

The γ -Radiolysis of Nylons: Molecular Rearrangement and Gas Production

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The γ -radiolysis of nylons 12, 11, 6/12, 6/9, 6/6, and 6 were investigated. The IR spectra of film samples before and after the γ -irradiation show the formation of amines, aldehydes, and ketones, and suggest that the cleavage of amide group is one of the major processes of radiolysis. The yields of gaseous products and their evolution from the bulk were measured with a quadrupole mass spectrometer. Four gases were determined as the major radiolytic products and their yields were found to be in the order $H_2 > CO > CO_2 > CH_4$ for all the nylons. The relationship between the gas yields and the chemical composition of the monomer unit shows that the H_2 yield increases with the relative number of H atoms. The results suggest a random distribution of energy leading to H_2 production. It was found that the yields of CO and CO_2 decrease with an increase in the relative number of amide groups on the nylon monomer unit. Since these later products must be derived from the amide group, chain scission and fragmentation at the amide group must decrease with increasing amide contribution to the monomer unit of the polymer chain. The diffusion coefficients of H_2 , CO, and CO_2 gases in the bulk polymer were determined and the results suggest that post-radiation processes exist in the γ -radiolysis of nylons.

Introduction

Nylon polymers have numerous applications and their degradation by mechanical deformation, heat, photolysis, and ionizing radiation have attracted research interests for decades.^{1–9} A number of physical and chemical changes such as sample yellowing, loss of mechanical strength, lowered melting point, and gas release have been observed in nylon degradation, suggesting that processes such as the decomposition of the amide group, chain scission, decreased crystallinity, and others are occurring. The practical effects of ionizing radiation on nylons are important to many fields such as the nuclear industry,^{10,11} nylon modification by heavy-ion implantation,¹² and ionizing radiation initiated grafting, and polymerization of polyamides.^{13,14} Fundamental studies on the radiolysis of nylons are especially interesting because one can observe the difference in products due to the variation in repeating groups making up the polymer main chain. The examination of volatile gases as a function of the type of nylon gives considerable knowledge on the degradation mechanism of these polymers, while IR spectroscopy provides information on the remaining high molecular weight products.

The different types of amides are characterized by the methylene chain length making up the amide monomer. For instance, nylon 6 (polycaprolactam) has the structure $[-CO-NH-(CH_2)_5-]_n$. A number of different radical species can be formed by bond breakage following the absorption of energy from ionizing radiation. ESR studies on the products from the high-energy irradiation of polyamides show that the predominant main-chain free radical species is formed by removal of a hydrogen atom from the carbon adjacent to the amide nitrogen ($-CO-NH-\bullet CH-CH_2-$).^{5,15–18} Simulations of the ESR spectra by Igarashi¹⁸ suggest that the radical $-CO-NH-\bullet CH-CH_2-$ accounts for 75% of all free radical species observed in the γ -radiolysis of nylon 6. Zimmerman¹⁴ proposes that the high

degree of specificity of free radical formation in the γ -radiolysis of nylons is due to a concentration of energy in the vicinity of the amide group prior to elimination of the α hydrogen atom, even though the initial ionization or excitation occurs randomly along the chain. The radiation chemical yield, G value, is estimated to be 5.8 main-chain radicals per 100 eV of energy absorbed in nylon 66.¹⁹ This value is typical for a liquid hydrocarbon and suggests that a large amount of H atoms are produced in this system.

Only a few investigations have examined the gas production in the degradation of nylons, even though such analysis can provide significant insight on the chemical mechanisms of the decomposition. Stephenson et al. used gas chromatography techniques to find that molecular hydrogen and methane were the two dominant gases produced in the UV photolysis of nylon 6/6.²⁰ Do et al. determined gaseous products in the UV photolysis of nylon 6 and nylon 6/6 from their IR spectra.²¹ They observed CO, CH_4 , NH_3 , and various carbonyl gaseous compounds and proposed that the amino end groups in nylon 6 were involved in the ammonia formation. Krasnansky et al. investigated the gas production in the γ -radiolysis of polymers including nylon 11, nylon 6/6, and MXD-6 (m-xylene diamine) by mass spectrometry.²² Their results showed that H_2 is the predominant gas in all the nylons, and they suggest that cross-linking and double bond formation on the main chains are the dominant radiolytic induced reactions. They also show that the total gas yield decreases with decreasing length of the aliphatic chain, indicating that the amide group increases the stability of the polyamides.

