

# Polymers Having Stable Radicals: Electrochemical and Chemical Behaviors of the Polymer Having Nitroxyls.

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As a part of this series on polymers having stable radicals, evaluation of oxidation-reduction potentials by polarography and oxidative reactivities toward hydrazine and hydrazobenzene has been dealt with on nitroxyl stable radicals. Poly (4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (III) as a polymer having stable radicals, and its prototypes, 4-oxy-2,2,6,6-tetramethylpiperidine-1-oxyl (I) and 4-isobutyroyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (II), have been employed for purpose of the study.

The electrode reactions of (I) in a range of pH. 8.0-10.1 in aqueous media were observed to be quasi-reversible and the reduction half-wave potentials ( $E_{1/2}$ ) being between 0.120-0.200 V (vs. SCE) depending on pH. In the other pH. regions, the reactions seemed to be irreversible and the reduction halfwave potentials depended upon pH. as well. In addition, polarographic data in a non-aqueous medium ensured that all the nitroxyls (I), (II) and (III) might have the same redox potential values.

The oxidation reactions, using (I), (II), and (III), on hydrazine and hydrazobenzene have been performed, of which extent was pursued spectrophotometrically. From the kinetics, it was elucidated that, (1) the reactions were bimolecular, (2) the rate determinant steps were in the first hydrogen abstraction and, (3) the reactions with hydrazine were reaction controlled ( $\Delta E$ ; 11.2-11.3 Kcal/mol) while the reactions with hydrazobenzene were diffusion controlled ( $\Delta E$ ; 5.9-3.9 Kcal/mol). Thermodynamic analysis indicated that the case of reaction with hydrazobenzene differed mechanistically whether the reactant was monomeric (II) or polymeric (III) ( $\Delta S^\ddagger$ : -17.9 e. u., (II); -21.8 e. u., (III), at 20°C in THF) and that a steric hindrance presumably took place in the latter.

## INTRODUCTION

Since the discovery of the nitroxyl radicals, a class of stable organic free radicals, in 1956<sup>1),2)</sup>, it was not until recently that applications of these compounds were found. Up to the present, these stable radical compounds have been of use in the field of biochemistry

as spin-labeling reagents<sup>3)-5)</sup> and the formation of stable radicals has become a useful tool as spin-trapping technique<sup>6)</sup>. Thus, chemistry and synthesis of stable radicals are now receiving increasing attention<sup>7)-9)</sup> in new research areas. In the previous papers<sup>10),11)</sup> of this series on the polymer having stable radicals, poly (4-methacryloyl-amino-/-oxy-2,2,6,6-tetramethylpiperidine-1-oxyl) s, a new synthetic approach through their precursor polymers has been presented, and some of their physicochemical and electrochemical properties such as UV, IR, EPR, and reduction potentials etc., have been discussed. The discussion has been focused

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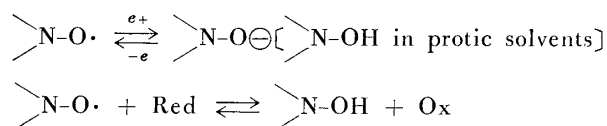
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also on comparison with their prototype of low molecular weight to define the behaviors of polymeric and monomeric nitroxyl radicals, taking account of dense distribution of unpaired electrons along a polymer chain, which may have a relation to any physical or chemical changes if these happened. In fact, some of differences in EPR have been found to exist between them<sup>11)</sup>.

In this report, we are concerned on reduction-oxidation properties of nitroxyls as described below:

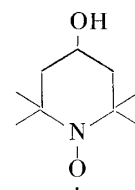


Especially, it attracts our attention that the latter is recently referred as a color developer<sup>12)</sup> among many other possible applications. Here, we present the polarographic results which confirmed the previous data under more sophisticated conditions and the chemical reactivities toward hydrazine and hydrazobenzene of which elucidation could be of the basis for more complicated redox reactions involving nitroxyl radicals.

