



## Effects of aromatic diacetylenes on polyurethane degradation by gamma irradiation



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### ABSTRACT

The effects of four aromatic diacetylenes on the gamma-irradiation-induced degradation of a commercial polyurethane were studied. Addition of 1 wt% of diphenylbutadiyne, which is homogeneously distributed in the polymer, effectively suppressed the polymer chain degradation. The dose required to decrease tensile strength by 50% was found to be 582 kGy for the polyurethane with 1 wt% of diphenylbutadiyne, while a dose of only 310 kGy for the polyurethane itself. The Young's modulus of the polyurethane alone decreased with dose; meanwhile the films with diphenylbutadiyne did not change. The films with *p,p'*-dinitrodiphenylbutadiyne behaved differently from others due to their inhomogeneous composition. The amide substituted diacetylenes also showed protecting effect, but in less extent due to the steric effect.

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## 1. Introduction

The resistance of polymers towards ionizing radiation has been an important topic of study from the point of view of applications as insulators and packing in nuclear plants and high intensity proton accelerators. The radiation effects on the mechanical properties of different polymers have been summarized in a review article [1], in which the polyurethanes (PUs) have shown higher radiation resistance compared with other common polymers such as polyolefins and vinyl polymers. Therefore, there are several works on the effects of gamma ray on PUs. They include CO<sub>2</sub> gas elimination [2], color changes [3], studies on stability of polyurethanes by chemiluminescence measurements [4], and degradation of PUs by Shintani [5], Ravat [6] and more recently by Sui et al. [7]. The effects of UV irradiation on PUs have been also studied by Ravat [8] and Wilhelm [9].

In order to increase radiation resistance of polymers various additives are usually used, which are called antirads, and they include aromatic amines [10], and more recently nanoparticles [11,12]. The effect of radiation on polymers involves free radical formation, and antirads are free radical scavengers. The present

authors have previously found that aromatic diacetylenes (DAs) stabilize transient free radicals. When some vinyl monomers such as ethylacrylate, methacrylate, methacrylonitrile, and styrene were polymerized in the presence of small amounts of aromatic DAs, intense ESR signals of propagating polymer radicals were detected at temperatures of polymerization [13–15]. Interestingly, the polymers did not contain any fragment of the DAs. The ESR signals of the propagating radicals were observed after polymerization, while the system was kept in vacuum; however, the signals diminished when the aromatic DAs having electron donor groups were employed. It is noteworthy that no such effect is observed with aliphatic DAs and the vinyl polymerization is not affected by their presence. These findings indicate that aromatic DAs scavenge free radicals stabilizing sufficiently enough to be detected by ESR spectroscopy. Some aromatic DAs such as diphenylbutadiyne (DPB) do not polymerize by irradiation with UV light or gamma ray in the solid state at room temperature [16], although it undergoes polymerization to give low molecular oligomers when irradiated at 110 °C by gamma ray [17] or heated at around 200 °C [18]. So far, no study has been reported on the effects of aromatic DAs on the radiation induced degradation of polymers. In this work, DPB and other aromatic DAs such as *p,p'*-dinitrodiphenylbutadiyne (DN) and *p,p'*-(dialkylaminocarbonyl)diphenylbutadiynes (PR and ET) were added to a commercial aromatic polyurethane and the

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changes on mechanical properties with gamma irradiation were studied.

## 2. Experimental

### 2.1. Materials

Anhydrous dimethylformamide (DMF) was purchased from Aldrich and Laripur S860, an aromatic poly(ester-urethane) for synthetic leather was provided by Novotex, Italy and they were used as received. The aromatic DAs employed in this work are shown in Table 1. They were synthesized by the oxidative coupling of the corresponding acetylenes [18]. PR and ET were chosen as they were thought to have good miscibility with the PU due to their amide groups. DN was expected to be a stronger electron acceptor due to nitro groups.