In the present paper, the γ -radiolysis of a series of nylons was carried out. The yields and dynamic evolution of several gaseous products were determined in order to provide both fundamental information on the polymer degradation and to give practical knowledge on the observation of gaseous products. IR spectra of the irradiated nylons were also obtained so that the residual state of the polymer could be determined. Chemical mechanisms in the γ -radiolysis of nylons are discussed as based

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TABLE 1: Physical Properties of the Nylons Examined Here

Nylon	density (g/cm ³)	melting temperature (°C)	shape ^a
12	1.010	178	sphere
11	1.026	198	pellet
6/12	1.040	218	pellet
6/9	1.080	210	sphere
6/6	1.090	267	sphere
6	1.084	228.5	sphere

^a Spheres are 2.0 mm diameter and pellets are 3.5 mm \times 2.2 mm.

on the analysis of the IR spectra and the gas yields from the different nylon samples.

Experimental Section

Materials and the γ -Source. Six types of nylons were investigated in this paper. They include nylon 12, nylon 11, nylon 6/12, nylon 6/9, nylon 6/6, and nylon 6. The pertinent physical properties of these polymers are listed in Table 1. Because the vender did not provide the specific density of nylon 6/12, it was determined by using a "flotation method" at room temperature.⁷ Carbon tetrachloride ($\rho = 1.5942$ g/cm³) and toluene ($\rho = 0.8669$ g/cm³) were used as the two floating liquids. By gradually dropping carbon tetrachloride into toluene, the polymer particles originally sitting on the bottom of the liquid began to float when a certain volume of carbon tetrachloride was added. A linear relationship was observed between the specific density of the other five nylons and the mixing ratio of the liquids. The specific density of nylon 6/12 was found to be 1.04 by interpolation using a straight line fitted to the data of the other five nylons.

The γ -irradiations were carried out with a Shepherd ⁶⁰Co source with a dose rate of about 200 Gy/min. The dosimetry was determined with a Fricke dosimeter as described elsewhere.²³ Electron density normalization was used to convert to the equivalent dose for each nylon investigated.

Measurement of the IR Spectra. For the determination of the IR spectra, the nylon pellets or spheres were cast into films before irradiation. Nylon films were cast using an *m*-cresol solution in which 3% of the nylon by weight was dissolved. The cast films were placed in a vacuum oven at 100 °C for about one week to allow the cresol to evaporate. The prepared films are white, half transparent, and less than 0.01 cm thick. The IR spectra of the films were taken by transmission scanning using a BIO-RAD FTS175 FT-IR spectrometer (resolution 8 cm⁻¹) with air as the reference. It was found that the IR spectra obtained are very similar to standard reference spectra,²⁴ indicating that the structures of the nylon molecules were preserved and the cresol remaining in the films was negligible. The irradiations of the nylon films were carried out by placing the films in a Pyrex cell containing an inlet and outlet for flushing with an inert gas. The cell was loaded with the film samples and flushed with ultrahigh-purity (UHP, > 99.999% pure) argon for 2 h before the γ -irradiation was conducted to ensure that the amount of residual air, as determined by mass spectrometry, was negligible. The sample was purged during the irradiation and for about 2 h after the irradiation. The film samples were then immediately moved to a vacuum oven for 3 or 4 days to prevent the oxygen from reacting with the long-lived free radicals. The IR spectra of the nylon films were then taken. The above procedure was repeated to obtain the IR spectra at different doses.

