C}$ for homopolymer, and at the ranges of $26\text{-}110^\circ\text{C}$ and $110\text{-}150^\circ\text{C}$ copolymer, 10-poly(PV-co-CMPV).

FT-IR Spectrum of a copolymer containing 10 mole % of CMPV units, 10-poly (PV-co-CMPV), is compared with that of the precursor polymer film in Figure 3. The precursor polymer film exhibits a broad absorption peak at $3100\text{-}3600\text{ cm}^{-1}$ due to the absorbed water, which disappears in the spectrum of the eliminated film. Strong absorption peaks at 968 and 3022 cm^{-1} after elimination indicated that the vinylene $\text{C}=\text{C}$ bonds formed are entirely of trans configuration.¹⁵ A small, but sharp absorption peak at 968 cm^{-1} in the spectrum of the precursor films results from a premature elimination reaction occurred during film casting. Both of the precursor and eliminated films exhibit sharp absorption peaks at 2235 cm^{-1} due to $-\text{C}\equiv\text{N}$ bonds.

UV-visible spectra of the fully eliminated polymer films shown in Figure 4 reveal significantly different behaviors between PV rich (CMPV units < 10 mole %) and CMPV rich (CMPV units > 31 mole %) polymers especially in the range near 430 nm . The broad, long wavelength absorption with maxima around 430 nm appeared in PV rich polymers is due to $\pi\text{-}\pi^*$ transition of the conjugated system. The absorption peak almost disappeared when the CMPV contents are above 31 mole % in the copolymer and the absorption spectra of the copolymers are similar to the PCMPV homopolymer. The reason why PCMPV does not show the $\pi\text{-}\pi^*$ transition peak may come from the electronic nature of the strong electron-withdrawing CN substituents which greatly distort the π bond electron cloud in phenylene and vinylene so that no more $\pi\text{-}\pi^*$ transition is observed. We also observed similar phenomenon for nitro-substituted PPV system.¹⁶

Table 2 shows draw ratios, the maximum conductivity values and degrees of doping of FeCl_3 -doped PCMPV and copolymers. The degree of doping and the maximum conducti-

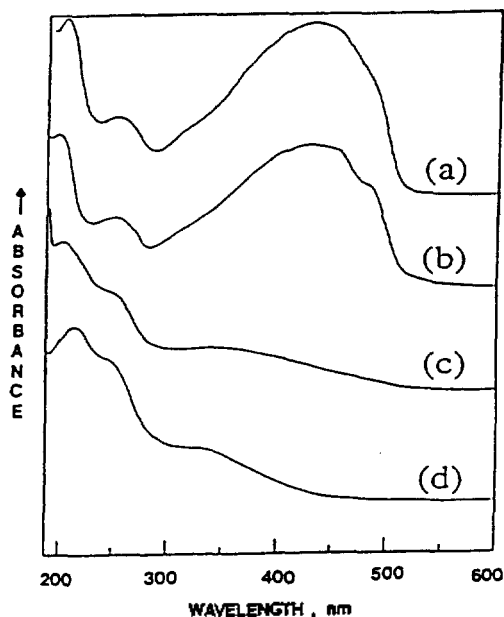


Figure 4. UV-VIS spectra of polyconjugated polymers of: (a) PPV, (b) 10-poly (PV-co-CMPV), (c) 31-poly(PV-co-CMPV), and (d) PCMPV.

Table 2. Maximum Conductivities of FeCl₃-Doped Polymers

Polymers	Draw Ratio, L/Lo	Conductivity, Scm ⁻¹	Degree of Doping, FeCl ₃ ⁺ /RU ^a
PCMPV	1	9.1 × 10 ⁻⁵	0.01
	5	7.2 × 10 ⁻⁴	
76-poly(PV-co-CMPV)	1	3.0 × 10 ⁻⁴	0.09
	5	4.0 × 10 ⁻⁴	
31-poly(PV-co-CMPV)	1	7.8 × 10 ⁻³	0.25
	5	1.0 × 10 ⁻¹	
10-poly(PV-co-CMPV)	1	1.2 × 10 ⁻²	0.94
	5	3.5 × 10 ⁻¹	
5-poly(PV-co-CMPV)	1	9.6 × 10 ⁻¹	0.53
	5	4.1	

^aRU stands for average repeating unit.

Conductivity values are very much parallel each other. PCMPV is not readily doped with FeCl₃, so the maximum conductivity is far lower than that of PDMPV.¹⁷ Even the stretched film of PCMPV with a draw ratio of 5 after doping with FeCl₃ had the electrical conductivity of only 7.2 × 10⁻⁴ Scm⁻¹. But the drawn copolymer films containing 5 mole% of CMPV unit, 5-poly(PV-co-CMPV), when doped with FeCl₃, showed maximum conductivity value of 4.1 Scm⁻¹. This conductivity value is 10⁴ times higher than that of PCMPV. On the other hand, as the content of CMPV unit in the copolymer increased further, the electrical conductivity steadily decreased as shown in Table 2. It was originally expected that the presence of the electron-withdrawing property of CN group raises the oxidation potential of the polymer chain resulting in reduced dopability. As mentioned above, at higher CMPV contents than 31 mole %, the π -electron delocalization is st-

rongly distorted and obstructed by the electron-withdrawing CN group. Therefore, the conductivity values of CMPV rich polymers are not high. Because of these reasons, we also observed that PCMPV homopolymer could not be doped with weak oxidant such as I₂.

