JOURNAL OF APPLIED POLYMER SCIENCE VOL. V, ISSUE NO. 16, PAGES 478-481 (1961)

Electron Spin Resonance Studies of Polyvinyl Chloride Irradiated in NH_3 Gas

HISASHI UEDA, ZEN'ICHIRO KURI, and SHOJI SHIDA

Tokyo Laboratories, Japanese Association for Radiation Research on Polymers, Kamifujimaecho, Bunkyoku, Tokyo, Japan

INTRODUCTION

The electron spin resonance spectra of polyvinyl chloride (PVC) irradiated in vacuum and at room temperature have been reported in previous studies.[1,2] The radical transformation of the radicals produced in PVC irradiated in vacuum at room temperature has also been reported by the present authors.[2] It was also reported by the present authors that PVC becomes insoluble on irradiation in NH_3 gas.[3] To obtain further data on the effect of NH_3 irradiation of PVC the electron spin resonance spectra of PVC irradiated in NH_3 and PVC subjected to post-irradiation reaction with SO_2 were studied.

EXPERIMENTAL

NH_3 and SO_2 were dried with CaO and P_2O_5, respectively, and distilled twice. After evacuation to more than 10^{-4} mm. Hg, these gases were introduced into the samples from the gas reservoir through a breakable seal.

The measurement of electron spin resonance (ESR) was carried out with an x-band spectrometer at 9400 Mcycles/sec. and at 20–30°C., except the case of low temperature measurement. Low temperature measurements were performed in a Dewar flask whose top was inserted into the microwave cavity. As a cooling medium a Dry Ice–petroleum ether mixture was used.

Gas absorption was measured in a glass vessel equipped with a manometer.

Nitrogen analysis of PVC irradiated in NH_3 with 5×10^7r was made. The nitrogen content was 1.5%, which corresponds to a G value of 22.5 for NH_3 absorption. This nitrogen content is the sum of both NH_4Cl occluded and nitrogen-containing groups bonded to PVC.

Infrared spectra obtained for PVC film irradiated in liquid NH_3 and then dried for 100 hr. at 10^{-4} mm. Hg show absorption peaks at 3030 and 3150 cm.$^{-1}$, and spectra obtained with NH_4Cl have their peaks at 1406 and 3200 cm.$^{-1}$. It may be impossible to distinguish the absorption bands for NH_4Cl from those for corresponding to nitrogen-containing groups bonded to PVC, as the sample cannot be purified by reprecipitation because of its insolubility.

RESULTS

ESR Spectra of PVC after Irradiation in NH_3

The effect of NH_3 on the ESR spectra is small, except that spectra of PVC obtained in NH_3 are a little broader than those obtained in vacuum (Fig. 1).

Plots of the radical concentration in PVC irradiated in vacuum versus dosage shows a tendency to level off at 10^7r, but the curve for the radical concentration obtained with irradiation in NH_3 does not level off up to a dose of 10^8 r (Fig. 2).

Absorption of NH_3 and Other Gases by Polyvinyl Chloride under Irradiation

Before studying the effect of gases, it is necessary to ensure that the gases are not consumed before the irradiation is complete. Plots of pressure versus irradiation dosage show some changes in slope as a result of changes in the types of gas present atmosphere during irradiation. These breaks divide the course of the whole pressure change into several periods as shown in Figure 3. These values are listed in the Table I, in which gas absorption is expressed by positive G values and gas evolution is expressed by negative G values.

The G values for gas evolution by PVC at various temperatures have been reported by Miller,[4] and his result at 20°C. is not different from our data (−7.5). The absorption of NH_3 by PVC shows an initial linear change and a subsequent nonlinear change, as shown in Figure 3. The broken line shows the absorption of NH_3 if it is assumed that

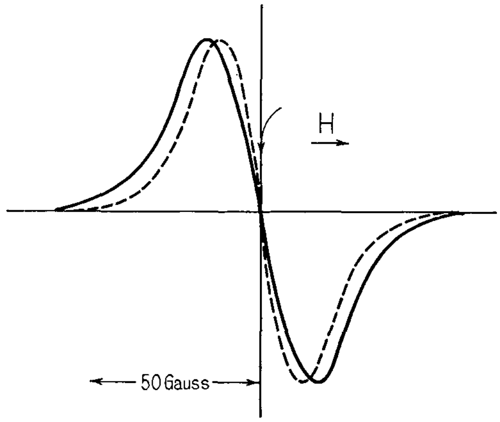

Fig. 1. Electron spin resonance spectra of PVC: (——) irradiated in NH_3; (- -) irradiated in vacuum. Dose: 10^8r. The arrow pointing downward shows the resonant point for DPPH.

