Migration Distances of Electrons Generated in Organic Solids by Ionizing Radiation

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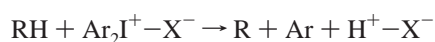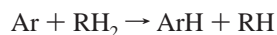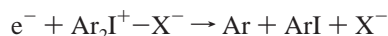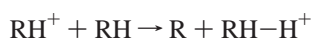Sapporo, 060-8628 Japan*

For estimating the final spatial resolution of lithography using ionizing radiation as a light source, the migration distances of electrons in γ-irradiated cryogenic organic matrices of polar alcohols and nonpolar methylcyclohexane have been determined by analyzing the transverse and the longitudinal electron spin−echo relaxations of radical pairs generated from the electrons and their counterpart cations. The intrapair distance of the radical pairs does not depend on the concentration of electron scavengers, which indicates that ejected electrons react with scavengers after losing their kinetic energies and being stabilized as trapped electrons. The intrapair distance decreases with increasing the concentration of polar molecules in the matrices, which indicates that charge−dipole interactions with polar molecules play significant roles in the slowing down process of the ejected electrons.

Introduction

Ionizing radiation is expected to be the light source for nanometer scale lithography because of its shorter wavelength than UV light. Although the decrease of wavelength causes the increase of spatial resolution for UV light lithography, this is not necessarily true for ionizing radiation. The action of UV light to resist materials is the dissociation of chemical bonds, so that photochemical reactions are localized within the field of exposure. The action of ionizing radiation is, however, not limited within the field of exposure. The major action of ionizing radiation is the ejection of electrons from resist molecules. The energy of the ejected primary electrons is generally much higher than that of the ionization energy of molecules, so that one primary electron generates many secondary electrons with the energy less than the ionization energy. Although the primary electrons with high kinetic energy move parallel to the incident radiation, the motion of the secondary electrons with low kinetic energy is rather isotropic. The secondary electrons travel in resist materials and are captured by electron scavengers to induce chemical reactions far from the parent cations and therefore from the field of exposure. For example, although the formation of acid from diphenyliodonium salt ($Ar_2I^+-X^-$), one of the typical acid generators for acid-catalyzed lithography, in resist materials (RH) by UV light is localized within the field of exposure as[1]

$$Ar_2I^+-X^- + h\nu \rightarrow ArI + Ar^+ + X^-$$

$$Ar^+ + RH + X^- \rightarrow ArR + H^+-X^-$$
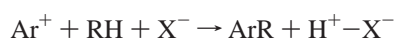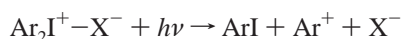
the formation by ionizing radiation is extended beyond the field of exposure[1−4]

$$RH + \text{ionizing radiation} \rightarrow RH^+ + e^-$$

$$RH^+ + RH \rightarrow R + RH-H^+$$

$$e^- + Ar_2I^+-X^- \rightarrow Ar + ArI + X^-$$

$$Ar + RH_2 \rightarrow ArH + RH$$

$$RH + Ar_2I^+-X^- \rightarrow R + Ar + H^+-X^-$$

since the ejected electrons travel a long distance before being captured by the onium salt. The spatial resolution is therefore limited by the migration distance before reacting with electron scavengers. To know the migration distance is therefore important for the estimation of the spatial resolution. The migration distance may be determined by two factors. One is the concentration of molecules scavenging the electrons. If the probability of electron capture by scavenger molecules is proportional to the number of collisions with the molecules, the spatial resolution can be improved by increasing the concentration of scavengers. Another factor is the nature of resist materials. If electrons are captured by scavenger molecules after losing their excess kinetic energy, the spatial resolution primarily depends not on the concentration but on the molecular nature of resist materials. It should be noted that the migration distance does not depend on the incident energy of ionizing radiations as long as the energy is much higher than the ionization energy, since the mean energy of secondary electrons does not depend on the incident energy.

In the present paper, the intrapair distances of radical pairs generated from ejected electrons and parent cations in γ-irradiated alcohol and alkane matrices at 77 K are determined by analyzing their paramagnetic relaxations. Kevan and co-workers determined the radius of spurs in γ-irradiated organic glassy matrices by means of the electron spin resonance (ESR) power saturation method.[5] They found that the value of $(T_1T_2)^{1/2}$, where T_1 and T_2 are longitudinal and transverse paramagnetic relaxation times, respectively, of trapped electrons did not depend on the dose up to some value where spatial overlapping of spurs was considered to take place. We have measured the paramagnetic relaxation rates of free radicals generated in γ-irradiated alcohol[6,7] matrices by means of electron spin−echo (ESE) methods and found that each spur consists of approximately one radical pair. On the basis of the fact that the radius of a spur corresponds to the intrapair distance of the radical pair, we have determined the intrapair distances of radical pairs in alcohol matrices and polymers[8,9] by analyzing their longitudinal spin relaxation. We have also shown that the intrapair distances can also be determined by the 2 + 1 ESE method,[10,11] which selectively detects transverse spin relaxation due to instantaneous

diffusion. However, control factors for the intrapair distances have not been elucidated yet.

We will show in the present paper that the intrapair distance does not depend on the concentration of electron scavengers but is determined by the thermalization distance of ejected electrons, which then depends on the concentration of polar molecules in the irradiated matrices.