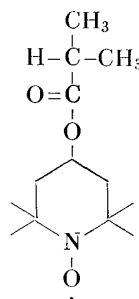
## RESULTS AND DISCUSSION

### Evaluations of Reduction-Oxidation Potentials

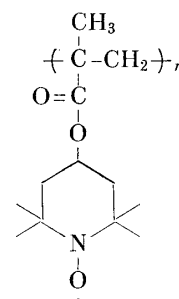
In our preceding paper<sup>11)</sup>, reduction half-wave potentials of monomeric (I), (II) and polymeric nitroxyls (III) were evaluated by means of polarography using a dropping mercury electrode vs. a mercury pool in pyridine and acetonitrile, and it was found that their half-wave potentials were comparable among them in the systems. The compounds which have been used are shown next:



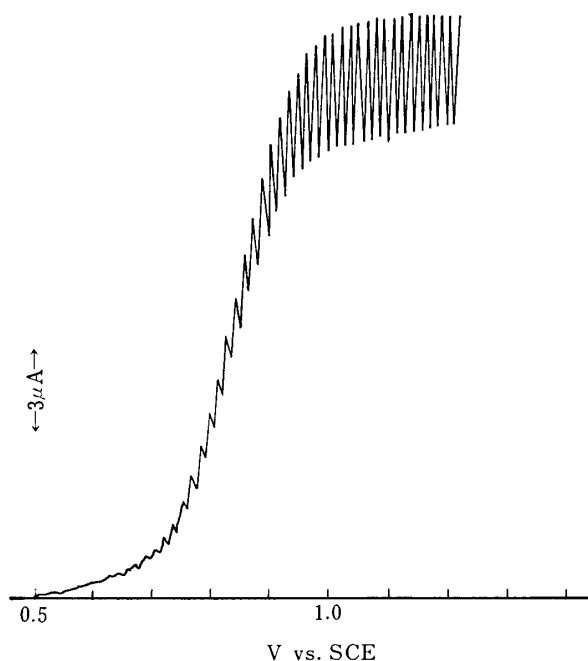
4-Oxy-2,2,6,6-tetramethylpiperidine-1-oxyl  
Monomeric radical  
(I)



4-Isobutyroyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl  
Monomeric radical  
(II)



Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl)  
Polymeric radical  
(III)



**Fig. 1** Polarographic current-voltage curve of polymeric oxyl (III): Sample concentration,  $5 \times 10^{-4}$  mol/l as radical; electrode, DME vs. SCE; solvent, pyridine; supporting electrolyte, tetra-*n*-butylammonium bromide, 0.1 M; temperature, 20°C.

In order to ensure the former results it was attempted to conduct polarography on the same compounds, (I), (II), and (III), by using a dropping mercury electrode (DME) and a standard calomel electrode (SCE) as a reference in stead of a mercury pool (Hg). The choice of the SCE is only just due to its higher stability than that of the mercury pool. A typical example of the polarograms is shown in Fig. 1, and  $E_{1/2}$ 's, diffusion currents ( $i_d$ ) and slopes of  $E$  vs.  $\log\{i/(i_d-i)\}$  are summarized in Table I.

**Table I** Reduction Half-Wave Potentials of Polymeric Nitroxyl (III), and their Related Compounds, (I), (II), in Non-aqueous Medium\*.

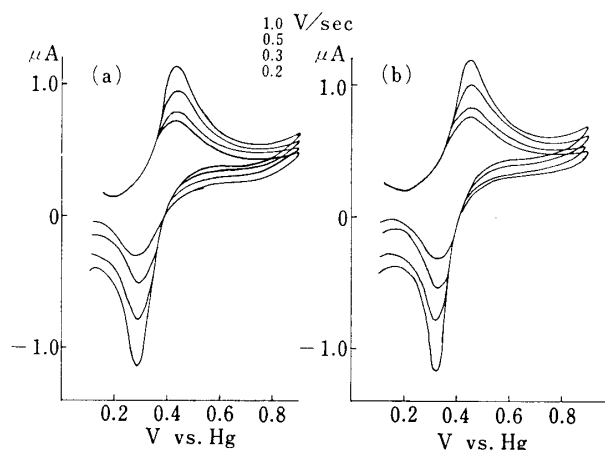
	$E_{1/2}$	$i_d$ ( $\mu\text{A}$ )	Slope (mV)
I	$0.94 \pm 0.02$	17.7	99
II	$0.94 \pm 0.02$	20.0	97
III	$0.94 \pm 0.02$	18.0	100

\* Experimental conditions are given in Fig. 1.

Although the values of  $E$  are inevitably accompanied by liquid junction potential in a non-aqueous medium, the factor could be disregarded when the reductive property is discussed relatively among the compounds used. Based on view of the point, it can be concluded again from the above results that the levels of oxidation power are equal of the three. As the slopes indicated in Table I are deviated from 60 mv which is theoretically obtainable in the case of reversible one-electron reduction, the electrode reactions in the systems are suggested to be irreversible. Furthermore, both the polarograms of polymeric and monomeric oxyls show such a similar one-step and one electron reduction wave that there would not exist any interactions among radicals on the polymers with which to affect their polaro-

graphic behaviors; the energy levels of the lowest vacant orbitals of these nitroxyls, which are closely associated with reduction potential and electron affinity, are identical each other.

