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The Synthesis of Poly[*N*-(*p*-vinylbenzylidene)-*t*-butylamine *N*-oxide] and Characterizations of Reaction with Nitrogen Dioxide

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Polymer-supported spin trap, poly[*N*-(*p*-vinylbenzylidene)-*t*-butylamine *N*-oxide] (polyPBN), was prepared by using *p*-chlorostyrene as a starting material, followed by Grignard reaction, condensation with *t*-butylamine, reduction, polymerization, and oxidation. The adsorption ability of NO_2 by polyPBN was investigated in a closed-circulation system. PolyPBN maintains its original NO_2 adsorbing ability in the mixed gas of nitrogen and nitrogen dioxide saturated with water vapor even after repeated (5 times) use. However, when the gaseous phase is freed from water, polyPBN exhibits less efficiency to adsorb NO_2 and its adsorbing ability decreases gradually with the repeated use.

The atmosphere has been fairly well improved by the recent high technologies for protecting the environment. However, the nitrogen oxides in atmosphere is rather increasing in spite of various efforts to remove them. They are generated both from static sources such as heavy oil and coal boiler, and mobile sources such as automobile, plane etc.[1,2] Most of the NO_x generated in the combustion system is in the form of nitrogen monoxide. However it is converted to nitrogen dioxide in the atmosphere. As a result, a considerable amount of nitrogen dioxide (NO_2) is accumulated in atmosphere. Since NO_2 is toxic for human body and causes photochemical smog, advanced technology for the removal of NO_2 is strongly desired.[3] Several methods of combustion modification and after-treatment have been proposed in order to reduce NO_x from exhaust gases. At the present time, many absorbents for NO_x has been proposed.[4,5]

Our recent study[6] showed the fact that α-(*N*-*t*-butyl-*N*-hydroxyamino)benzyl nitrate was produced by the reaction of nitrogen dioxide with *N*-benzylidene-*t*-butylamine *N*-oxide (PBN), which is known as a spin trap. The nitrate is a white solid; its yield is largely dependent on the solvent and becomes almost quantitative when NO_2 was bubbled into the methanol solution of PBN. When the nitrate was treated with water, PBN was recovered quantitatively. Simultaneously NO_2 was converted to nitric acid. In order to apply the reaction to the analysis and the removal of NO_2, polymer-supported spin trap, poly[*N*-(*p*-vinylbenzylidene)-*t*-butylamine *N*-oxide] (polyPBN) was prepared.

In general, the immobiliztion of active functional group on the polymer acquires several new properties advantageous to small molecules. 1) Easy recovery and repeated use because of low solubility. 2) an improvement in the activity and the stabilization of active group by incorporating in the polymer structure. In this paper, the preparation and the reaction with NO_2 of polyPBN will be reported in detail.

Experimental

Ultraviolet spectra was taken with a JASCO double beam spectrophotometer UVIDEC-610c. Infrared spectra were measured with a JASCO fourier transform infrared spectrophotometer FT/IR-5M on KBr pellets. ESR spectra were observed with a JEOL ME-3X. Mass spectra and ^{1}H NMR were obtained with a JEOL JMS-AX-500 and a JEOL EX-270, respectively. The measurement of surface area was carried out with a β Scientific Corp. automatic surface area analyzer model 4200. Molecular weight was made with a TOSOH CP 8000 series high performance liquid chromatography.

Preparation of PolyPBN (i) *p*-Vinylbenzaldehyde (3).[7] A solution of 7.3 g (0.1 mol) of dimethylformamide in 50 ml of dry tetrahydrofuran was added dropwise over a 30 min period to a solution of *p*-vinylphenylmagnesium chloride (0.1 mol, from 13.8 g *p*-chlorostyrene and 2.5 g of magnesium) in 75 ml of tetrahydrofuran. The temperature was maintained at 20 °C during the addition. The reaction mixture was stirred for 2 h at the room temperature. The product was hydrolyzed with saturated aqueous ammonium chloride solution and extracted with ether. The organic layer was dried over anhydrous sodium sulfate and evaporated on a rotary evaporator. The crude product was distilled, giving 5.6 g (42.1%) of *p*-vinylbenzaldehyde: bp 73—79 °C (3 mmHg, 1 mmHg=133.322 Pa); Lit,[8] bp 92—93 °C (14 mmHg).