Experimental Section

Two kinds of solid samples were used for the measurement of the migration distance of electrons. One was perdeuterated methanol, CD_3OD, containing 5 vol % D_2O, 3.3 vol % D_2O and 1.7 vol % D_2SO_4, and 5 vol % D_2SO_4, respectively. The other was the mixture of perdeuterated 2-propanol, $(CD_3)_2$-CDOD, and perdeuterated methylcyclohexane, $C_6D_{11}CD_3$, containing chlorocyclohexane, $C_6H_{11}Cl$, as an electron scavenger. Methanol samples were used for studying the effect of the concentration of an electron scavenger, D_2SO_4, on the intrapair distance, whereas the mixture samples were used for studying the effect of matrix composition. All of the samples gave homogeneously mixed glassy solids at 77 K. They were irradiated with a ^{60}Co γ-ray source at 77 K to generate stable free radicals. The concentration of free radicals was changed by changing the radiation dose and was determined by double integration of their ESR spectra.

The following reactions are known to be induced by irradiation of methanol samples with ionizing radiation;[12] the first event is the formation of radical cation−electron pairs

$$CD_3OD + \text{ionizing radiation} \rightarrow CD_3OD^+ + e^-$$

The radical cations immediately convert to hydroxymethyl radicals CD_2OD by proton transfer.[12]

$$CD_3OD^+ + CD_3OD \rightarrow CD_3OD_2^+ + CD_2OD$$
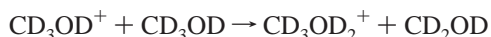
The ejected electrons are captured by deuterons to generate hydroxymethyl radicals

$$e^- + D^+ \rightarrow D \quad D + CD_3OD \rightarrow CD_2OD + D_2$$

or stabilized as solvated electrons, which can be converted to hydroxymethyl radicals by photoillumination.[13]

$$e^- + 4(CD_3OD) \rightarrow e^-(CD_3OD)_4$$

$$e^-(CD_3OD)_4 + h\nu \rightarrow 2CD_3OD + CD_2OD + CD_3O^- + D_2$$
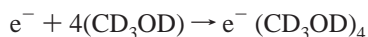
γ-irradiation thus generates CD_2OD- -CD_2OD radical pairs.

The intrapair distances of radical pairs were determined by the 2 + 1 ESE method. Because the detailed theory of the 2 + 1 ESE method has been given in previous papers,[10,14] only the principle of the method is briefly mentioned. The 2 + 1 ESE method is a pulsed ESR technique that selectively detects the relaxation of transverse magnetization arising from magnetic dipole−dipole interactions between electron spins.

Figure 1 shows the train of microwave pulses used for the measurement of the transverse spin relaxation by the 2 + 1 ESE method. The first pulse generates a coherent transverse magnetization of an electron spin system. The refocusing pulse applied at time τ after the first pulse refocuses the transverse magnetization at time τ after the refocusing pulse. The refocusing would be perfect if the precession frequency of each electron spin was kept constant during time interval 2τ. The precession frequency was determined by the local magnetic field of each
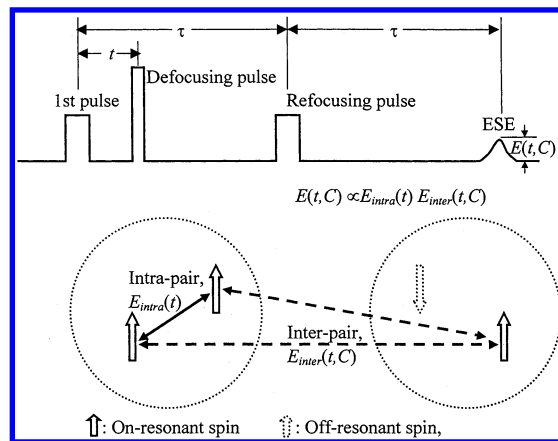

Figure 1. Pulse train for the 2 + 1 ESE method used for the detection of transverse relaxation due to instantaneous diffusion of CD_2OD radicals generated in perdeuterated methanol matrices by ionizing radiation (upper) and magnetic interactions causing the instantaneous diffusion of CD_2OD radicals (lower). An observed relaxation $E(t,C)$ is given by a product of relaxations due to intrapair electron spin−spin interaction $E_{intra}(t)$ and interpair electron spin−spin interaction $E_{inter}(t,C)$, which depends on the concentration C of CD_2OD radicals.

electron spin, which was given as a vector sum of an external magnetic field and magnetic fields generated by electron and nuclear spins surrounding observed electron spins. The thermal motion of molecules in the spin system causes the fluctuation of local magnetic fields generated by electron and nuclear spins, so that the degree of refocusing generally decreases with increasing τ.

Application of a defocusing pulse causes an additional fluctuation of the local magnetic fields by changing the states of on-resonant electron spins interacting with observed electron spins. The intensity of an ESE signal therefore decreases. This forced relaxation is called instantaneous diffusion (of an ESR spectrum) and can be selectively detected by measuring the intensity of ESE as a function of time interval t between the first pulse and a defocusing pulse while fixing time interval τ.