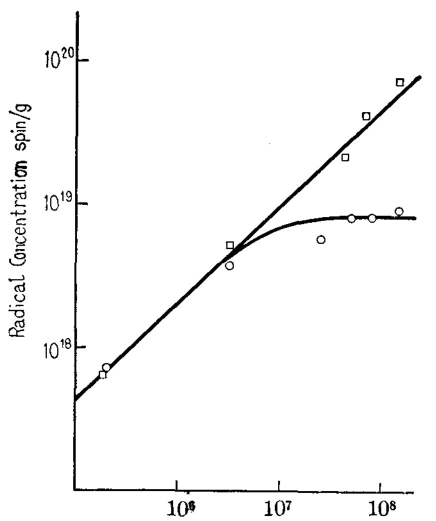

Fig. 2. Plot of radical concentration vs. dosage for the irradiation (○) in vacuum; (□) in NH_3; abscissa: dose, r.

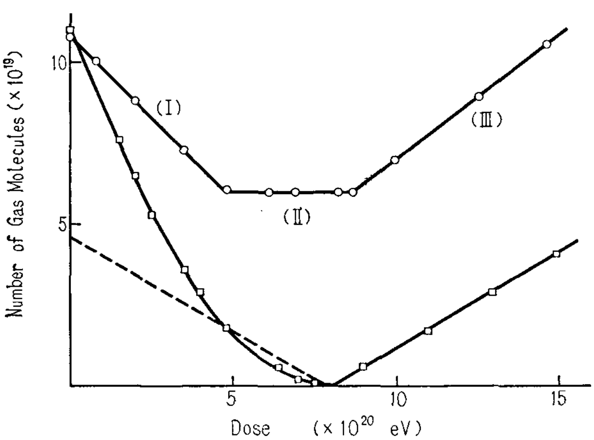

Fig. 3. Gas absorption by 1 g. PVC under irradiation: (○) absorption of NO; (□) absorption of NH_3.

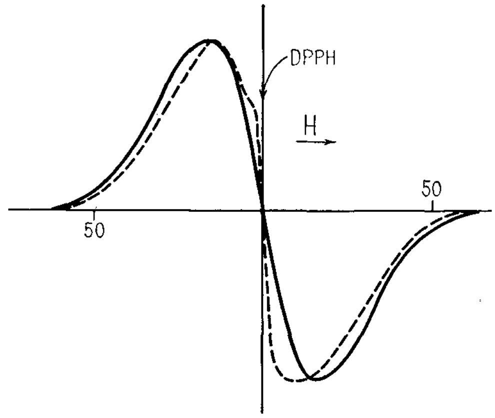

Fig. 4. ESR spectra of irradiated PVC before and after reaction with SO_2: (——) irradiation in vacuum; (- -) irradiation after reaction with SO_2.

NH_3 reacts only with the evolved hydrogen chloride to precipitate as ammonium chloride. The fact that the solid line crosses the broken line indicates that the elimination of HCl is prevented by NH_3, at least at lower pressures. The ultraviolet and visible light spectra of irradiated PVC shows the coloration which appears in PVC is caused by the radically induced chain reaction of hydrogen halide elimination with formation of long, conjugated double-bonding systems. Then the fact that less NH_3 is absorbed under irradiation agrees with the fact that the coloration of PVC in NH_3 under irradiation is much less than that in vacuum, and that the coloration appearing on irradiation after the complete consumption of NH_3 is much stronger than that appearing after irradiation in vacuum.

Effect of NH_3 on the Reactivity to SO_2

PVC irradiated in SO_2 shows ESR spectra typical of the $RSO_2\cdot$ radical, but PVC irradiated in vacuum does not react with SO_2 after irradiation. This result was found not to be true always. At a lower dose (less than 10^5r), a partial reactivity to SO_2 remains in PVC irradiated in vacuum and at 20°C. (Fig. 4).

However, considerable reactivity for SO_2 remains when the PVC is irradiated in NH_3 gas, as shown in Figure 5. The reactivity to SO_2 decreases gradually as the radiation dosage increases.

Electron Spin Resonance Spectra of PVC Irradiated at −78°C.