(ii) *N*-(*p*-Vinylbenzylidene)-*t*-butylamine (4). A solution of 4.5 g (0.034 mol) of **3**, 10.0 g (0.136 mol) of *t*-butylamine in 20 ml of anhydrous benzene was heated with stirring for 3 h at 60 °C with the addition of a molecular sieve 3A (1/16) as dehydrating agent. Upon cooling, the solution was dried over anhydrous sodium sulfate, filtered, and evaporated to afford a light-yellow liquid in a 62.5% yield.

IR (CCl_4): 2960—2850 (CH_3, CH_2), 1640 (CH=N), 1600 (Ar), 980 and 900 cm^{-1} (vinyl); ^{1}H NMR ($CDCl_3$) δ=1.25 (s, 9H, $3CH_3$), 5.25 (d, 1H, vinyl), 5.80 (d, 1H, vinyl), 6.70 (q, 1H, vinyl), 7.20—7.80 (m, 4H, ArH), 8.25 (s, 1H, CH); Mass spectrum m/z 187 (M^+).

(iii) *N*-*t*-Butyl-*p*-vinylbenzylamine (5). To a methanol (30 ml) solution of 2.1 g (0.011 mol) of **4**, 0.42 g (0.011 mol) of sodium borohydride was added gradually at room temperature for 15 min. When the addition of sodium borohydride was complete, the reaction solution was refluxed an additional 15 min and then cooled. The product was extracted with ether and washed with water. The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated to give a light-yellow liquid in an 85.9% yield.

IR (CCl_4) 3400 (NH), 2960—2850 (CH_3, CH_2), 1600 (Ar), 1190 (CH_2–NH), 980 and 900 cm^{-1} (vinyl); ^1H NMR ($CDCl_3$) $\delta=1.15$ (s, 9H, $3CH_3$), 3.72 (s, 2H, CH_2), 5.15 (d, 1H, vinyl), 5.70 (d, 1H, vinyl), 6.70 (q, 1H, vinyl), 7.30 (q, 4H, ArH). Mass spectrum m/z 189 (M^+).

(iv) Poly(*N*-*t*-butyl-*p*-vinylbenzylamine) (6). A solution of 1.5 g (7.94 mmol) of **5** and 0.075 g of α,α'-azobisisobutyronitrile in 2 ml of tetrahydrofuran was put into a glass ampule, which was evacuated, filled with nitrogen and sealed in a conventional manner. Polymerization was carried out at 70 °C for 24 h. The polymer was obtained in 90.5% conversion. The resulting polymer was easily soluble in benzene, tetrahydrofuran, and dichloromethane. IR spectrum of this polymer indicated the disappearance of vinyl absorptions at 980 and 900 cm^{-1}.

(v) Poly[*N*-(*p*-vinylbenzylidene)-*t*-butylamine *N*-oxide] (7).[9] To a mixture of 1.0 g (ca. 5.3 mmol) of **6**, 102.5 mg (0.3 mmol) of sodium tungstate, and 186.5 mg (0.6 mmol) of tetrabutylammonium bromide in 5 ml of dichloromethane, 2.4 g (0.021 mol) of 30% aqueous hydrogen peroxide was added dropwise with stirring and with ice cooling over a period of 10 min. After the reaction mixture was kept stirring for 6 h at room temperature, 40 ml of dichloromethane was added. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, and evaporated to afford with a light-yellow solid in a 95% yield.