As schematically represented in Figure 1, the instantaneous diffusion of free radicals generated in pair in solid matrices arises from two types of magnetic interactions, intra- and interpair electron spin−spin interactions. The former interaction does not depend on the concentration C of radicals, whereas the latter depends on the concentration. Because both interactions simultaneously affect the relaxation, the 2 + 1 ESE relaxation $E(t,C)$ is expressed by a product of relaxations due to intrapair interaction $E_{intra}(t)$ and interpair interaction $E_{inter}(t,C)$ as[10]

$$E(t,C) = E_0(C) \, E_{intra}(t) \, E_{inter}(t,C) \tag{1}$$

where $E_0(C)$ is the intensity of an ESE signal at $t = 0$. $E_{intra}(t)$ and $E_{inter}(t,C)$ are normalized to unity at $t = 0$. Because $E_{intra}(t)$ solely arises from electron spin−spin interactions between radicals and their paired ones, one can determine the distribution of the intrapair separation distance by analyzing $E_{intra}(t)$ that can be extracted from an observed $E(t,C)$. The method of the extraction will be shown in the following section.

Because the 2 + 1 ESE method necessitates the excitation of a considerable amount of electron spins surrounding observed electron spins, this method is not applicable to a system with a wide ESR spectrum. This is the reason that perdeuterated methanol was used as matrix molecules. CD_2OD radicals generated from perdeuterated methanol give a very sharp ESR spectrum so that magnetic dipole interactions among on-resonant spins are possible to be detected by the 2 + 1 ESE method.

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The 2 + 1 ESE measurements were carried out on a homemade X-band ESE spectrometer with the pulse widths of 80, 40, and 80 ns for the first, the second, and the third microwave pulses, respectively. The intensity of the second defocusing pulse was four times those of the first and the third pulses. The 2 + 1 ESE signals were measured at 77 K by fixing τ at 2.3 μs.

Because γ-irradiation of the mixture matrices of $(CD_3)_2CDOD$ and $C_6D_{11}CD_3$ gave radical species with rather wide ESR spectra, the 2 + 1 ESE method was not applicable for the determination of the intrapair distances of free radicals in the mixture matrices. The intrapair distances in the mixture matrices were determined by analyzing the longitudinal relaxation of C_6H_{11} radicals generated by the reaction of ejected electrons with $C_6H_{11}Cl$, as

$$MD + \text{ionizing radiation} \rightarrow MD^+ + e^-$$

$$MD^+ + MD \rightarrow M + MD_2^+$$
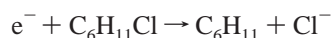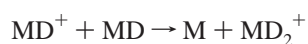
$$e^- + C_6H_{11}Cl \rightarrow C_6H_{11} + Cl^-$$

where MD denotes perdeuterated matrix molecules. γ-Irradiation thus generates C_6H_{11}- -solvent radical (M) pairs. $C_6H_{11}Cl$ was selected as an electron scavenger since the transverse relaxation of the generated C_6H_{11} radicals was slow enough to detect strong two pulse ESE signals.[15] In addition, the ESR spectrum of C_6H_{11} radicals was much wider than those of free radicals generated from perdeuterated matrix molecules. The longitudinal relaxation of C_6H_{11} radicals was therefore selectively measured without spin excitation of matrix radicals.

Longitudinal spin relaxation is the recovery of the energy distribution of electron spin systems from the excited to the thermally equilibrium ones by dissipating their excess spin energies to the surrounding and is induced either by the spectral diffusion of on-resonant hot spins to off-resonant spectral region and the concomitant diffusion of off-resonant cool spins to the on-resonant spectral region or by the change of the quantum states of on-resonant spins. The spectral diffusion of alkyl radicals mainly arises from the fluctuation of hyperfine inter-actions due to their thermal motion[16,17] and is negligibly slow for C_6H_{11} radicals, since the motion of β-protons is very slow for cyclic alkyl radicals. The change of the spin quantum states is induced either by cross-relaxation or by spin−lattice relax-ation. The cross-relaxation is the flip-flop of spin quantum states between on- and off-resonant spins through magnetic dipole−dipole interactions between them. The spin−lattice relaxation is the conversion of the excess energy of on-resonant spins to lattice vibration and is also enhanced by magnetic dipole−dipole interactions. Therefore, analysis of the longitudinal relaxation makes it possible to determine the intrapair distance of free radicals.

Figure 2 shows the train of microwave pulses used for the measurement of longitudinal spin relaxation by the two pulse ESE method. A saturation pulse transfers the longitudinal magnetization of on-resonant electron spins to the transverse direction. The longitudinal magnetization recovered at time t after the saturation pulse by spin relaxation is then detected by the two pulse ESE method. The difference between the ESE intensities with and without the saturation pulse at radical concentration C, $E(t,C)$, plotted against t is a longitudinal relaxation curve and is the amount of magnetization that is not longitudinally relaxed after time t.
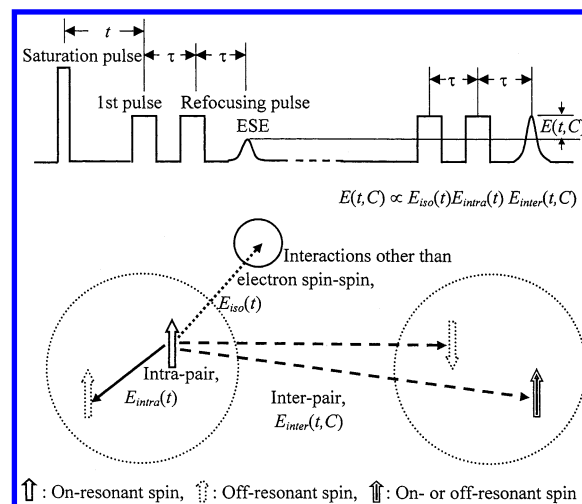