The ESR spectrum of PVC irradiated at −78°C. shows some hyperfine structure, as shown in

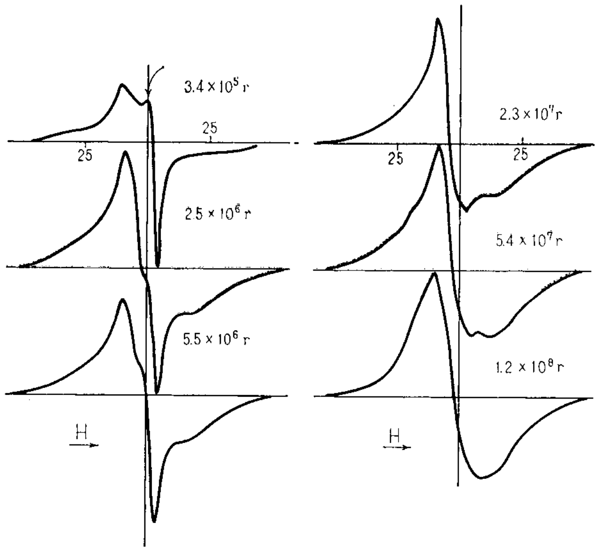

Fig. 5. ESR spectra of PVC after post-irradiation reaction with SO_2 at various doses.

Figure 6, although the spectrum obtained by irradiation at room temperature shows no such structure. This hyperfine structure is attributed to the discontinuous configurational interaction between an unpaired electron and a proton, as the radical electrons produced at low temperature have little or no double-bonding systems conjugating to them. Coinciding with this fact, experiments[4] on the yield of HCl at various temperature show that G_{HCl} becomes constant at temperatures lower than −70°C. The reactivity to SO_2 also remains in this temperature region. The coloring is also very faint.

On irradiation at −78°C. the reactivity remains unchanged, even at a dosage of 10^7r, the spectrum of the $RSO_2\cdot$ radical being obtained on the post-irradiation reaction of SO_2 as shown in Figure 6.

TABLE I
G Values for the Absorptions of Various Gases by PVC during Irradiation

Gas	*G* value		
	Period I	Period II	Period III
In vacuum	−7.5	—	—
H_2S	−2.5	−7.5	—
NO	+10.0	±0	−7.5
SO_2	−5.0	—	—
O_2	+20.0[a]	−10.0	—
NH_3	+22.5	−5.0	—

[a] Miller[4] reported the post-irradiation *G* value for O_2 absorption of PVC irradiated at −196°C. to be about 2[4], 24 hr. after development of coloration.

But on reaction with oxygen after irradiation at −78°C., a spectrum which coincides with the spectrum obtained on reaction with oxygen after irradiation at 20°C. is obtained.

DISCUSSION

The coloring of PVC irradiated at both −78 and 20°C. is evidence for the fact that the length of conjugated double bonds is greater at higher temperatures. The color of PVC irradiated in vacuum at 20°C. changes when exposed to air. This shows the unpaired electron to be conjugated with the double-bonding system in this sample. The spectrum obtained on irradiation in NH_3 is merely broader than that obtained in vacuum; however, the spectrum obtained after irradiation at −78°C. shows some hyperfine structure. This indicates that the conjugation length in PVC irradiated in NH_3 at 20°C. is greater than that of PVC irradiated at −78°C. in vacuum if we assume that the greater the conjugation length, the less the sigma character of the π-electron of the radical.

According to Miller,[4] the total radical concentration produced in PVC at −190°C. remains constant through the course of warming up to room temperature in the absence of oxygen, even though a brown color developed. The reactivity to SO_2 of radicals produced in PVC is therefore concluded to be controlled by the length of the double bond systems, with which they are conjugated.

$$—CH_2—CHCl— \rightarrow —CH_2—\dot{C}H— + Cl\cdot$$
$$—CH_2—\dot{C}H— + SO_2 \rightarrow —CH_2—CH(SO_2\cdot)—$$
$$—CH_2—(CH{=}CH)_n—\dot{C}H— + SO_2 \rightarrow \text{no reaction}$$

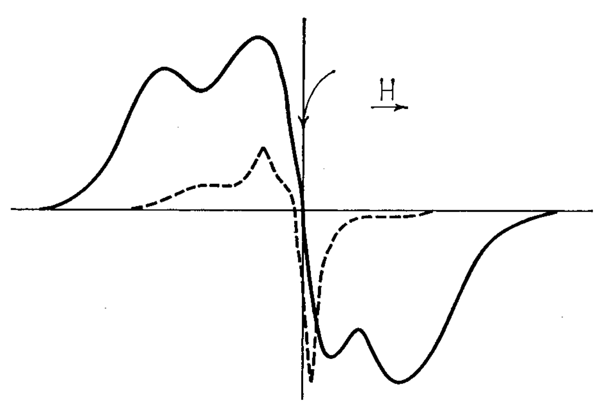

Fig. 6. ESR spectra of PVC (——) before and (- -) after reaction with SO_2. The irradiation was at −78°C. The measurements were made at −78°C. for the spectrum before reaction; (——) and at 20°C. for the spectrum after reaction.