Measurement of NO_2 Adsorption. NO_2 and nitrogen were purchased from Japan Oxgen Co. and Kawasaki Sogo Gas Center, and were used without further purification. The adsorption experiments of NO_2 by polyPBN were carried out by using a closed-circulation apparatus depicted in Fig. 1. Nitrogen dioxide and nitrogen were introduced into this apparatus and were circulated with gas-circulating pump at the rate of 100 dm^3 min^{-1}. In order to keep the NO_2 concentration constant during the process of sampling the mixed gas, the gas chamber is connected with gas burette. The volume of sampled mixed gas was made up by adjusting the height of leveling liquid. Prior to the circulation on polyPBN, the mixed gas was saturated with the vapor of solvent used as leveling liquid. The amount of absorbed NO_2 was traced by sampling the mixed gas. The sample was reacted with the Saltzman's reagent and the amount of NO_2 was determined by measuring the intensity of absorption at about 545 nm.[10]

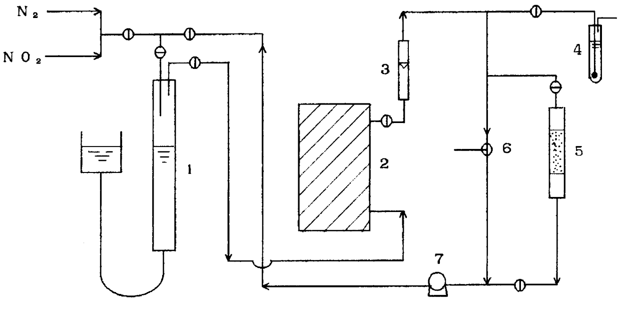


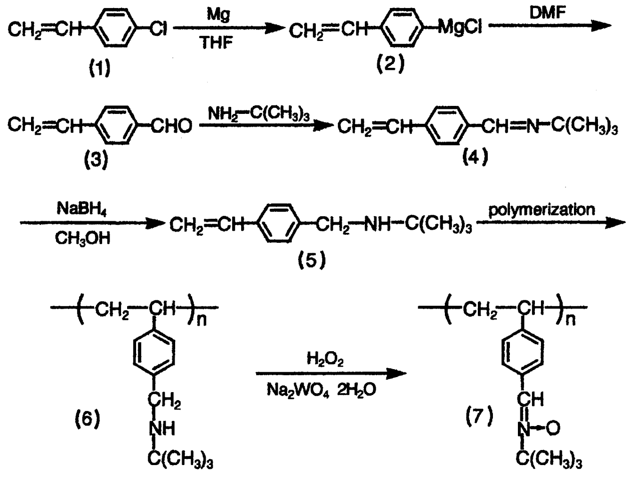
Fig. 1. Schematic diagram of gas adsorption apparatus. 1. Gas burette. 2. Gas chamber. 3. Flow meter. 4. Analyzer. 5. Adsorbent column. 6. Gas outlet. 7. Gas-circulating pump.

Regeneration of PolyPBN. The regeneration experiments of polyPBN from its NO_2 adduct were carried out by flowing water through the sample tube packed with polyPBN. In order to regenerate polyPBN completely, a prolonged treatment with water becomes necessary. After washing this adduct with water for 3 h, regenerated polyPBN was dried in vacuo completely.

Spin Trapping Experiments. After repeated use (5 times) for NO_2 capturing experiment, the intrinsic spin trapping ability of the regenerated polyPBN was checked. This reaction was performed by heating benzene (10 ml) solution of recovered polyPBN (0.0124 g) and α,α'-azobisisobutyronitrile (AIBN) (0.0026 g, 0.016 mmol) at 80 °C until the evolution of nitrogen ceased. The solution was quenched and degassed with nigrogen for 5 min before measuring ESR specta. Measurements were made under ordinary conditions.