### 2.2. Film preparation

Pellets of the polyurethane (PU) were dissolved in DMF at room temperature and 1 wt% of aromatic DAs was added. The clear solutions were degassed in an ultrasonic bath, and then cast onto Teflon petri dishes and allowed to dry in a vacuum oven at 50 °C for 48 h, and then at 70 °C for 2 h in order to remove the residual solvent. The PU film without DA is hereafter named as Blank, while those with DAs are named using the abbreviation showed in Table 1 for each DA. To enhance the miscibility of aromatic amide DAs with PU, mixtures of PR, DPB and ET were used in weight ratio of 1:1.

### 2.3. Mechanical testing

The mechanical properties of films were determined using an INSTRON 4301 at a crosshead speed of 10 mm min<sup>-1</sup> at room temperature. The films sizes were approximately of 50 mm × 5 mm. Four films were tested for each PU to average each mechanical testing data.

### 2.4. Gamma irradiation

The films were irradiated in air using a Nordion Gamma Beam 651 PT with a Cobalt 60 source at the Institute of Nuclear Science (ICN-UNAM). The dose rate was 5.43 kGy h<sup>-1</sup> at room temperature.

### 2.5. Characterization

X-Ray diffraction measurements were performed on a Bruker Model D8 Advance diffractometer with detector of PSD Vantec-1, using a Cu K $\alpha$  radiation source of 1.5406 Å.

### 2.6. Gel content

The irradiated films were immersed into DMF for 96 h at room temperature; they were filtered and dried at 60 °C in a high vacuum oven for two days. The gel percent was calculated as follows:

$$\% \text{ gel} = [W_f/W_i]100 \quad (1)$$

where  $W_f$  is the weight of the insoluble part and  $W_i$  is the initial weight of film.

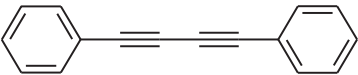
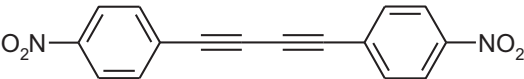
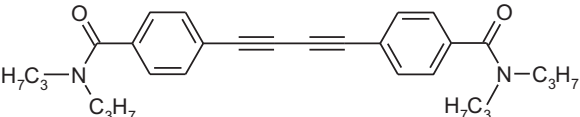
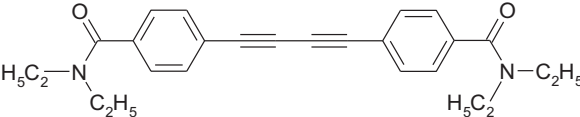
### 2.7. Radiation chemical yield

The radiation chemical yield was calculated according to the Charlesby–Pinner equation [19];

$$S + S^{1/2} = (p_o/q_o) + 1/(q_o\mu D) \quad (2)$$

where  $S$  is the sol fraction;  $p_o$  and  $q_o$  are the chain degradation and crosslinking per unit dose in kGy<sup>-1</sup> (or the probability of being degraded or crosslinked) respectively;  $\mu$  is the number average degree of polymerization before irradiation and  $D$  is the absorbed dose in kGy.  $p_o$  and  $q_o$  are obtained from the experimental curve of  $S + S^{1/2}$  versus  $1/D$ . The radiation chemical yields  $G_d$  is the number of polymer chain scissions per 100 eV absorbed and  $G_c$  is the

**Table 1**  
Aromatic diacetylenes employed as antirads

ID	Chemical structure	mp (°C)	Appearance
DPB	 Diphenylbutadiyne	83	White needle crystals
DN	 <i>p,p'</i> -dinitrodiphenylbutadiyne	–	Pale yellow powder
PR	 ( <i>p,p'</i> -dipropylaminocarbonyl)diphenylbutadiyne	140–142	White crystals
ET	 ( <i>p,p'</i> -diethylaminocarbonyl)diphenylbutadiyne	139–143	White crystals