In order to examine chemical decay of nitroxyls during the course of reduction and subsequent oxidation, cyclic voltammetry was employed for (II) and (III) under the similar conditions to those given to polarography. The cyclic voltammograms obtained with change of the electrode potential scan rate are illustrated in Fig. 2.



**Fig. 2** Cyclic voltammograms of (II) and (III): (a), monomeric oxyl (II); (b) polymeric oxyl (III); sample concentration,  $5 \times 10^{-4}$  mol/l as radical; electrode, DME vs. Hg; solvent, pyridine; supporting electrolyte, tetra-*n*-butylammonium bromide, 0.1 M; temperature, 20°C; scan rate, as indicated in figure.

Fig. 2 indicates clearly oxidation and reduction waves on both substrates and that the values for peak potentials move linearly with increasing peak currents. The cathodic peaks become more cathodic and the anodic peaks become more anodic as the scan rate is increased. Consequently, the peak potentials were determined by extrapolating, for a range of scan rates, the line through the peak maxima to zero current. The values thus obtained,

together with the corresponding anodic and cathodic currents, are presented in Table II.

**Table II** Cyclic Voltammetric Values Obtained for One Electron Process on (II) and (III)\*<sup>1,2,3</sup>.

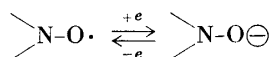
	(II)	(III)
Peak Potential (V)		
$E_{pa}$ (anodic)	-0.42	-0.43
$E_{pc}$ (cathodic)	-0.33	-0.34
$E_{pa}-E_{pc}$	0.09	0.09
Peak current ( $\mu A$ )		
$i_{pa}$ (anodic)	0.80	0.80
$i_{pc}$ (cathodic)	0.95	1.00

\*<sup>1</sup> Experimental conditions are given in Fig. 2.

\*<sup>2</sup> Electrode scan rate is 0.5 V/sec.

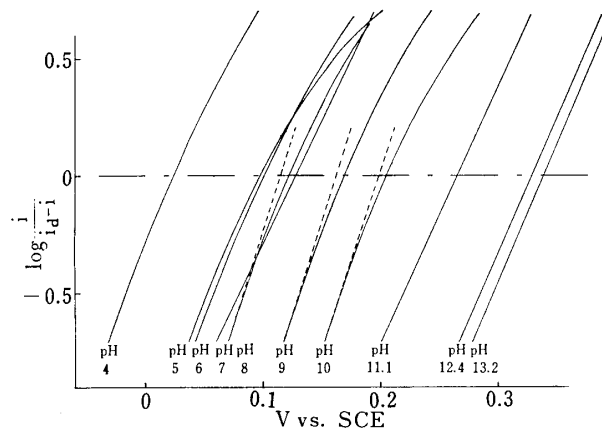
\*<sup>3</sup> The peak potential was measured by extrapolating them to zero current.

It should be noted that the cathode and anode peaks are of similar heights, thus chemical reactions of any species subsequent to electron transfer are not incorporated in these scan periods; actually no chemical decay during the electrode reaction and the process being chemically reversible as shown below;



Because of insolubility of the materials concerned to water, polarography has been performed in non-aqueous media to evaluate reductive characteristics. In spite of making sure that the reduction potentials of the three compounds, (I), (II), and (III), were practically same, the values obtained there have been a sort of relative. This has led us to the investigation of a polarography in an aqueous medium, using the sole water soluble compound, (I), of the three, for evaluating the genuine reduction potentials. Providing that the other nitroxyls will be of same values as above-mentioned, estimation of considerably valid reduction pot-

entials would be possible, this time, while the problem of irreversibility of electrode reactions still remains. Polarography was carried out on (I) at a variety of pH values controlled by the Kolthoff buffer solutions. The logarithmic current-voltage plots are indicated in Fig. 3, and numerical values from which obtained are summarized in Table III.



**Fig. 3** Logarithmic current-voltage plots of monomeric nitroxyl (I) at a variety of pH's: Sample concentration,  $5 \times 10^{-4}$  as radical; electrode, DME vs. SCE; medium, aqueous solution of which pH was controlled by the Kolthoff buffer solutions; supporting electrolyte, KCl, 0.1 M; 20°C; temperature, pH, as indicated in figure.