Results and Discussion

Preparation and Characterization of PolyPBN. Polymer-supported spin trapping reagent poly[*N*-(*p*-vinylbenzylidene)-*t*-butylamine *N*-oxide] (polyPBN) was prepared according to Scheme 1. *p*-Chlorostyrene in tetrahydrofuran reacted smoothly with magnesium to form *p*-vinylphenylmagnesium chloride. *p*-Vinylbenzaldehyde was obtained from the reaction of *p*-vinylphenylmagnesium chloride with dimethylformamide in a comparatively low yield (42.1%), presumably due to partial polymerization. The other reactions to the precursor polymer were carred out without any difficulty. Because spin traps have the ability to trap free radicals, vinyl polymer having nitrone moiety can not be obtained with conventional polymerization. Polymer of *N*-*t*-butyl-*p*-vinylbenzylamine was synthesized as a precursor polymer and then was subjected to oxidation by



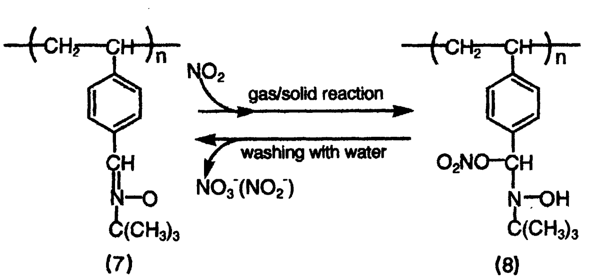
Scheme 1. Preparation of polyPBN.

Table 1. Analytical Results of the Obtained PolyPBN

Polymer	IR (KBr) cm^{-1}	NMR ($CDCl_3$) ppm
PolyPBN	2860—3100 (alkyl), 1630 (C=N), 1610 (aryl), 1370 and 1180 (N–O)	7.8—8.1 (CH=N), 6.4—8.0 (aryl), 1.0—2.5 (alkyl)

Table 2. Properties of the Obtained PolyPBN

Polymer	M_n	M_w	Surface area	UV (λ_{max})/nm	
	$\times 10^3$	$\times 10^4$	m^{2}g^{-1}	in THF	in MeOH
PolyPBN	9.74	1.64	0.7369	305	299



Scheme 2. Reaction with NO_2 and regeneration of polyPBN.

H_2O_2 at room temperature to form polyPBN.

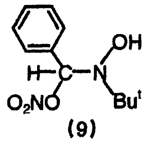
The analytical results of polyPBN are shown in Table 1. From the IR and NMR spectra, it was confirmed that this method afforded nitrone moiety in the polymer chain. But, the complete disappearance of CH_2 peak of **6** in NMR can not be attained. This can be attributed to the difficulty of polymer reaction. The amount of nitrone moiety in polymer chain is estimated to be 63% by comparison of absorption with that of PBN.

The properties of polyPBN were investigated briefly, as indicated in Table 2. High molecular weight polymer was not obtained, owing to the existence of amino group which acts as inhibiting or retarding substance in the radical polymerization of *N*-*t*-butyl-*p*-vinylbenzylamine. The feature of polyPBN and PBN in the UV spectra is that both show absorption at 290—308 nm due to nitrone moiety. The former absorption shifts about 4 nm in THF solution and 7 nm in MeOH to longer wavelength, respectively, which might imply the existence of interaction among nitrone moieties in the polymer chain. When solvent changed from THF to MeOH, the absorption of PBN shifted from 301 to 292 nm. In contrast, the change in the absorption maximum of polyPBN is smaller (from 305 to 300 nm) than that of PBN. This may be due to the coordination of oxygen atom of nitrone moiety to a protic solvent. In the case of polymer, this sort of interaction was suppressed to some extent by steric effect around nitrone moieties.

Characterization of NO_2 Adduct of PolyPBN by IR, NMR, and ESR Spectroscopy. PolyPBN can absorb NO_2 under mild experimental conditions (Scheme 2).[11] PBN itself could absorb NO_2 with low efficiency, probably because it reacts with NO_2 only on the surface of solid material. In contrast, polyPBN can absorb NO_2 efficiently even in solid state and can be easily regenerated from its adduct by the treatment with water, thus, it has potential use for the removal of NO_2 in the air.