Figure 2. Pulse train for the 2 pulse ESE method used for the detection of longitudinal spin relaxation of C_6H_{11} radicals generated in mixture matrices of $(CD_3)_2CDOD$ and $C_6D_{11}CD_3$ by ionizing radiation (upper) and magnetic interactions causing the longitudinal relaxation of C_6H_{11} radicals (lower). An observed longitudinal relaxation $E(t,C)$ at total radical concentration C is given by a product of relaxations due to intrapair electron spin−spin interaction $E_{intra}(t)$, interpair electron spin−spin interaction $E_{inter}(t,C)$, and interactions other than electron spin−spin interaction $E_{iso}(t)$.

As schematically represented in Figure 2, the longitudinal spin relaxation of free radicals generated in pair in solid matrices arises from three types of interactions, intra- and interpair electron spin−spin interactions and interactions other than the electron spin−spin interactions. The longitudinal relaxation is therefore expressed as[6]

$$E(t,C) = E_0(C)\, E_{iso}(t)\, E_{intra}(t)\, E_{inter}(t,C) \qquad (2)$$

where $E_0(C)$ is the intensity of an ESE signal at $t = 0$, $E_{iso}(t)$ is the spin−lattice relaxation of isolated electron spins that is induced by g-anisotropy and electron−nuclear spin−spin in-teractions, and $E_{intra}(t)$ and $E_{inter}(t,C)$ are relaxations induced by intra- and interpair spin−spin interactions, respectively. $E_{iso}(t)$, $E_{intra}(t)$, and $E_{inter}(t,C)$ are normalized to unity at $t = 0$. $E_{iso}(t)$ and $E_{intra}(t)$ do not depend on the concentration of free radicals, whereas $E_{inter}(t,C)$ depends on the concentration. It is noted that C is not the concentration of on-resonant spins or C_6H_{11} radicals but is the total concentration of C_6H_{11} and solvent radicals, since the longitudinal relaxation takes place both between on- and on-resonant spins and between on- and off-resonant spins.

Determination of the intrapair separation distance from an observed longitudinal relaxation necessitates the extraction of $E_{iso}(t,C)$ from the observed relaxation. The procedure of the extraction will be shown in the following section.

The longitudinal relaxation was measured with the homemade spectrometer. The widths of 40, 60, and 60 ns were used for the saturation pulse and the first and the refocusing pulses, respectively. The intensity of the saturation pulse was three times those of the first and the third pulses. The two pulse ESE signals were measured at 77 K by fixing τ at 0.93 μs.

Results and Discussion

Effect of Scavenger Concentration. Figure 3 shows the transverse relaxation of CD_2OD radicals in CD_3OD + 5 vol % D_2O obtained by means of the 2 + 1 ESE method. The ESE intensities at $t < 0.3$ μs and at $t > 1.8$ μs were trustless due to interference effect by a defocusing pulse. Because the observed relaxation is the product of relaxations due to intra- and interpair
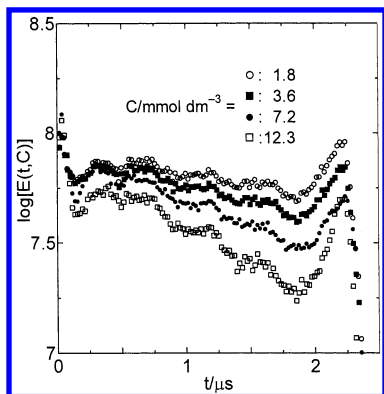
Figure 3. Observed 2 + 1 ESE relaxation of CD_2OD radicals at 77 K in CD_3OD + 5 vol % D_2O. C is the concentration of CD_2OD radicals.
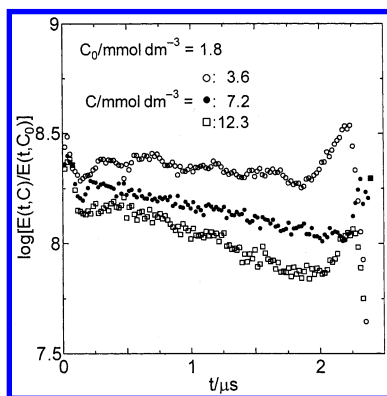

Figure 4. 2 + 1 ESE relaxation of CD_2OD radicals in CD_3OD + 5 vol % D_2O due to interpair spin−spin interaction. C and C_0 are the concentrations of CD_2OD radicals.

Figure 5. Rate constants for the 2 + 1 ESE relaxation of CD_2OD radicals in CD_3OD + 5 vol % D_2O due to interpair spin−spin interaction.

Figure 6. 2 + 1 ESE relaxation of CD_2OD radicals in CD_3OD + 5 vol % D_2O due to intrapair spin−spin interaction. The concentration of CD_2OD radicals is 1.8 mmol/dm^3 for all of the samples.

interactions, as $E(t,C) = E_0(C) E_{\mathrm{intra}}(t) E_{\mathrm{inter}}(t,C)$, the relaxation due solely to the interpair interaction is extracted by taking the intensity ratio of ESE signals from two samples with the same scavenger concentration and different radical concentrations, C and C_0, as

$$E(t,C)/E(t,C_0) = [E_0(C)/E_0(C_0)][E_{\mathrm{inter}}(t,C)/E_{\mathrm{inter}}(t,C_0)] \quad (3)$$

It is suitable to select the lowest radical concentration as C_0, since the relative contribution of the intrapair interaction to the relaxation is the highest for a sample with the lowest concentration.