Measurement of the Radiolytic Gases. Gas evolution experiments were conducted on the polymers as received,

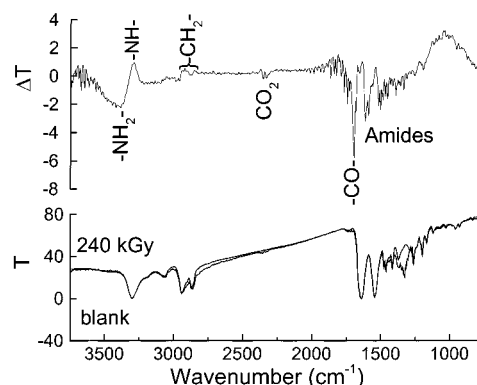


Figure 1. Transmittance, *T*, IR spectra of nylon 6 before and after radiolysis to 240 kGy. Difference of IR spectra, ΔT , due to radiolysis.

following a washing with water and a vacuum-dry. The samples were placed in a quartz cell containing an inlet and outlet port for gas purging. UHP argon with a flow rate of 50 mL/min was used to purge the air from the sample cell before irradiation and to flush the gaseous products from the cell following irradiation. Irradiations were performed at room temperature by lowering the sample cell into the irradiation zone of the cobalt source for a fixed period of time. In the dynamic, or real-time, experiments the argon gas purged the sample throughout the irradiation. Except for H₂, the evolution of products from the bulk polymers into the gas phase was slow. Some experiments were run in an isolation mode in which a four-way valve was used to close off the sample from the argon gas stream during the radiolysis. The valve remained closed for various delay times following the radiolysis in order to accumulate the gases and to obtain the time dependence of their evolution from the bulk. The valve was then opened and the gaseous species were flushed from the quartz cell.

A quadrupole mass spectrometer (Balzers QMA140 analyzer) was used to sample the effluents flowing from the irradiation cell using a capillary tube ($\phi = 50$ μ m, $L = 20$ cm) as the transfer line. A multiple-ion-detection mode was used to simultaneously monitor as many as four peaks at different mass channels. The dwell time for each mass channel was set to 50 ms. The time used to shift between the channels was dependent on the hardware and not longer than 50 ms. The time to obtain the data from 4 channels in one cycle was less than 0.4 s, which was short enough to minimize any sampling bias of the evolving peaks.

Air slowly entered the cell when the four-way valve was used to isolate it from the stream of argon. This phenomenon can interfere with the measurement of the peaks at mass numbers 27 and 28. Admission of atmospheric gases can occur by leaks at the joints connecting the quartz cell, plastic tubing, and the four-way valve, or by their diffusion through the plastic tubing. The amount of gas entering the system showed linear increases with isolation time and could be subtracted by conducting "blank" runs without irradiation.

Results and Discussion

IR Spectra of the Radiolytic Products. The changes in the IR spectra in the γ -radiolysis of nylons 6, 6/9, 11, and 12 films were determined. It was found that the spectra of the nylon films are quite similar to each other so the effects on only nylons 6 and 12 are fully discussed. Figures 1 and 2 show the transmittance, *T*, in the IR region before and after irradiation with a dose of 240 kGy for nylon 6 and nylon 12 films, respectively.

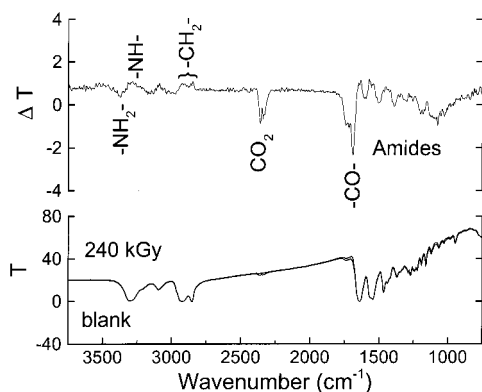


Figure 2. Transmittance, T , IR spectra of nylon 12 before and after radiolysis to 240 kGy. Difference of IR spectra, ΔT , due to radiolysis.

The similarity in their spectra is apparent, indicating that the nylon samples are similar in structure. All the bands in the spectra are at the expected frequencies as given in *The Aldrich Library of FT-IR Spectra*.²⁴ The important bands have been assigned in other studies^{9,21,25,26} and they include: 3300 cm^{-1} ($-\text{NH}-$ stretch); 2930 and 2860 cm^{-1} ($-\text{CH}_2-$, stretch); 1640 cm^{-1} (Amide I, the $\text{C}=\text{O}$ stretch) and 1540 cm^{-1} (Amide II, the $\text{C}-\text{N}$ stretch).