IR spectra indicated the changes in absorption peaks of polyPBN before and after the exposure to NO_2. When polyPBN adsorbs NO_2, strong and sharp adsorption bands appear at 1620 and 1390 cm^{-1}. These absorptions can be assigned to the asymmetric and symmetric stretching vibrations of nitrate ester, respectively. Nitrate ion has absorption in the ranges 1380—1350 cm^{-1} (very strong) and 840—815 cm^{-1} (medium), but does not absorb in the range 1640—1620 cm^{-1}. The presence of the 1620 cm^{-1} band can be evidence for the covalent nitrate structure. "PBN-nitrate", α-(*N*-*t*-butyl-*N*-hydroxyamino)benzyl nitrate (**9**) was also shown to absorb at 1638 and 1370 cm^{-1} (KBr pellet) (Chart 1).[6] This showed the formation NO_2 adduct of polyPBN whose structure is similar to the PBN–NO_2 adduct. The band at 3100—3500 cm^{-1} can be assigned to the stretching vibration of the OH group formed. However, the band is rather diffuse, and not suitable for the identification of the adduct. In the measurement after washing with water, drastic decrease in the intensities of the nitrate adsorption was observed. The whole spectrum became very similar to the orginal polyPBN, indicating its regeneration. In addition, NO_3^- and NO_2^- ions were detected in the aqueous solution by brucine/concentrated sulfuric acid test and the Griess–Romijn test.

In order to verify further the formation of NO_2 adduct of polyPBN, we also measured NMR spectrum of its adduct. NMR data showed the disappearance of nitrone moiety (CH=N) peak which was accompanied with the occurrence of new peak at about 5.4 ppm (Ph–CH). Similarly, the recovered polyPBN showed NMR spectrum which is almost same as the original one. This also indicated the fact that the reaction of polyPBN with NO_2 takes place and nitrate ester is formed. In ad-



(9)

Chart 1.

dition,during the adsorption of NO_2, the color of solid polyPBN turned dark yellow, indicating the occurrence of reaction. The ESR signal was not observed with this NO_2 adduct of polyPBN, suggesting the formation of a diamagnetic species. The fact also strongly supported the idea that the adsorption of NO_2 by polyPBN proceeds by the binding of NO_2 with nitrone moiety and the reaction product is a nitrate of polyPBN.

NO_2 Adsorption Experiment of PolyPBN in the Presence of Water Vapor. In the aim of characterizing the reaction of polyPBN with NO_2, the adsorption of NO_2 by polyPBN was studied under various conditions. In the first place, possibility of repeated use of polyPBN as the adsorbent of NO_2 was checked. Before starting the first experiment of NO_2 adsorption, polyPBN in the reaction apparatus (Fig. 1) was contacted with dry nitrogen at room temperature for 5 min, and then was subjected to a reduced pressure (2 mmHg) for 10 min. The mixed gas was introduced into this apparatus and was circulated. Because water was used as leveling liquid for gas burette, polyPBN certainly experienced the atmosphere saturated with water vapor. In order to suppress absorption of NO_2 by water as low as possible, aqueous sodium chloride solution which was saturated with gaseous NO_2 was used as leveling liquid in the gas burette. It was found from the blank experiments without polyPBN that the effect of the absorption of NO_2 by water is negligible within the experimental error. Figure 2 shows the time-adsorption curve of NO_2 on new polyPBN. The adsorption rate was not so rapid as expected, but more than 80% of NO_2 was adsorbed at equibrilium. The color of the polymer changed from light yellow to dark yellow in the process of NO_2 adsorption. The NO_2 adduct of polyPBN was characterized by IR and NMR spectroscopy. After the NO_2 adduct of polyPBN was washed with water, the color of this adduct faded clearly.