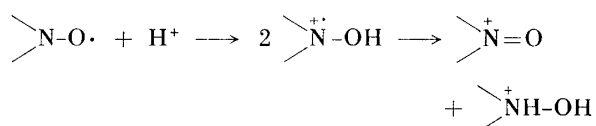
**Table III** Reduction Half-Wave Potentials of (III) at Various pH's in Aqueous Medium\*<sup>1</sup>.

pH	$E'_{L/2}$ (v)	$E_{L/2}$ (v)	Slope (mv)* <sup>2</sup>
4.0	-0.020		92
5.0	-0.100		92
6.0	-1.01		86
7.0	-0.129		97
8.0	-0.123	-0.120	78
9.0	-0.168	-0.162	78
10.1	-0.206	-0.200	78
11.1	-0.266		92
12.4	-0.330		89
13.4	-0.340		90

\*<sup>1</sup> Experimental conditions are given in Fig. 3.

\*<sup>2</sup> Measured between -0.3 and 0.3 A

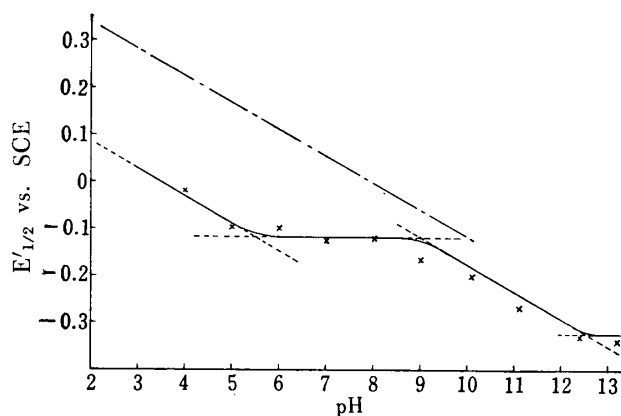
As indicated by the slopes, polarographic behavior of the nitroxyls appeared to be irreversible in the most cases, but those at pH. 8.0, 9.0 and 10.1 which were likely to be quasi-reversible. In Table III,  $E'_{1/2}$ 's are apparent reductive half-wave potentials obtained directly from the polarograms.  $E'_{1/2}$ 's of quasi-reversible systems were corrected for thermodynamically probable ones by extrapolating the tangent of a reversible part to zero value of the axis of ordinate and taking E value read for the potential. The corrected potentials are denoted as  $E_{1/2}$  in Table III. The irreversibility is possibly due to<sup>13</sup>: (1) Subsequent chemical reaction. (2) Irreversibility of the electron transfer process. The symmetry of the anodic and cathodic peaks and the equal peak separation eliminated the first possibility as already mentioned. In acidic media, however, there exists a possibility of (1) due to the chemical reaction arising by disproportionation of protonated nitroxyls as shown<sup>14,15</sup>;



This effect is presumably one of the causes of the irreversibility. As no chemical reaction has been reported under alkaline state, only (2) would contribute in an alkaline side.

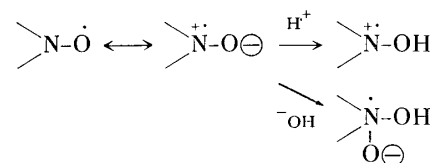
The pH dependency of  $E'_{1/2}$  is depicted in Fig. 4 together with that of a 1,4-p-quinone-1,4-p-hydroquinone system, where it is obvious that  $\text{>N-O}\cdot$  works as a weaker oxidant than quinone and *vice versa* on  $\text{>N-OH}$  as a reductant.

As nitroxyls are known to have the following resonance structures, the protonated ionic structure positively charged will enhance their oxidative power in an acidic medium while



**Fig. 4** pH dependency of reductive half-wave potentials of monomeric nitroxyl (I): Measuring conditions are identical with Fig. 3; —x— (I), - - - - hydroquinone.

the hydroxylated one negatively charged in an alkaline medium degrades it. The proposed processes are included below.

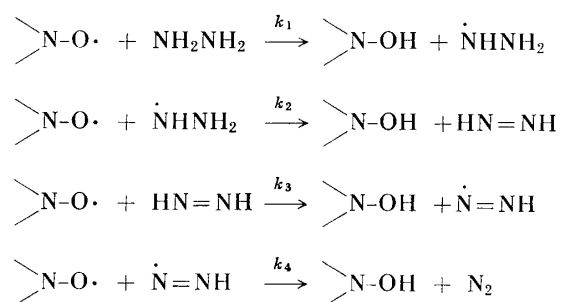


On the other hand, quinone does not take such an ionic structure that resulted in exclusion of unpredictable dependency upon pH.

More detailed consideration and calculations will be published elsewhere.