To examine the changes in the IR spectra caused by irradiation, the difference between the spectra before and after irradiation was taken. Irradiation causes the films to yellow, so the background shift of the irradiated spectrum was taken into account before comparing the spectra. The spectrum in the range of 1800–2200 cm^{-1} was used to calculate the background shift. After adjusting the background shift, the difference in transmittance, ΔT , was calculated. The difference spectrum obtained in this way was considered to represent the spectrum of the radiolytic products. The spectra of the radiolytic products in the 240 kGy irradiation of nylons 6 and 12 are presented in Figures 1 and 2, respectively. Note that a decrease in the transmittance is an increase in absorbance, or formation of a product and vice versa.

The difference spectra are very similar for both nylons 6 and 12. Both spectra show increases in the bands at about 3300 cm^{-1} , 2930 and 2860 cm^{-1} , and 1640 cm^{-1} , suggesting that the $-\text{NH}-$, $-\text{CH}_2-$, and amide groups, respectively, decrease in the radiolysis of the nylon samples. The decreases in the bands at about 2360 and 1690 cm^{-1} indicate the formation of CO_2 gas²¹ and the production of new carbonyl groups.^{9,21} Adjacent to the increasing $-\text{NH}-$ band at 3300 cm^{-1} , there is a decreasing band at about 3380 cm^{-1} . This band is assigned to the products due to the rupture of the amide $-\text{NH}-$ group in the radiolysis. According to the reference spectra,²⁴ many nonaromatic amines and amides show a band at about 3380 cm^{-1} (for compounds such as RNH_2) or a wider band ranging from 3200 to 3600 cm^{-1} (for compounds such as R_1NHR_2 and RCONH_2). This finding suggests that the cleavage of the amide bonds causes the $-\text{NH}-$ groups to transform into RNH_2 , R_1NHR_2 , and RCONH_2 . The increasing amine band at about 3380 cm^{-1} has different shapes in the spectra for nylon 6 and nylon 12. The band for nylon 6 is wider and expanded to the higher frequency, suggesting that the amine products in nylon 6 are more complicated than those in nylon 12.

The spectra of the radiolytic products for nylons 6 and 12 also show big differences in the range from 1250 to 1650 cm^{-1} . For nylon 12, a group of four bands at 1600, 1500, 1390, and 1300 cm^{-1} can be observed, whereas for nylon 6, there are many narrow bands with minima at 1617, 1593, 1509, 1455, 1398,

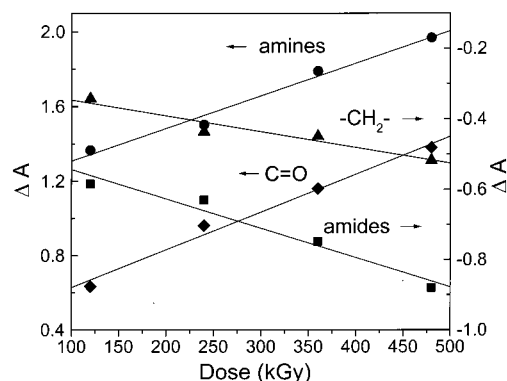


Figure 3. Changes in IR spectra bands, ΔA , as a function of dose for nylon 12: (●) amines, (■) amides, (▲) $-\text{CH}_2-$, (◆) $\text{C}=\text{O}$.

and 1339 cm^{-1} . The IR spectra of amines²⁴ suggest that the group of four bands at about 1600, 1470, 1380, and 1300 cm^{-1} are due to the absorption of N -alkylamines. For amines with more complicated structure than N -alkylamines and amides, many narrow bands are expected in the range between 1250 and 1650 cm^{-1} . Therefore, it is proposed that for nylon 12 most of the ruptured amide $-\text{NH}-$ groups result in the amines with the form of $\text{NH}_2-\text{CH}_2-\text{CH}_2-$. However, for nylon 6, other types of amines such as $\text{R}-\text{NH}_2$, R_1NHR_2 , and RCONH_2 are found. Photodegradation studies of nylon 6 and nylon 6/6 by Moor²⁷ and by Do et al.²¹ suggest that the aminyl radical $-\dot{\text{N}}\text{H}$ does not form amino end groups. Our observation on the radiolysis of nylons is not in agreement with this suggestion and is probably due to the use of higher energy radiation compared to the more specific photodegradation.