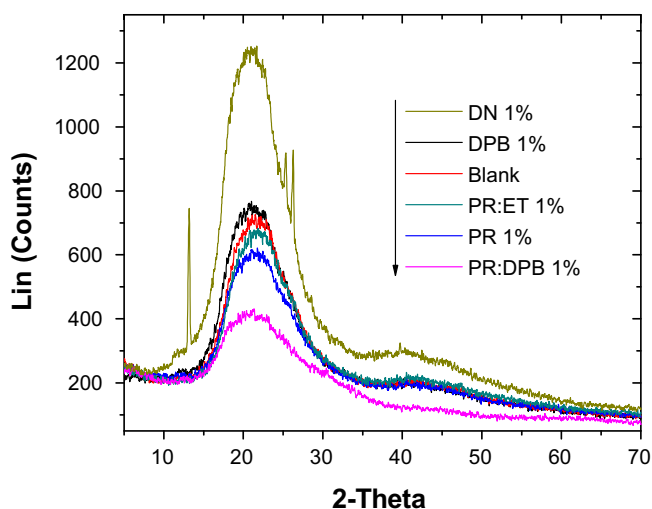


Fig. 1. X-Ray diffraction of PU films.

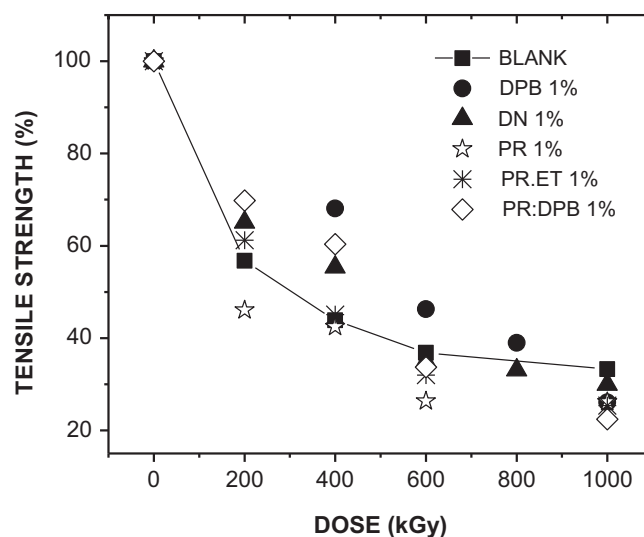


Fig. 2. Changes in relative tensile strength with dose.

number of polymer crosslink sites per 100 eV absorbed, they are related to  $p_0$  and  $q_0$  by the equation:

$$G_d/G_c = 2(p_0/q_0) \quad (3)$$

### 3. Results and discussion

The PU films without and with DPB, PR and the mixtures, are colorless and transparent, which indicates that the DAs are homogeneously mixed in the PU with their particle size less than the visible wavelength. In the case of DN films, the DN itself is yellow and the films were opaque yellow indicating the existence of DN crystals of which particle size in PU is larger than the visible wavelength.

All the films were amorphous as can be seen in the X-ray diffractogram (Fig. 1), except for DN films, which showed the existence of DN crystals. The X-ray diffractograms of the irradiated films were identical to those before irradiation, indicating there was no morphological change by the irradiation.

When the films were irradiated, they developed yellow color as reported in other studies [3]. However, in the case of DN films, they became orange due to the radiation induced oligomerization of DN itself and by the addition of radicals formed on the PU during irradiation.

The mechanical properties of the films before irradiation are shown in Table 2. The DN film showed somewhat inferior mechanical properties than Blank and DPB films. This is due to the poor miscibility of DN in PU and the DN crystals become the breaking points when the film was stretched. Young's modulus and tensile strength of DPB, PR and mixture of PR with DPB and ET

Table 2  
Mechanical properties of PU films before irradiation.

PU	Tensile strength (MPa)	Elongation at break %	Young's modulus (MPa)
Blank	51 ± 1.02	938 ± 18.76	41 ± 0.82
DPB 1%	62 ± 1.24	873 ± 17.46	51 ± 1.02
DN 1%	48 ± 0.96	867 ± 17.34	49 ± 0.98
PR 1%	56 ± 1.12	915 ± 18.30	53 ± 1.06
PR-ET 1%	57 ± 1.14	889 ± 17.78	51 ± 1.02
PR-DPB 1%	54 ± 1.08	967 ± 19.34	46 ± 0.92

before irradiation, were somewhat higher than those of the Blank. Such effects have been observed for PU containing carbon nanotubes [20] and silicates [21,22].