#### Oxidation Reactions by Nitroxyls.

Reaction with hydrazine<sup>17</sup>): The reaction of nitroxyls with hydrazine can be written in the following scheme;



If it is assumed that  $k_1 \ll k_2, k_3, k_4$  the rate of disappearance of the nitroxyl is of a first-order

with respect to the radical and the kinetic equation can be

$$\frac{d[>\text{NO}\cdot]}{dt} = 4k_1[>\text{NO}\cdot][\text{hydrazine}]$$

when hydrazine presents excess enough to remain unchanged during the reaction, the over-all reaction appears as a first-order and the rate constant observed ( $k_0$ ) should be

$$k_0 = 4k_1[\text{hydrazine}]$$

To study the kinetics, the reactions were carried out on (I), (II), and (III) in the presence of excess hydrazine in a mixture of methanol-pyridine (1:1) at 5°, 15°, 25°, and 35°. The course of the reaction was followed by measuring optical density at a visible region due to  $n-\pi^*$  electronic transition of nitroxyl radicals; (I) at 448 nm, (II) at 455 nm, (III) at 457 nm. The results reveal that the reactions are of first-order as for nitroxyls. A typical first-order plot for the reaction is shown in Fig. 5.

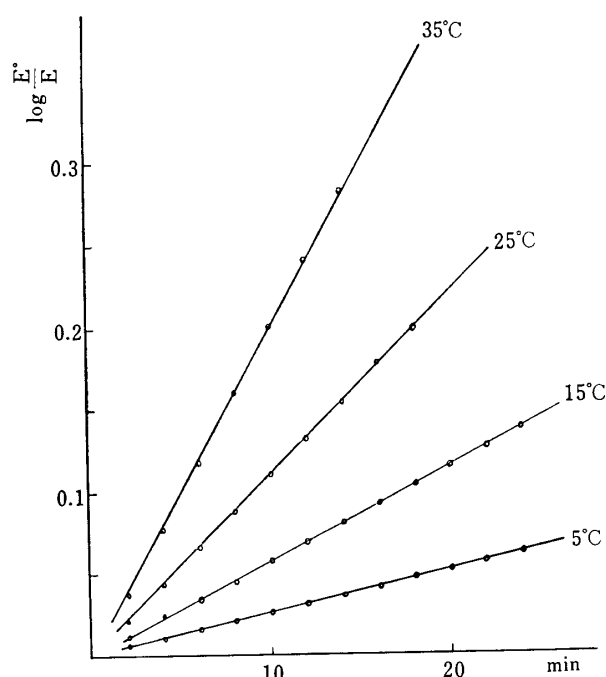


Fig. 5 First order plot of the reaction between polymeric oxyl (III) and hydrazine in a methanol-pyridine (1:1) mixture.

The apparent first-order rate constants ( $k_0$ ) and the second-order ones ( $k_1$ ) obtained by taking hydrazine concentration into consideration, are summarized in Table IV.

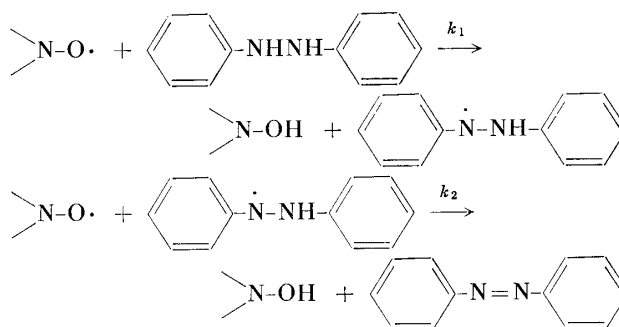
Table IV Rate Constants of the Reactions of (I), (II) and (III)\*<sup>1</sup>, with Hydrazine\*<sup>2</sup>.

	T°C	$k_0(\text{min}^{-1}) \times 10$	$k^1(1/\text{mol}\cdot\text{sec}) \times 10^5$
Model I	5	0.096	4.08
	15	0.19	8.08
	25	0.38	16.16
	30	0.53	22.53
	35	0.68	28.91
Model II	5	0.17	7.23
	15	0.31	13.18
	25	0.60	25.51
	30	0.84	35.71
	35	1.18	45.92
Polymer	5	0.14	5.95
	15	0.30	12.76
	25	0.59	25.09
	35	1.05	44.60

\*<sup>1</sup> Radical concentration;  $2.50 \times 10^{-2}$  mol/l.

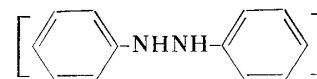
\*<sup>2</sup> Hydrazine concentration;  $9.80 \times 10^{-1}$  mol/l.