Figure 4 shows the relaxation thus extracted from the ESE signals shown in Figure 3 with $C_0 = 1.8$ mmol/dm^3. The relaxation due to the interpair interaction is expressed by

$$E_{\mathrm{inter}}(t,C)/E_{\mathrm{inter}}(t,C_0) = \exp[-k_{\mathrm{T}}(C - C_0)t] \quad (4)$$

where $k_{\mathrm{T}}(C - C_0)$ is the rate constant for the relaxation at the radical concentration of $C - C_0$. Figure 5 shows the rate constants for the relaxation thus obtained. The functional shape of $E_{\mathrm{inter}}(t,C)/E_{\mathrm{inter}}(t,C_0)$ accords well with the theoretical prediction that the relaxation due to interpair interaction is expressed by $\exp(-kCt)$.[14] The contribution of intrapair interaction, $E_{\mathrm{intra}}(t)$, was then extracted from the observed relaxation curve as

$$E_{\mathrm{intra}}(t) = [E(t,C) \exp(k_{\mathrm{T}}Ct)]/E_0(C) \quad (5)$$

Here $C = C_0$ should be used for minimizing errors arising from the elimination of the interpair interaction from the observed relaxation, since the contribution of the interpair interaction is the lowest at the lowest radical concentration.
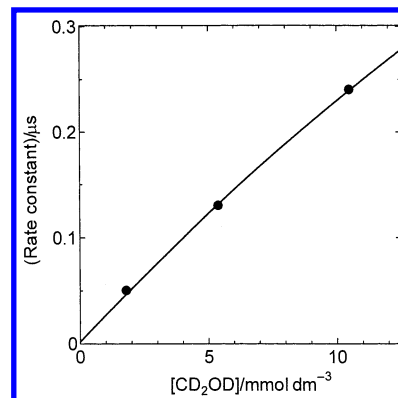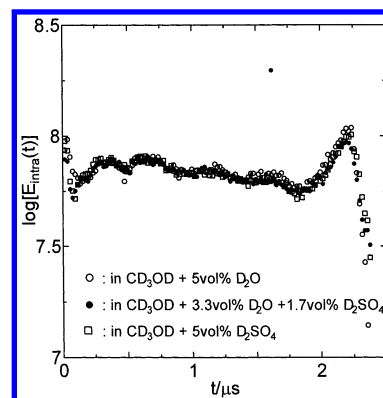
The same procedure was used for extracting $E_{\mathrm{intra}}(t)$ for methanol matrices containing D_2SO_4 as an electron scavenger. Figure 6 compares $E_{\mathrm{intra}}(t)$ for CD_3OD + 5 vol % D_2O, CD_3OD + 3.3 vol % D_2O + 1.7 vol % D_2SO_4, and CD_3OD + 5 vol % D_2SO_4. The relaxation curves shown in Figure 6 are for samples with the radical concentration of 1.8 mmol/dm^{-3}. The relaxation curves due to the intrapair interaction are, however, independent of the radical concentration. The three $E_{\mathrm{intra}}(t)$ completely overlap with each other, which indicates that the intrapair distance does not depend on the concentration of the electron scavenger.

In the present study, the distribution function $P(r)$ of the intrapair distance was not calculated from $E_{\mathrm{intra}}(t)$, since the intensities of microwave pulses affecting the decay rate of 2 + 1 ESE signals were not measured. However, it is evident that $P(r)$ is the same as that for CD_3OD + 0.45 vol % D_2SO_4 that was determined in our previous work by the 2 + 1 ESE method to be $P(r) = 3\exp[-(r/r_0)^6]/(2\pi^{3/2}r_0^3)$, where $r_0 = r_{\mathrm{m}}/0.764$ and $r_{\mathrm{m}} = 5.6$ nm is a distance within which a half of the partner radical is found.[6] Because the increase of the concentration of the electron scavenger more than 10 times does not cause the shortening of the intrapair distance, it is evident that the determinant process for the reaction of electrons with the scavenger is not the encounter with the scavenger but the slowing down of the electrons. Electrons may be captured by scavenger molecules after losing most of their kinetic energy. The distance necessary for losing their excess kinetic energy can be called the thermalization distance. Because the mean intrapair distance is the same as that in neat CD_3OD, it is also quite reasonable to assume that the electrons are captured by
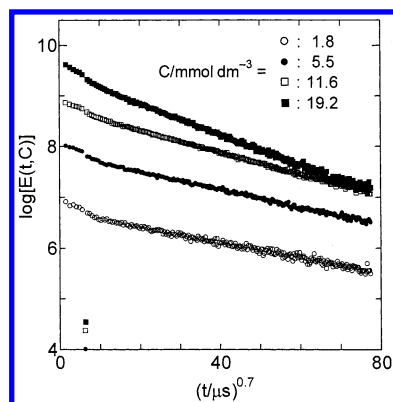
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Figure 7. Observed longitudinal spin relaxation of C_6H_{11} radicals at 77 K in the mixture matrix of $(CD_3)_2CDOD$ and 48 vol % $C_6D_{11}CD_3$. C is the total concentration of C_6H_{11} and solvent radicals.