The tensile strength of all films decreased similarly to each other with irradiation, as shown in Fig. 2. However, for the DPB films the decrease was noticeably less than the other films. At 1000 kGy the remaining strength was about the same for all the films, indicating that aromatic DAs have been consumed by the reactions with polymer radicals formed by irradiation and by the formation of DA oligomeric species. The low tensile strength of DN films was due to their inhomogeneous composition induced by the poor miscibility of DN with the PU.

The elongation at break decreased with dose for all the films as can be seen from Fig. 3, indicating that chain scission is taking place. The decrease in elongation for the DPB films was less than the others, as in the case of tensile strength, showing that DPB is effective for radiation protection.

The relationships between Young's modulus and dose are shown in Fig. 4, where the decrease in modulus for Blank indicates that chain scission predominates. The moduli before irradiation of

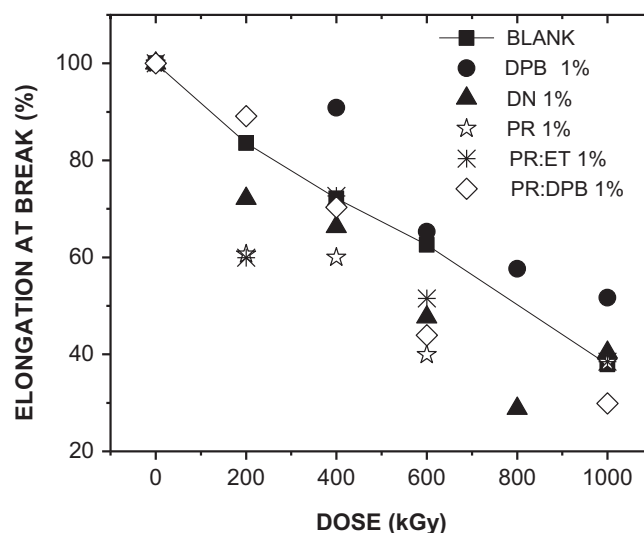


Fig. 3. Changes in relative elongation at break with dose.

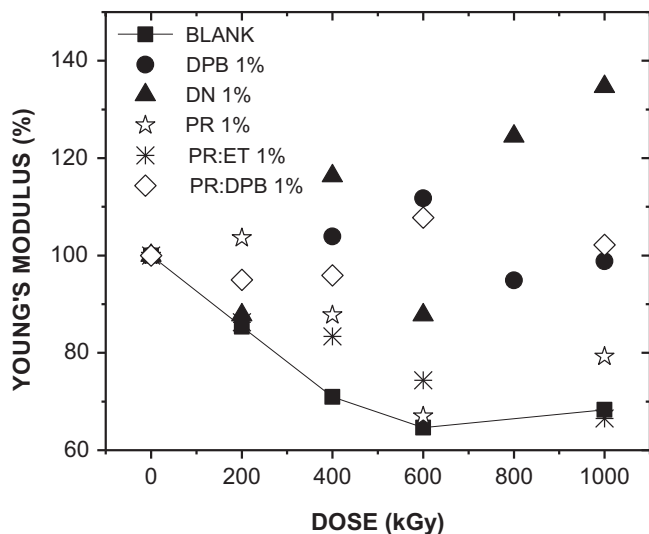


Fig. 4. Changes in Young's modulus with dose.

all the films with DAs were higher than that of Blank, as observed for tensile strength in Table 1. The modulus of films with DN showed increasing tendency with dose which is difficult to be explained because of its inhomogeneous consistency. In the case of DPB and PR:DPB, the modulus remained unchanged, while Blank, PR and PR:ET showed decreasing tendency indicating that they suffer more degradation than crosslinking. Therefore, DPB alone and the mixed can be used for radiation protection.