Reaction with hydrazobenzene<sup>18)</sup>: The reaction of nitroxyls is known to produce azobenzene. The reaction will undergo successively as that of hydrazine;



Assuming  $k_1 \ll k_2$ , the rate of consumption of hydrazobenzene can be

$$\frac{d[\text{C}_6\text{H}_5\text{-NHNH-C}_6\text{H}_5]}{dt} = 2k_1[\text{nitroxyl}]$$

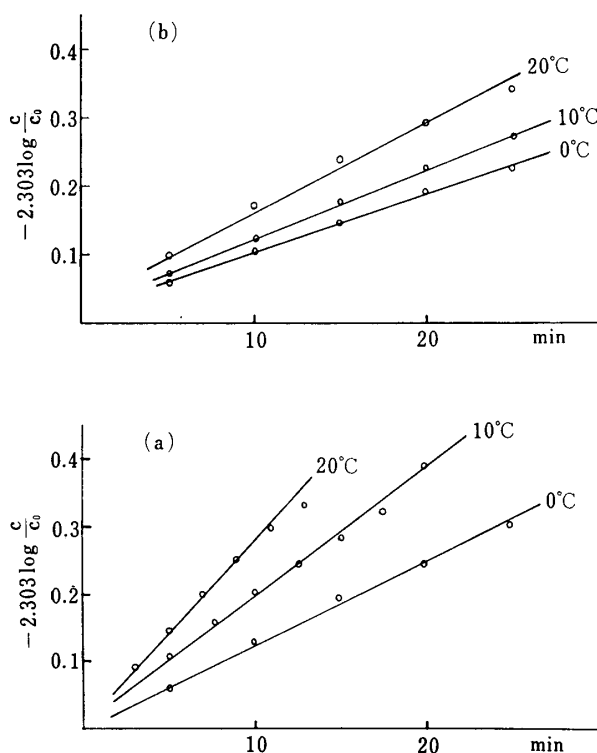


When nitroxyl is sufficiently excess, the over-all reaction order can be reduced to first-order and the rate constant observed ( $k_0$ ) should be

$$k_0 = 2k_1 [\text{nitroxyl}]$$

To establish kinetic relationship between nitroxyl and hydrazobenzene, the reaction was conducted on (II) and (III), in the presence of excess nitroxyl in contrast to the case of hydrazine, by measuring the optical density developed at 320 nm which is contributed by azobenzene formed. A first order-reaction resulted as expected, of which plot is shown in Fig. 6. The apparent first-order rate constants ( $k_0$ ) and the second-order ones ( $k_1$ ) calculated as before are listed in Table V.

Mechanistic consideration: Above two experiments help complementally support that the



**Fig. 6** First order plots of the reactions of monomeric (II) and polymeric oxyls (III), with hydrazobenzene in tetrahydrofuran: (a), in the case of (II); (b), in the case of (III).

**Table V** Rate Constants of the Reactions of (II) and (III)\*<sup>1</sup> with Hydrazobenzene\*<sup>2</sup>.

	$T^\circ\text{C}$	$k_0(\text{min}^{-1}) \times 10^{-2}$	$k_1(1/\text{mol sec}) \times 10^{-2}$
(II)	0	1.26	5.01
	10	1.90	7.56
	20	2.66	10.58
(III)	0	0.90	3.89
	10	1.13	4.90
	20	1.46	6.34

\*<sup>1</sup> Radical concentration;

$2.095 \times 10^{-3}$  mol/l for (II)

$1.920 \times 10^{-3}$  mol/l for (III)

\*<sup>2</sup> Hydrazobenzene concentration;

$0.390 \times 10^{-3}$  mol/l

order of the redox reactions, with respect to reductant (hydrazine or hydrazobenzene), is first-order and, with respect to oxidant (nitroxyls), neither second (supposing hydrazobenzene) nor fourth (supposing hydrazine) but first-order, and hence, as a whole, is second-order. This finding makes virtual the assumption that the first hydrogen abstraction process is rate determinant.