Figure 8. Longitudinal spin relaxation of C_6H_{11} radicals in the mixture matrix of $(CD_3)_2CDOD$ and 48 vol % $C_6H_{11}CD_3$ due to interpair spin−spin interaction. C and C_0 are the total concentrations of C_6H_{11} and solvent radicals.

scavenger molecules after being stabilized as trapped electrons, as

$$e^- \text{ (hot)} \rightarrow e^- \text{ (thermal)} \rightarrow e^- \text{ (trapped)}$$

$$e^- \text{ (trapped)} + D^+ \rightarrow D$$
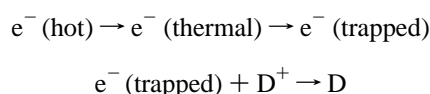
The enhancement of the spatial resolution by the increase of the concentration of electron scavengers may therefore not be expected.

Effect of Matrix Composition. Because the thermalization distance of electrons may depend on electronic interactions between electrons and matrix molecules, such as charge−dipole interactions, addition of nonpolar molecules to polar alcohol matrices is expected to increase the intrapair distance and therefore to decrease the longitudinal spin relaxation of free radicals.

Figure 7 shows the observed longitudinal spin relaxation of C_6H_{11} radicals in $(CD_3)_2CDOD$ + 5 vol % $C_6H_{11}Cl$ + 48 vol % $C_6D_{11}CD_3$. Decrease of the concentration of electron scavenger $C_6H_{11}Cl$ to 2.5 vol % did not change the relaxation behavior, which certifies that the intrapair distance between C_6H_{11} and solvent radicals depends not on the concentration of the scavenger but on the thermalization distance of electrons. Increase of the relaxation rate with increasing concentration of C_6H_{11} radicals is due to the increase of interpair magnetic dipole−dipole interactions, which leads to the increase of the rate of cross-relaxation and spin−lattice relaxation. Using the relation of eq 2, $E(t,C) = E_0(C) E_{iso}(t) E_{intra}(t) E_{inter}(t,C)$, the relaxation due solely to the interpair interaction is extracted by taking the intensity ratio of ESE signals from two samples with the same matrix composition and different total radical concentrations, C and C_0, as

$$E(t,C)/E(t,C_0) = [E_0(C)/E_0(C_0)][E_{inter}(t,C)/E_{inter}(t,C_0)] \quad (6)$$

It is suitable to select the lowest radical concentration as C_0, since the relative contribution of the intrapair interaction to the relaxation is the highest for a sample with the lowest concentration. Figure 8 shows the relaxation thus extracted from the ESE signals shown in Figure 7 with $C_0 = 1.8$ mmol/dm^3. The relaxation due to the interpair interactions is expressed by

$$E_{inter}(t,C)/E_{inter}(t,C_0) = \exp[-k_L(C - C_0)t^{0.7}] \quad (7)$$

where $k_L(C - C_0)$ is the rate constant for the relaxation at the concentration of $C - C_0$. The functional shape of $E_{inter}(t,C)/E_{inter}(t,C_0)$ is close to $\exp(-kCt^{0.5})$, which is theoretically
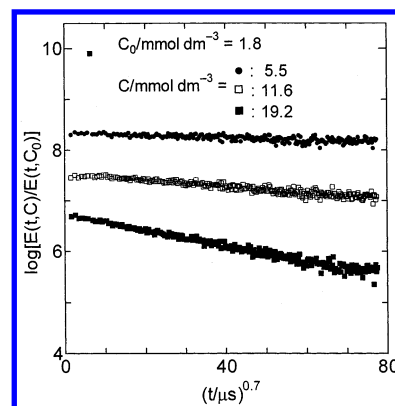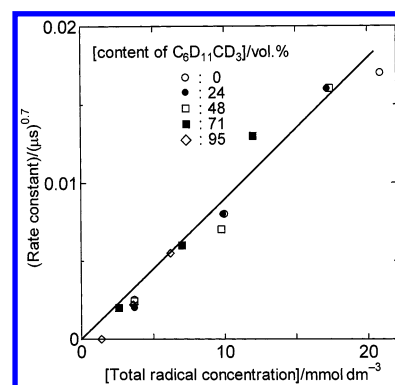

Figure 9. Rate constants for the longitudinal spin relaxation of C_6H_{11} radicals in the mixture matrices of $(CD_3)_2CDOD$ and $C_6D_{11}CD_3$ arising from interpair spin−spin interaction.

obtained under the assumption of random distribution of dilute electron spins around observed electron spins.[18]

Figure 9 shows the rate constants for the relaxation by the interpair interactions thus obtained. The value of k_L scarcely depends on the concentration of $C_6D_{11}CD_3$, which indicates that the nature of matrix affecting the longitudinal relaxation does not depend on the matrix composition. This strongly suggests that $E_{iso}(t)$ is also independent of the matrix composition.