The carbonyl band at about 1690 cm^{-1} has different shapes for nylons 6 and 12. For nylon 12, the $\text{C}=\text{O}$ band is at 1690 cm^{-1} , with a shoulder expanding to 1770 cm^{-1} . The area of the shoulder is nearly as large as that of the band itself. For nylon 6, the $\text{C}=\text{O}$ band is at 1698 cm^{-1} , with a shoulder about half its area. The reference IR spectra of various ketones and aldehydes²⁴ indicate that only the ketones and aldehydes with carbon-carbon double bonds conjugated to the $\text{C}=\text{O}$ groups display shoulders expanding to higher frequency. Ketones and aldehydes without conjugated carbon-carbon double bonds show a narrower band around 1700 cm^{-1} . Therefore, it is suggested that for nylon 12 a large part of the ruptured amide $\text{C}=\text{O}$ groups form the ketones and aldehydes with carbon-carbon double bonds conjugated to the carbonyl groups. For nylon 6, a variety of the ketones and aldehydes with and without conjugated double bonds are produced in the radiolysis.

The characteristic bands in the spectra of the radiolytic products were further investigated by varying the radiation doses. Similar shapes were found for all the bands at different doses. The differences in the areas of the absorbance bands (ΔA) before and after the irradiation were found to be approximately linear in the dose range from 120 to 480 kGy. Figure 3 illustrates the near linear dependence of ΔA on the irradiation doses for the radiolysis of nylon 12. The only exceptions to the linearity are the ΔA of the bands between 1250 and 1630 cm^{-1} for nylon 6. For all the nylons, an increase in dose leads to an increase in amines and carbonyl groups with a concurrent decrease in amides and $-\text{CH}_2-$ bands. These results are consistent with carbon-hydrogen bond breakage and the cleavage of the monomer chain at the amide group. Although the changes in ΔA are linear with dose, the IR spectra obtained in this work is not useful for determining yields. It can be observed in Figure 3 that the ΔA values do not extrapolate through the origin. This result is due to the large doses, >120 kGy, used to obtain

observable changes in the absorbance. The IR data is useful for qualitative analysis.

Aldehydes and ketones with conjugated carbon–carbon double bonds are observed mainly in the radiolysis of nylon 12. However, amines, aldehydes, and ketones with various forms are observed in the radiolysis of nylon 6. Do et al.²¹ suggest that hydrogen bonding in nylon might produce more complicated radiolytic products in the radiolysis of nylons with high concentrations of amide groups. It can be concluded that the cleavage of the amide group is a major process in the radiolysis of nylons. For nylons with longer aliphatic chains, the cleavage of the amide group favors formation of *N*-alkylamines, aldehydes, and ketones. Carbon–carbon double bonds tend to form in positions conjugated with the carbonyl groups. For nylons with shorter aliphatic chains, the cleavage of the amide group follows more complicated mechanisms to produce amines, aldehydes, and ketones in various forms.

Constitution of the Gaseous Products. The gaseous species were identified and their yields were measured in the radiolysis of all the nylon samples. A four-way valve was used to isolate the quartz cell containing the nylon samples during the radiolysis in order to increase the detection sensitivity. Doses varying from 200 Gy to 24 kGy were used in the radiolysis. It was found that the peak intensities at masses 2, 15, 28, and 44 increase with increasing radiation dose, while the peak intensities at masses 17, 26, 27, and 30 do not vary with the dose. This observation was true for all six nylons, although the variation of the intensity of peaks at 44 and 15 becomes slight as the aliphatic chain length in the nylons decreases. Masses 17, 26, 27, and 30 correspond to the parent peaks of NH_3 , C_2H_2 , HCN , and C_2H_6 and the results suggest that there is no evolution of these gases. The parent mass of C_2H_4 is at 28, but this molecule also has substantial peaks at masses 26 and 27, which do not vary with dose suggesting that it too is not a major product in the radiolysis of the nylons. The production of these gases is lower than the detection limit of the apparatus, which means their yields are less than 0.05% of the total gas yield. The observed peaks at 2, 15, and 44 can readily be assigned to H_2 , CH_4 , and CO_2 , respectively. The peak at 28 has a contribution from both CO and CO_2 . Standard mass spectral reference data show that the peak for CO_2 at 28 is about 7% as large as the peak at 44.²⁸ The CO_2 yield as determined from mass 44 was found to be less than 20% of the CO yield so it was concluded that the contribution of CO_2 to the peak at 28 is negligible compared to CO . Therefore, the peak at 28 was assigned to CO and may represent an overestimate by no more than 14%.