The radiochemical yields,  $G_d/G_c$  for Blank, DPB and DN were found to be 3.16, 3.4 and 3.25, respectively, calculated according to the Charlesby-Pinner equation [19] indicating that this PU generally suffers more chain scission than crosslinking. However, the Charlesby-Pinner plot was not helpful to indicate individually the magnitudes of degradation and crosslinking due to the low gel fraction as shown in Fig. 5. Then, the mechanical properties are represented by more than 80% of soluble parts of the material, as the gel percentage is less than 17%.

The modulus is affected not only by crosslinking, but also by the molecular weight, and the results of Fig. 4 are the balance between

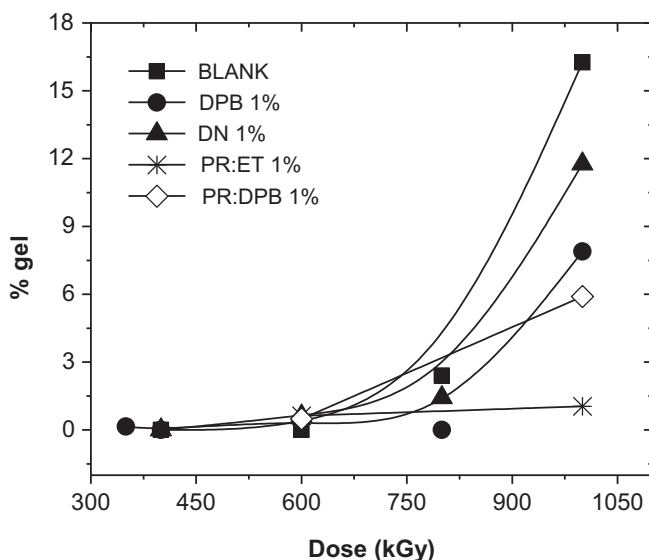
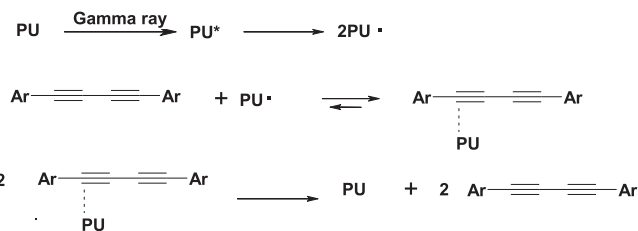


Fig. 5. Gel formation with dose.



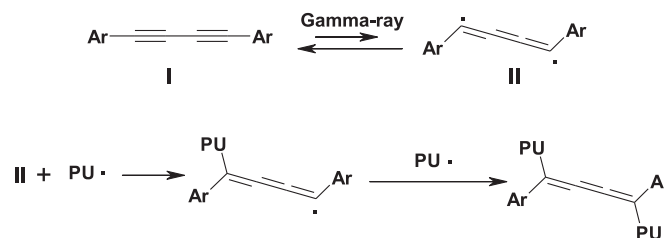
Scheme 1. Stabilization of free radicals by aromatic diacetylenes.

chain scission and cross-linking. It is obvious that the chain scission is suppressed by the DAs, and thus less decrease in modulus and tensile strength was observed.

Considering the role of aromatic DAs in free radical vinyl polymerization [13–15], the PU radicals, formed by irradiation, are trapped by the DA thus further chain degradation or crosslinking is suppressed, as shown in Scheme 1. The stabilized radicals can be released from the DA and recombine each other to return the original form. Although the DAs do not form bonds with transient radicals [15], the diradicals of aromatic DAs formed by heat or radiation can couple each other [18,23], and combine with other free radicals present in the system, as shown in Scheme 2. The radicals formed on the film surface will be converted to peroxy radicals and abstract nearby hydrogen to form peroxides, but in the presence of aromatic DAs, this could also be controlled. This interaction of free radicals with aromatic DAs is enhanced by electron acceptor groups in the benzene rings [14], and it was expected that the DN, PR and ET would trap free radicals more than DPB as they have electron withdrawing groups. However, in the case of DN their real effects could not be evaluated due to its poor miscibility with the PU. The PR and ET were somewhat less effective than DPB, although they were miscible, and this is due to the steric effect of the dialkylamide groups, which make the approaching of PU radicals to the DA more difficult. This agrees with the results in Fig. 4 in which less crosslinking is taking place for PR and ET.