Because the rate constant for the interpair interaction linearly depends on the radical concentration, it is reasonable to assume that $E_{inter}(t,C) = \exp(-k_L Ct^{0.7})$. The longitudinal relaxation of isolated radical pairs without contribution of the interpair interaction is then derived by substituting $E_{inter}(t,C) = \exp(-k_L Ct^{0.7})$ into eq 2, as

$$E(t,C)/E_{inter}(t,C) = E(t,C) \exp(k_L Ct^{0.7}) =$$
$$E_0(C) E_{intra}(t) E_{iso}(t) \quad (8)$$

Figure 10 shows the longitudinal relaxation curves thus obtained from the observed relaxation curves for samples with the total radical concentrations of 1.8 mmol/dm^3 for 0 vol %, 24 vol %, and 48 vol % $C_6D_{11}CD_3$, 1.2 mmol/dm^3 for 71 vol % C_6D_{11}-CD_3, and 0.6 mmol/dm^3 for 95 vol % $C_6D_{11}CD_3$. The relaxation curves are, however, independent of the radical concentration since the contribution of the interpair interaction is eliminated from the observed relaxation curves. Although the rate of the relaxation at $t < 500$ μs decreases with increasing concentration of $C_6D_{11}CD_3$, they are the same at $t > 500$ μs and follow an exponential function of $\exp(-k_I t)$. The decay component of $\exp(-k_I t)$ is obviously due to $E_{iso}(t)$. The contribution of the
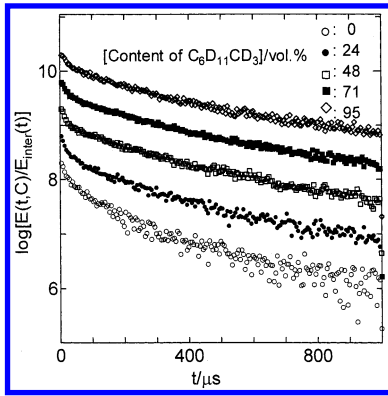
Figure 10. Longitudinal spin relaxation of isolated pairs of C_6H_{11} and solvent radicals in the mixture matrices of $(CD_3)_2CDOD$ and $C_6D_{11}CD_3$ obtained by eliminating the contribution of interpair spin−spin interaction from observed relaxation curves. The total concentrations of C_6H_{11} and solvent radicals are 1.8 mmol/dm³ for 0, 24, and 48 vol % $C_6D_{11}CD_3$, 1.2 mmol/dm³ for 71 vol % $C_6D_{11}CD_3$, and 0.6 mmol/dm³ for 95 vol % $C_6D_{11}CD_3$.

Figure 11. Longitudinal spin relaxation of C_6H_{11} radicals in the mixture matrices of $(CD_3)_2CDOD$ and $C_6D_{11}CD_3$ due solely to intrapair spin−spin interaction. The total concentrations of C_6H_{11} and solvent radicals are 1.8 mmol/dm³ for 0, 24, and 48 vol % $C_6D_{11}CD_3$, 1.2 mmol/dm³ for 71 vol % $C_6D_{11}CD_3$, and 0.6 mmol/dm³ for 95 vol % $C_6D_{11}CD_3$.
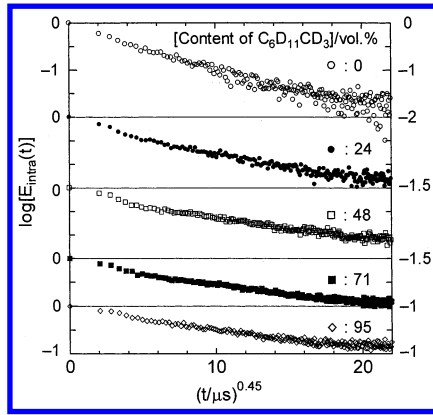
TABLE 1: Longitudinal Spin Relaxation Components of C_6H_{11} Radicals in γ-Irradiated Mixture Matrices of $C(CD_3)_2DOD$, $C_6D_{11}CD_3$, and 5 Vol % $C_6H_{11}Cl$

vol % of $C_6D_{11}CD_3$	$E_{inter}(t,C)$ C (mol dm⁻³)	$E_{iso}(t)$	$E_{intra}(t)$	$r_{s,m}$ (nm)^b
0	$\exp(-0.9Ct^{0.7})$	$\exp(-0.0007t)$	$\exp(-0.10t^{0.45})$	5.3
24	$\exp(-0.9Ct^{0.7})$	$\exp(-0.0007t)$	$\exp(-0.065t^{0.45})$	6.2
48	$\exp(-0.9Ct^{0.7})$	$\exp(-0.0007t)$	$\exp(-0.050t^{0.45})$	6.9
71	$\exp(-0Ct^{0.7})$	$\exp(-0.0007t)$	$\exp(-0.044t^{0.45})$	7.2
95	$\exp(-0.9Ct^{0.7})$	$\exp(-0.0007t)$	$\exp(-0.042t^{0.45})$	7.3

^{a} t is in μs. ^{b} r_m is a mean intrapair distance within which a half of the partner radical is found.

intrapair interaction to the relaxation is finally extracted by using the equation

$$E_{intra}(t) = [E(t,C)\exp(k_L Ct^{0.7})\exp(k_I t)]/E_0(C) \quad (9)$$

Figure 11 shows the longitudinal relaxation by the intrapair interaction. The relaxation rate decreases with increasing concentration of $C_6D_{11}CD_3$, which indicates that the intrapair or the thermalization distance increases with increasing concentration. The relaxation terms contributing to the observed longitudinal relaxation are summarized in Table 1. The relax-
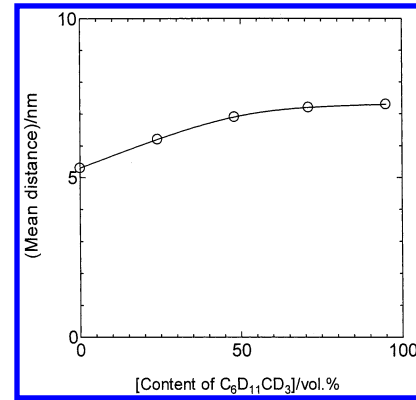