The mechanism of radical formation and of development of the conjugated double bond system has been discussed by Miller.[4] According to Miller, the reaction leading to the formation of HCl and conjugated unsaturation is propagated by two processes, one including and one not including Cl atoms. If this process of HCl formation involves only Cl atoms, the formation of unsaturation may be quenched completely by NH_3 when PVC is irradiated in NH_3:

$$—\dot{C}H—CH(Cl)— \rightarrow —CH{=}CH— + Cl\cdot$$

$$Cl\cdot + NH_3 \rightarrow NH_3Cl\cdot, \text{ etc.}$$

However, the reactivity to SO_2 gradually decreases with increasing dosage, which may be accepted to be the result of both processes acting at the same time. The partial reactivity of the radical produced at 20°C. at low dosage may show that the unsaturation formation is not so rapid.

The leveling off of PVC radical concentration produced on irradiation in vacuum at 20°C. may be interpreted by the intramolecular recombination of the radicals. The radicals produced in NH_3 have shorter conjugated double bonding systems, so the probability of intramolecular radical recombination is low. At the point where the radical concentration approaches saturation, each polymer molecule has about one radical on the average, as the mean degree of polymerization of the sample used is about 1000.

The effect of NH_3 on the gelation of PVC is not as yet clear, but the great initial G value for the absorption of NH_3 with less coloring may involve some chain reactions of gaseous free radicals containing a nitrogen atom, such as $\cdot NH_3Cl$ or $\cdot NH_2$, and as a result of these, some unknown reactions leading to gelation of PVC may be promoted.

References

1. Abraham, R. J., and D. H. Whiffen, *Trans. Faraday Soc.*, **54,** 1291 (1958).
2. Kuri, Z., H. Ueda, and S. Shida, *J. Chem. Phys.*, **32,** 371 (1960).
3. Shinahara, K., S. Shida, Z. Kuri, and H. Ueda, *Kôgyô Kagaku Zasshi*, **63,** 350 (1960).
4. Miller, J. A., *J. Phys. Chem.*, **63,** 1755 (1959).

Synopsis

The electron spin resonance of polyvinyl chloride (PVC) irradiated in NH_3 was studied. The radicals produced on irradiation in NH_3 do not differ greatly from those obtained on irradiation in vacuum, but the reactivity of the former to SO_2 to form $RSO_2\cdot$ radicals is far higher than that of those obtained in vacuum. The radicals produced by irradiation at −78°C. and in vacuum was also studied. The spectra of these radicals were different from those of the radicals produced at 20°C. and in vacuum. The reactivity of the radicals produced in PVC is interpreted on the basis of the length of double bonds conjugating with the radical π-electron.

Résumé

On a étudié la résonance de spin électronique du chlorure de polyvinyle (P.V.C.) irradié dans NH_3. Les radicaux produits par irradiation dans NH_3 ne sont pas tellement différents de ceux obtenus dans le vide, mais leur sélectivité vis à vis de SO_2 avec formation de $RSO_2\cdot$ est beaucoup plus élevée que celle obtenue dans le vide. On a également étudié le radical produit par l'irradiation à −78°C, ainsi que dans le vide et leurs spectres sont différents de ceux des radicaux produits à 20°C dans le vide. La réactivité des radicaux produits dans le P.V.C. est interprêtée à partir de la longueur des doubles liaisons conjuguées et conjuguée avec l'électron π du radical.

Zusammenfassung

Die Elektronenspinresonanz von Polyvinylchlorid (PVC), in NH_3 bestrahlt, wurde untersucht. Die durch Bestrahlung in NH_3 erzeugten Radikale unterscheiden sich nicht sehr stark von den im Vakuum erhaltenen, jedoch ihre Reaktionsfähigkeit mit SO_2 unter Bildung von $RSO_2\cdot$ Radikalen ist wesentlich grösser als bei den im Vakuum erhaltenen. Weiters wurden die durch Bestrahlung bei −78°C und im Vakuum erzeugten Radikale untersucht; ihre Spektren unterscheiden sich von denen der Radikale, die bei 20°C und im Vakuum hergestellt wurden. Die Reaktionsfähigkeit der im PVC erzeugten Radikale wird durch die Anzahl der konjugierten Doppelbindungen, die zum π-Elektron des Radikals konjugiert sind, erklärt.

Received December 27, 1960