Gas measurement experiments with an isolation time of 420 min gave linear relationships for the amount of H_2 , CO , and CO_2 with dose for all six nylons. The isolation time refers to the post-irradiation period in which the gas is allowed to diffuse from the bulk polymer. Figure 4 illustrates the variation of the product gas volumes as a function of the radiation dose for the radiolysis of nylon 11. It can be seen that the experimental points for H_2 , CO , and CO_2 can be readily fit to straight lines. For CH_4 , the linear correlation between the amount of gas and the dose was not good because the amount of gas produced in the radiolysis is low, especially in the case of nylon 6/9, nylon 6/6, and nylon 6. It can be seen in Figure 4 that the fitted lines for CO , CO_2 , and CH_4 do not go through the origin as the dose approaches zero. Unavoidable air leaks during the isolation are responsible. The linear relationships between the gas volume and the dose are good and the isolation time is always much longer than the irradiation time. The results indicate that the amount of air entering the system does not change if the isolation

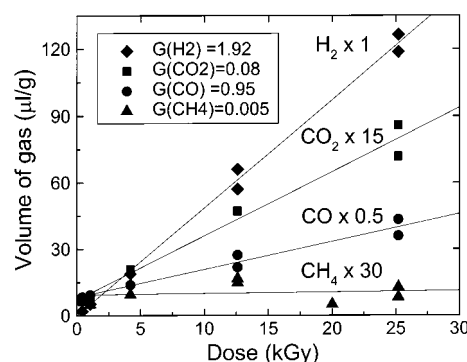


Figure 4. Production of gases as a function of dose in the radiolysis of nylon 11: (◆) H_2 , (■) CO_2 , (●) CO , (▲) CH_4 .

TABLE 2: *G* Values (molecules/100 eV) for the Gases in the Radiolysis of the Nylons

polymer	$G(\text{H}_2)$	$G(\text{CO})$	$G(\text{CO}_2)$	$G(\text{CH}_4)$	G_{total}
Nylon 12	2.1	0.88	0.07	0.006	3.06
Nylon 11	1.92	0.95	0.08	0.005	2.96
Nylon 6/12	1.67	0.59	0.05	0.004	2.31
Nylon 6/9	1.29	0.38	0.05	0.004	1.72
Nylon 6/6	0.96	0.24	0.03	0.002	1.23
Nylon 6	0.92	0.17	0.04	0.002	1.13

time and other machine conditions are fixed. Therefore, the gas yields can be calculated from the slopes of the fitted lines and expressed as *G*-value, which is defined as the number of the molecules produced per 100 eV energy deposited in the sample.

Table 2 lists the gas yields measured in the γ -radiolysis of the six nylons. It can be seen that the total gas yields for these nylons range from 3.06 to 1.13 molecules/100 eV. Of the four main gaseous products in all of the nylons examined, H_2 is the predominant component with a relative yield ranging from 60 to 80% of the total. The relative order for other three components is CO (15–32%) > CO_2 (2–3%) > CH_4 (~0.2%). It is interesting that the yields of all gas products gradually decrease in the order of nylons 12, 11, 6/12, 6/9, 6/6, and 6; that is, with decreasing number of $-\text{CH}_2-$ units in the monomer. This decrease is attributed to the gradual increase in the stabilizing effect of the amide group.