Figure 12. Mean intrapair distances of C_6H_{11}−solvent radical pairs in γ-irradiated glassy matrices composed of $(CD_3)_2CDOD$, $C_6D_{11}CD_3$, and 5 vol % of $C_6H_{11}Cl$.

ation due to the intrapair interaction is approximately expressed by

$$E_{intra}(t) = \exp(k_s t^{0.45}) \quad (10)$$

where k_s is the rate constant for the relaxation due to intrapair spin−spin interaction in a matrix containing s vol % of $C_6D_{11}CD_3$.

Intrapair distances between C_6H_{11} and solvent radicals can be obtained from $E_{intra}(t)$ as follows. The longitudinal relaxation due to intrapair magnetic dipole−dipole interaction is given by[6]

$$E_{intra}(t) = \int_0^\infty dr \int_0^\pi 2\pi r^2 P_s(r) \times$$
$$\exp[-kt(1 - 3\cos^2\theta)^2/r^6]\sin\theta \, d\theta \quad (11)$$

where r is an intrapair distance, $P_s(r)$ is the distribution function of the distance for a matrix containing s vol % of $C_6D_{11}CD_3$, and k is a constant that is independent of the matrix composition. Assuming the functional shape of the distribution to be the same for all of the matrices, the distribution function can be expressed with that of a standard sample containing no $C_6D_{11}CD_3$, $P_0(r)$, as

$$P_s(r) = P_0(r \cdot r_{0,m}/r_{s,m}) = P_0(r/\alpha_s) \quad (12)$$

where $r_{0,m}$ and $r_{s,m}$ are mean intrapair distances within which a half of the partner radical is found, and $\alpha_s = r_{s,m}/r_{0,m}$. The mean distance $r_{0,m}$ has already been determined by the 2 + 1 ESE method to be 5.3 nm. Using eq 12, eq 11 is rewritten as

$$E_{intra}(t) \propto \int_0^\infty d(r/\alpha_s) \int_0^\pi 2\pi (r/\alpha_s)^2 P_0(r/\alpha_s) \neq$$
$$\exp[-k(t/\alpha_s^6)(1 - 3\cos^2\theta)^2/(r/\alpha_s)^6]\sin\theta \, d\theta =$$
$$E_{0,intra}(t/\alpha_s^6) \quad (13)$$

where $E_{0,intra}(t)$ is the ESE decay of the standard sample due to intrapair spin−spin interaction. The above equation shows that the relaxation curves at different s overlap with each other if time t is normalized with $(r_{s,m})$.[6] Because $E_{0,intra}(t/\alpha_s^6)$ is equal to the observed $E_{intra}(t)$ that is approximately expressed by $\exp(-k_s t^{0.45})$, we obtain

$$k_s t^{0.45} = k_0(t/\alpha_s^6)^{0.45} \quad \therefore \quad r_{s,m} = (k_0/k_s)^{1/2.7}r_{0,m} \quad (14)$$

where k_0 is the rate constant for the standard sample containing no $C_6D_{11}CD_3$.

Figure 12 shows the mean intrapair distances thus obtained. The intrapair distance increases with decreasing the concentra-

Migration Distances of Electrons in Organic Solids

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tion of polar alcohol molecules, which indicates that charge−dipole interactions between electrons and polar molecules play significant roles in the dissipation of the excess kinetic energy of electrons. Electrons ejected from matrix molecules by ionizing radiation are slowed by giving their excess kinetic energy to matrix molecules in the forms of electronic, vibrational, rotational, and phonon excitations. Interactions causing these excitations are generally induced by short and long range interactions. The short range interaction is essentially the inelastic collision of electrons with matrix molecules through the overlapping of the electronic wave functions of electrons and matrix molecules. The long range interaction is charge−dipole interactions between electrons and matrix molecules. The long range interactions causing the vibrational, rotational, and phonon excitations increase with increasing the permanent dipole moment of matrix molecules. Addition of polar alcohol molecules into nonpolar matrix therefore reduces the thermalization distance.

Although the thermalization distance of electrons in solids has not been studied, those in nonpolar liquids have been determined by means of electron conductivity measurements. The mean thermalization distance in liquid cyclohexane[19] at 293 K (0.025 eV) is 7.3 nm, which is equal to the mean distance in methylcyclohexane at 77 K (0.0063 eV). The difference of the temperature does not affect the thermalization distance, which indicates that electrons are captured by trapping sites or scavengers before their exact thermalization.

Conclusion

The intrapair distance of radical pairs generated in resist materials by ionizing radiation determines the final resolution of the radiation resists. The intrapair distance is in turn determined by the distance necessary for losing the excess kinetic energy of electrons ejected from resist molecules by ionizing radiation. The intrapair distance cannot be shortened by increasing the concentration of electron scavengers, since the electrons react scavengers after losing their excess kinetic energy. The distance for losing the excess energy is shorter in matrices containing more polar molecules, so that the final resolution can be improved by adding polar molecules into resist materials.

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