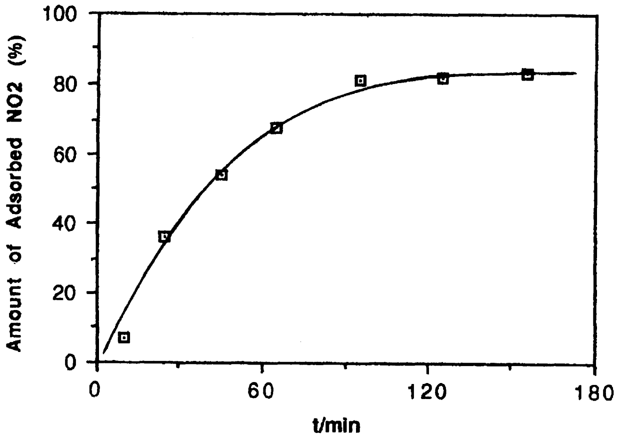


Fig. 2. Adsorption of NO_2 by polyPBN at room temperature under 1 atm in the presence of water vapor. polyPBN (1.1 g, mesh: 22) was packed with a glass tube (inside diameter: 11 mm).

The NO_2 adsorption experiments of the regenerated polyPBN were carried out four times by repeating exactly the same procedure as was used in the adsorption experiment of the new polyPBN. The results are given in Table 3. Table 3 compares the amount of NO_2 adsorbed by the new polyPBN and the regenerated polyPBN. The results clearly indicate that the adsorption rate and the NO_2 adsorbing capacity of the regenerated polyPBN does not change even after four times recycle-use for NO_2 adsorption. This experimental results suggested that the NO_2 adduct of polyPBN was returned to the orginal polyPBN by washing with water and the nitrone group of polyPBN was not destroyed during the process of reaction and after-treatment for regeneration.

Generally, owing to the lack of mobility of polymer in solid states, solid surfaces are likely to be very complex in structure. In heterogeneous reaction of solid material with a gas, it can be expected that the reaction rate will be influenced by several factors such as the concentration of gas, the surface area of solid, and diffusion. Therefore, the effect of concentration on the reaction rate will provide an important information on the reaction. When an NO_2 molecule goes into the pores of polyPBN, it will encounter with nitrone moiety to form chemical bond. If there are many nitrone moieties on the surface of this polymer and the diffusion of NO_2 into the inside is very fast, the collision probability between NO_2 molecules and nitrone moieties will increase to generate the NO_2 adduct of polyPBN. We investigated the effect of NO_2 concentration on NO_2 adsorption of polyPBN. The result was summarized in Table 4. Due to the technical difficulty in our reaction apparatus, it is very difficult to adjust the initial concentrations of NO_2 in a wide range. Although the initial adsorption rate could not be determined clearly, this table indicated that the adsorption rate of NO_2 increases with the increase in the initial concentration of NO_2. The diffusion of NO_2 into the inside of polyPBN appears to have strong effect on the NO_2 adsorption. The reaction of NO_2 with nitrone moiety occurs first on the surface of polyPBN, and then the NO_2 diffuses from the surface to the inside. Therefore, the diffusion is rather slow because of the small surface area of this polymer and the low mobility of nitrone moiety.

We also investigated the dependence of NO_2 adsorption on the amount of polyPBN. Figure 3 indicated that the adsorption rate of NO_2 increased with the increase in the amount of polyPBN. As shown in the curves 1 and 2 in Fig. 3, the amount of adsorbed NO_2 reached a saturation point when the amount of polyPBN is less than equimolar to NO_2. The position of the saturation point depends on the molar ratio of polyPBN to NO_2 and corresponds to the (almost) complete consumption of the nitrone group in the polymer. However, when the molar amount of polyPBN is equal or beyond NO_2, it can adsorb NO_2 in the reaction ap-

Table 3. Effects of Repeated Use on the Adsorbing Capability for NO_2 in the Presence of H_2O Vapor[a)]

Repetition number (n)	Initial concentration of NO_2 (volppm)	Amount of adsorbed NO_2[b)]	
		After 45 min	At equilibrium
1	537	0.54	0.83
2	553	0.60	0.80
3	401	0.66	0.87
4	746	0.62	0.86
5	870	0.63	0.83

a) Amount of polyPBN: 1.1 g. Leveling liquid in gas burette: water. Flow rate of circulating gas: 100 dm^3 min^{-1}. b) Ratios to the initial concentrations.