According to Baughman [16] the radiation induced polymerization of DPB in the solid state is negligible in the crystalline state by Gamma irradiation, however, it is possible that the diradicals of aromatic DAs [23] (II in Scheme 2) formed by irradiation can couple with the PU radicals resulting in crosslinking, as shown in Scheme 2. In the case of DPB and its mixture, the PU radicals are stabilized to avoid further degradation and crosslinking. In the cases of PR and ET however, the steric effect of amide groups makes the approach of PU radicals more difficult, and therefore, there will be less interaction between the DAs and PU radicals, resulting in lower stabilization and crosslinking could take place.

As a summary, the doses required for the changes in tensile strength and elongation at break by 25 and 50% are shown in Figs. 6 and 7. It can be seen that the films with DPB give much higher radiation resistance than others. The elongation at break decreased more rapidly with the DAs except for the DPB. Thus, it can be said



Scheme 2. Crosslinking through diradicals.

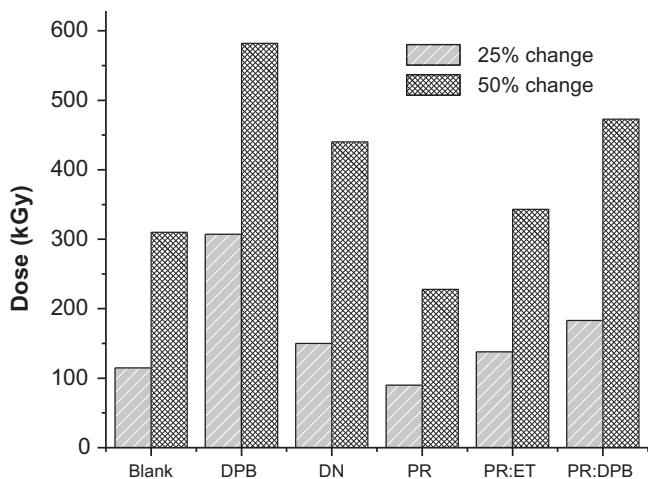


Fig. 6. Dose required for changes in tensile strength by 25 and 50%.

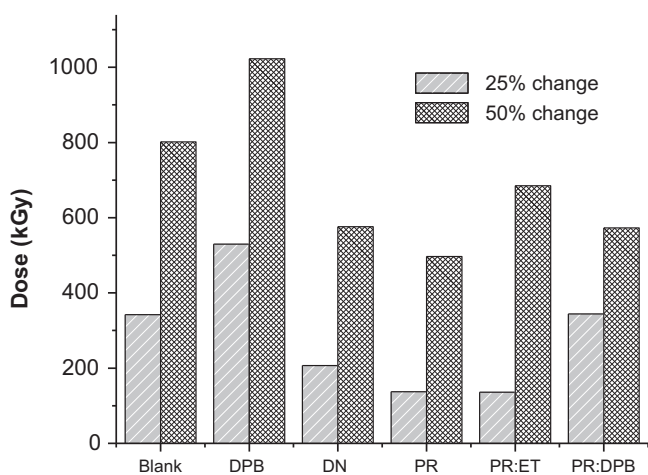


Fig. 7. Dose required for changes in elongation by 25 and 50%.

that DPB can be used as a stabilizer for radiation-induced degradation of polymers. Further studies for other polymers are being studied, and the results will be reported in future.

#### 4. Conclusion

DPB showed better radiation protecting effects than other aromatic DAs for a commercial PU for synthetic leather. The radiation protecting effects depended on the miscibility, electron-accepting capacity, steric effect and resonance stability of aromatic DAs. The effects of these aromatic DAs on the PU are: (1) Stabilization of the PU radicals formed by irradiation, inhibiting the polymer chain scission (Scheme 1), and (2) in some extent, cross-linking through coupling of PU radicals with DA diradicals (Scheme 2). Thus, DPB can be used as an antirad for the polyurethane at least within a dose of around 600–800 kGy. The addition of 1 wt% DAs improved the mechanical properties of PU.

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