It is well known that unsubstituted PPV films could not be doped with FeCl₃ dopant. Nevertheless, the copolymer films containing small amounts of CMPV units show significantly high conductivity values. These observations suggest that the presence of electron-withdrawing CN substituents on phenylene ring causes a morphological change in such a way that it makes easier for the doping species to approach and oxidize polymer chains. In other words, the positive effects by the morphological changes due to the presence of CN group overtake its negative electronic effect at low levels of CMPV units. At a higher content of CMPV structure in the copolymer, however, electronic effect by the CN substituent starts to overwhelm the morphological effect and, thus, diminish conductivity of the doped materials.

We recently observed that the precursor copolymers containing 11 mole % and 31 mole % of CMPV units exhibit much higher value of 2nd order non-linear optical responses (electro-optic coefficients) when these materials were corona poled during elimination. Surprisingly, the electro-optic response for the 11-poly(PV-co-CMPV) copolymer film was remained stable up to 100°C for several hours. The thermal stability and mechanical strength of PPV derivatives, and easy processibility from precursor polymers suggest a new approach for the molecular design of the thermally stable 2nd order nonlinear optical polymers.

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Theoretical Investigation of the Vibrational Relaxation of NO($v=1-7$) in Collisions with O₂ and N₂

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The vibrational relaxation rate constants of NO($v=1-7$) by O₂ and N₂ have been calculated in the temperature range of 300-1000 K using the solution of the time-dependent Schrödinger equation. The calculated relaxation rate constants by O₂ increase monotonically with the vibrational energy level v , which is compatible with the experimental data, while those by N₂ are nearly independent of v in the range of $3.40 \pm 1.60 \times 10^{-16}$ cm³/molecule-sec at 300 K. Those for NO(v)+N₂ are about 2-3 orders of magnitude smaller than those for NO(v)+O₂, because the latter is an exothermic processes while the former an endothermic. Relaxation processes can be interpreted by single-quantum V-V transition. The contributions of V-T/R transition and double-quantum V-V transition to the relaxation are negligible over the entire temperature range.

Introduction

Nitric oxide is a prominent infrared radiator in the ionosphere. Its vibrational energy transfer rate with atmospheric species is necessary to describe properly nonequilibrium infrared radiative phenomena in the excited atmosphere. In particular, quenching of vibrationally excited NO by O₂, N₂, and O in the upper atmosphere is of great significance. The vibrational relaxation of nitric oxide through collisions with atoms, diatomic and simple polyatomic molecules have been extensively studied over wide temperature ranges.¹⁻¹² There have been several measurements of the relaxation rates of the first excited vibrational level of NO in the X²I state by O₂ and N₂, and the rate constants for these processes are well established.⁴⁻⁶

However, little has been known on the relaxation of vibrational levels $v>1$ for these collision systems. Murphy *et al.* mentioned⁴ that "Based on the assumption that quenching of NO(v) by O₂ is proportional to v , the quenching rate constant obtained for NO($v=1$) by O₂ is $2.4 \pm 1.5 \times 10^{-14}$ cm³/sec. If the quenching of NO(v) by O₂ is independent of v , the reported rate constant is increased by 75%. The quenching rate of NO($v=1$) by N₂ obtained is $1.7 \pm 0.7 \times 10^{-16}$ cm³/sec where the uncertainty includes both the quenching models proportional and independent of v ." Using Lambert-Salter probability scaling for $v=1$ and their experimental data, Whitson, Darnton, and McNeal⁷ have placed the bounds on the rate coefficients of the processes NO(v)+O₂→NO($v-1$)+O₂ for $v=1-7$. Their reduced scaling is sub-linear with v . Green *et al.*⁸ have also determined the room temperature rate coefficients for the above process for $v=1-7$, and have found that the rate coefficient increases monotonically with

v . To our knowledge, however, the vibrational relaxation rate of NO(v) by N₂ for $v>1$ has never been reported.

The present study was aimed to calculate the vibrational relaxation of NO($v=1-7$) by O₂ and N₂ through a semiclassical procedure. In this collision system, the vibrational relaxation appears through V-V and V-T/R processes. However, the V-T/R relaxation rates are expected to be very small compared with the V-V rate. Thus, the relaxation of NO was considered as through the V-V process. But, the V-T/R processes were also discussed.

Theory for V-V process

In this section we described NO+O₂ collision, and NO+N₂ collision can be described by the similar way.

Interaction Model and Potential Energy. We set up the intermolecular potential as the sum of four atom-atom interaction terms, each of which is assumed to be the Morse type:^{12,13}

$$V(\gamma_1, \gamma_2, \gamma_3, \gamma_4) = \frac{1}{4} D \sum_{i=1}^4 \left[\exp\left(-\frac{\gamma_i}{a}\right) - 2 \exp\left(\frac{l}{2} - \frac{\gamma_i}{2a}\right) \right] \quad (1)$$

Where, D , l , and a are the potential constants to be determined. For the relative separation which is significantly larger than the equilibrium bond lengths d_1 and d_2 , these atom-atom distances are approximated as

$$r_{12} = r - \gamma_1(d_1 + x_1)\cos\theta_1 \pm \frac{1}{2}(d_2 + x_2)\cos\theta_2 \quad (2a,b)$$

$$r_{34} = r + \gamma_2(d_1 + x_1)\cos\theta_1 \pm \frac{1}{2}(d_2 + x_2)\cos\theta_2 \quad (2c,d)$$