Table 4. Effects of Initial Concentration of NO_2 on the Adsorption Capability for NO_2[a)]

Initial concentration of NO_2 (volppm)	Amount of adsorbed NO_2[b)]		
	After 25 min	After 45 min	At equilibrium
242	0.26	0.48	0.89
416	0.28	0.52	0.86
537	0.36	0.54	0.83
709	0.40	0.59	0.88
959	0.49	0.65	0.87

a) Amount of polyPBN: 1.1 g. Leveling liguid in gas burette: water. Flow rate of circulating gas: 100 dm^3 min^{-1}. b) Ratios to the initial concentrations.

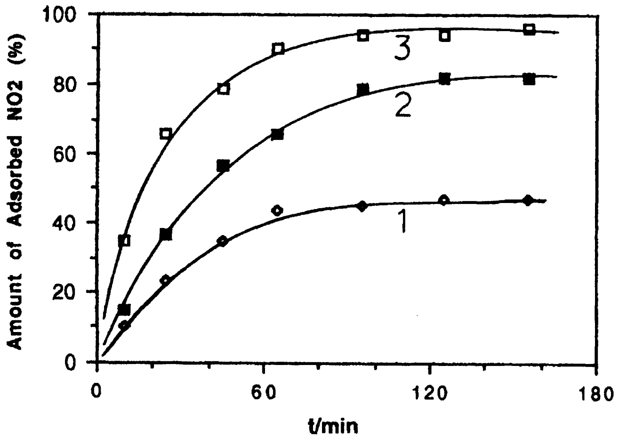


Fig. 3. Dependence of NO_2 adsorption on the amount of polyPBN. 1: polyPBN, 0.6 g, 2: polyPBN, 1.1 g, 3: polyPBN, 2.2 g.

paratus exhaustively as shown in curve 3 of Fig. 3.

Effect of Carbon Tetrachloride on the Capability of PolyPBN to Adsorb NO_2. In analogy with the formation of α-(*N*-*t*-butyl-*N*-hydroxyamino)benzyl nitrate (**9**) from PBN, the solvent molecule should also play a crucial role in the formation of product **8**. From this point of view, the reaction product **8** can be expected to be formed by the hydrogen abstraction from water vapor. In order to examine further the role of solvent vapor in the reaction of polyPBN with NO_2, we carried out the NO_2 adsorption experiments by using carbon tetrachloride as leveling liquid (see gas adsorption apparatus in Fig. 1). As the reaction was run in the dry nitrogen atmosphere saturated with carbon tetrachloride vapor, the NO_2 adduct of polyPBN can not abstract any hydrogen atom from its surrounding gas. The NO_2 adsorption experiments were carried out with the new and regenerated polyPBN. The results are listed in Table 5. It can be seen from the table that the NO_2 adsorption capability of the regenerated polyPBN gradually decreases as the number of repetition increases. During these runs, irreversible coloration of polyPBN took place, the color did not fade away clearly even after the exhaustive washing with water. In conctrast, neither irreversible coloration nor decrease in the NO_2 adsorbing capability was observed with the runs using water as leveling liquid.