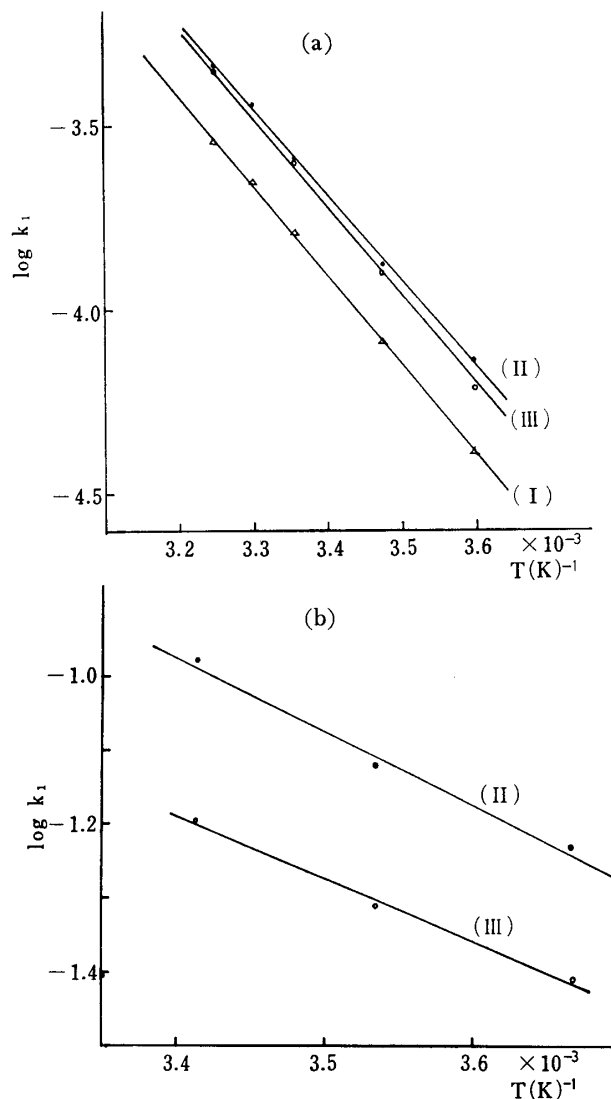
Fig. 7 illustrates the Arrhenius plots of these reactions, and the energies and entropies of activation calculated are in Table VI.

In the reaction with hydrazine, the activation energy ranged around 11.2-11.5 Kcal/mol is

**Table VI** Activation Energies ( $\Delta E$ ) and Activation Entropies ( $\Delta S^\ddagger$ ) of the Reactions of Nitroxyls, (I), (II), and (III) with Hydrazine and Hydrazobenzene.

	Hydrazine		Hydrazobenzene	
	$\Delta E$ (Kcal/mol)	$\Delta S^\ddagger$ (e. u.)	$\Delta E$ (Kcal/mol)	$\Delta S^\ddagger$ (e. u.)
(I)	$11.2 \pm 0.2$	-42.4		
(II)	$11.3 \pm 0.2$	-41.4	$5.9 \pm 0.2$	-17.9
(III)	$11.5 \pm 0.3$	-40.5	$3.9 \pm 0.2$	-21.8

Reaction medium: Hydrazine; methanol-pyridine (1:1), hydrazobenzene; tetrahydrofuran  
 $\Delta S^\ddagger$ : at 20°C



**Fig. 7** Arrhenius plots of the reactions of (I), (II) and (III), with hydrazine and hydrazobenzene: (a), reactions with hydrazine; (b), reactions with hydrazobenzene.

probable for hydrogen abstraction and the value of 4-6 Kcal/mol in the reaction with hydrazobenzene is very likely to be that of diffusion; the former seems to be reaction controlled, whereas the latter is rather diffusion controlled. This diversity in the mechanisms is also supported by the difference of  $\Delta S^\ddagger$  between both systems and would be a consequence of much easily oxidizable property of hydrazobenzene.

In the reactions with hydrazine, no particular difference in energy and entropy of activation was observed among the three compounds; all the nitroxyls, regardless whether monomeric or polymeric, were found to have a similar reactivity. In the reactions with hydrazobenzene, however, difference of  $\Delta E$  between them is pretty significant. This must effect the rate faster by 3-4 times on polymer but this factor looks like being compensated by decrease of  $\Delta S^\ddagger$ , due to a steric hindrance on the side of polymer. This contrasting issue of steric effect in the reactions with hydrazobenzene to hydrazine is well explained by bulkiness of the substrates. In the more bulky substrate, hydrazobenzene, the factor of steric effect predominated, which caused reaction the more to be influenced by bulkiness of counter-part reactant, polymeric nitroxyl.

## EXPERIMENTAL

### Materials

#### 4-Hydroxy-2, 2, 6, 6-tetramethylpiperidine.

This starting material was supplied from San-kyo Co. Ltd., and used as received, mp. 71.5°C.

#### 4-Hydroxy-2, 2, 6, 6-tetramethylpiperidine-1-

oxyl. To 800 ml of a methanolic solution containing 94 g (0.6 mole) of 4-hydroxy-2, 2, 6, 6-tetramethylpiperidine, 1.6 g of EDTA, and 1.04 g of sodium tungstate were added 120 ml of a 30% aqueous hydrogen peroxide and 120 ml of distilled water. The mixture was stirred for 30-35 hr at room temperature. The crude product was obtained by evaporation of liquid, followed by stirring in 200 ml of a saturated aqueous solution of potassium carbonate for 1 hr, filtration, and washing with distilled water. The crude product was recrystallized from cyclohexane, orange rhombic crystals, mp 72-



73°C; yield 104 g (100%). The infrared spectrum showed bands at 3400 (OH) and 1350 (NO·)  $\text{cm}^{-1}$ . Ultraviolet peaks were observed at 243 and 450 nm.