Role of Coexisting Water Vapor on the Adsorption of NO_2. Just like PBN itself, polyPBN has nitrone groups on the side chain. Thus it has an excellent spin trapping ability. On the other hand, NO_2 is known to be a kind of reactive paramagnetic species. Quite analogous to the reaction of PBN with NO_2, the nitrone moiety of polyPBN can react with NO_2.[12)] When an NO_2 molecule is passing through polyPBN, it has a chance to go through pores in the polymer structure and to encounter with the nitrone moiety. The encounter in the pore should afford a prolonged period of the contact of the two reactants which is favorable to generate the adduct. It can be seen from the experiments in which solvent vapor was saturated with water, water vapor plays an important role in the adsorption of NO_2 by polyPBN and in the regeneration of polyPBN. Oxygen atom of nitrone moiety can form a strong hydrogen bond with hydroxylic compounds. Thus, the adsorbed water should be hydrogen-bonded on the oxygen of nitrone moiety. This hydrogen bond should be

Table 5. Effects of Repeated Use on the Adsorbing Capability for NO_2 in the Presence of CCl_4 [a)]

Repetition number (n)	Initial concentration of NO_2 (vol ppm)	Amount of adsorbed NO_2 [b)] After 45 min	At equilibrium
1	831	0.57	0.73
2	887	0.46	0.67
3	741	0.38	0.52
4	723	0.32	0.44
5	750	0.28	0.37

a) Amount of polyPBN: 1.1 g. Leveling liquid in gas burette: Carbon Tetrachloride. Flow rate of circulating gas: 100 dm^3 min^{-1}. b) Ratios to the initial concentrations.

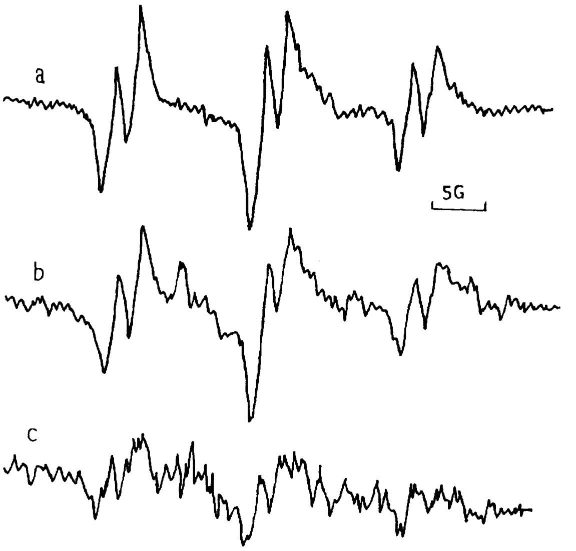


Fig. 4. ESR spectra of spin adducts of the new polyPBN (a), the recovered polyPBN (b) in water vapor and in carbon tetrachloride vapor (c).

considerably strengthened in the hydrophobic circumstance around the nitrone moiety. If paramagnetic NO_3 or NO_2 species attack to the α-carbon, C–O(N) covalent bond is formed easily through probably a concerted single hydrogen transfer from RO group. This process must be coupled with the single electron transfer through the hydrogen bond forming RO free radical. Thus generated hydroxyl or alkoxyl radical might annihilate by the abstraction of hydrogen atom or by the coupling with other free radical.

In the experiment in the dry atmosphere containing carbon tetrachloride vapor, the decrease in the NO_2 adsorption capability of the regenerated polyPBN indicated that the nitrone moiety was destroyed gradually so that the ability to adsorb NO_2 was declining. The fact suggests that the formation of NO_2 adduct of polyPBN can proceed through a different mechanism depending on various reaction conditions.

In order to examine the spin trapping ability of the recycled polyPBN, ESR spectra of regenerated polyPBN after repeated (5 times) use were measured under the same conditions and shown in Fig. 4. When water was used as leveling liquid, the recovered polyPBN could trap 1-cyano-1-methylethyl radical and a characteristic triplet of doublets pattern similar to the new polyPBN was observed without decrease in intensity. However, the polyPBN used in the experiment of dry carbon tetrachloride vapor-containing atmosphere did not give clear ESR spectrum after the treatment with AIBN. Weaker signal intensity suggests lower reactivity of nitrone moiety towards radical trapping. It is also concluded from this result that solvent vapor must play a crucial role in the formation of NO_2 of polyPBN.

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