4-Isobutyroxyloxy-2, 2, 6, 6-tetramethylpiperidine-1-oxyl. In a 200 ml flask with a condenser protected by a calcium chloride drying tube, a mechanical stirrer, and a 20-ml dropping funnel, were placed 6 g (0.035 mole) of 4-hydroxy-2, 2, 6, 6-tetramethyl-piperidine-1-oxyl and 4.26 g (0.042 mole) of triethylamine. Then 4.45 g (0.042 mole) of isobutyroyl chloride dissolved in 30 ml of benzene was added dropwise, the temperature being maintained at 20-25°C under stirring. One hour after finishing the addition, the temperature of the reaction mixture was raised to 70°C and maintained for 3 hr. The reaction mixture was then subjected to vacuum distillation. The crude product which was collected at 80°C/0.4 mmHg was recrystallized from a mixture of ethanol and water (1 : 1 by weight); orange crystals; mp 54°C; yield 6.0 g (71%).

Anal. Calcd for  $\text{C}_{13}\text{H}_{24}\text{N}_1\text{O}_3$ : C, 64.46%; H, 9.92%; N, 5.79%.

Found: C, 64.40%; H, 9.95%; N, 5.86%.

4-Methacryloyloxy-2, 2, 6, 6-tetramethylpiperidine-1-oxyl. A mixture of 34.4 g (0.2 mole) of 4-hydroxy-2, 2, 6, 6-tetramethyl-piperidine-1-oxyl, 21.2 g (0.21 mole) of triethylamine and 22.0 g (0.21 mole) of methacryloyl chloride in 600 ml of dry benzene was processed as previously described in the synthesis of 4-isobutyroxyloxy-2, 2, 6, 6-tetramethylpiperidine-1-oxyl. The crude product was recrystallized from cyclohexane; orange crystals; mp 82-83°C; yield 38 g (80%).

Anal. Calcd for  $\text{C}_{13}\text{H}_{22}\text{N}_1\text{O}_3$ : C, 64.97%; H, 9.23%; N, 5.83%.

Found: C, 65.03%; H, 9.11%; N, 5.91%.

4-Methacryloyloxy-1-hydroxy-2, 2, 6, 6-tetramethylpiperidine Sulfate. In a 200-ml Erlenmeyer flask, were placed 3.21 g (0.013 mole) of 4-methacryloyloxy-2, 2, 6, 6-tetramethylpiperidine-1-oxyl dissolved in 50 ml propanol and 1.47 g (0.015 mole) concentrated  $\text{H}_2\text{SO}_4$ , and the mixture was allowed to stand at room temperature for 30 hr. The reaction mixture was concentrated to one fifth the initial volume and mixed with 150 ml of ether to precipitate white solid; yield 4.3 g (95%).

Anal. Calcd for  $\text{C}_{13}\text{H}_{25}\text{N}_1\text{O}_7\text{S}_1$ : C, 46.02%; H, 7.37%; N, 4.13%.

Found: C, 45.79%; H, 7.74%; N, 4.20%.

Precursor Polymer. Polymerization was conducted by using an ampul technique with froze degassing. The polymerization conditions are: solvent; t-BuOH, monomer/solvent=1/3, catalyst; AIBN, 0.5 wt% of monomer, polymerization period, 10 hr; polymerization temperature 60°C; yield, 90%;  $\eta_{sp}/C$ , 2.12, polymer/6.0 wt% NaCl aqueous solution=1/100 at 30°C.

Poly-4-methacryloyloxy-1-hydroxy-2, 2, 6, 6-tetramethyl-piperidine Sulfate. Calcd for  $\text{C}_{13}\text{H}_{25}\text{N}_1\text{O}_7\text{S}_1$ : N, 4.13%. Found: N, 4.01% (Kjeldahl).

Nitroxyl Stable Radical Polymer. Precursor polymer was dissolved in pyridine or dioxane containing a twofold excess of triethylamine (ca. 10 wt-% solution); then air was passed through the reaction mixture for 40 hr at room temperature. The resulting yellow-orange reaction mixture was precipitated by pouring into water. The nitroxyl stable stable radical polymer thus obtained was reprecipitated in water from the THF solution. An orange powder was obtained in a 70-90% yield.

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