Few studies are available that contain data on the gas yields obtained in the radiolysis of nylons. Krasnansky et al. reported a study on the gas production in the γ -radiolysis of nylon 6/6 and nylon 11 in a vacuum with doses of 30, 60, and 360 kGy.²² The gaseous components they found are same as those observed here, i.e. H_2 , CO , CO_2 , and CH_4 . The relative gas yields obtained by Krasnansky et al. are also similar to those observed in this paper. For example, in the radiolysis of nylon 11 at a dose of 60 kGy, they found that the relative gas yields are 66%, 29%, 1%, and 4% for H_2 , CO , CO_2 , and CH_4 , respectively. These results compare well with the values of 64%, 32%, 2.7%, and 0.2% for the corresponding species observed here with dose ranging from 200 Gy to 24 kGy. However, the total gas yields reported by Krasnansky et al. are smaller than those observed here. With a dose of 360 kGy, they report that the total yields of gases are 28 mol/10⁶ g for nylon 6/6 and 56 mol/10⁶ g for nylon 11. These yields translate to radiation chemical yields of 0.8 and 1.6 molecules/100 eV, and are smaller than the corresponding values of 1.23 and 2.96 molecules/100 eV observed here at a dose of 24 kGy. One possible reason for the discrepancy is in the time evolution of the gases from the sample as discussed below.

Production of H_2 Gas. It can be seen from Table 2 that the H_2 gas yields of the nylons, $G(\text{H}_2)$, increases gradually in the

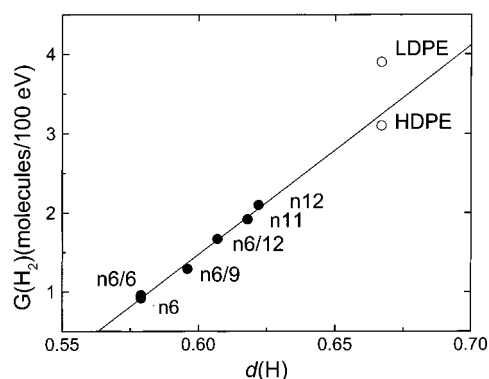


Figure 5. $G(\text{H}_2)$ as a function of the relative number of H atoms in the monomer of the nylons, low-density polyethylene (LDPE) ref 29, and high-density polyethylene (HDPE) ref 30.

order of nylon 6 ~ nylon 6/6 < nylon 6/9 < nylon 6/12 < nylon 11 < nylon 12. This result shows that $G(\text{H}_2)$ increases with increasing number of $-\text{CH}_2-$ units in the monomer of the nylons. A plot of the $G(\text{H}_2)$ value as a function of the relative number of H atoms in the monomer unit, $d(\text{H})$ (i.e., the ratio of the number of H atoms to the number of all the atoms in the monomer unit), shows a good linear relationship, see Figure 5. Such a relationship may be useful for predicting the production of H_2 gas directly from the chemical composition of a particular class of polymers.

The H_2 gas yields for low-density polyethylene (LDPE, $G(\text{H}_2) = 3.9$)²⁹ and high-density polyethylene (HDPE, $G(\text{H}_2) = 3.1$)³⁰ are also shown in Figure 5. It can be seen that the $G(\text{H}_2)$ for HDPE agrees better than LDPE with the value predicted by extrapolation of the nylon data. The reason for $G(\text{H}_2)$ for HDPE being lower than that of LDPE is usually attributed to the difference in their crystallinities.³¹ A number of investigations have shown that radical processes in the amorphous phase are faster than in the crystalline phase.^{32–34} The crystallinity of nylons range from 10% to 40%,³⁵ which is closer to that of LDPE (about 40–50%) than to that of HDPE (about 80–90%). Crystallinity arguments would predict the LDPE to be closer to the extrapolated line. However, the amide group may possess a stabilizing effect on carbon–hydrogen bond rupture that lowers the H_2 production in the radiolysis of nylons.

The observations suggest the following mechanisms for the production of H_2 in the radiolysis of nylons.

(a) The production of $\text{H}\cdot$ free radicals is proportional to the relative number of H atoms in the nylon monomer unit. If the initial ionization and excitation takes place randomly along the chain in the radiolysis,¹⁴ it is reasonable to assume that the yield of $\text{H}\cdot$ is proportional to the relative number of H atoms along the nylon chain, $G(\text{H}\cdot) \propto d(\text{H})$.

(b) Various free radical reactions are possible as the $\text{H}\cdot$ radicals diffuse. However, the linear relationship of $G(\text{H}_2)$ to $d(\text{H})$ suggests that abstraction and H_2 elimination reactions dominate. The following abstraction and elimination reactions are possible:

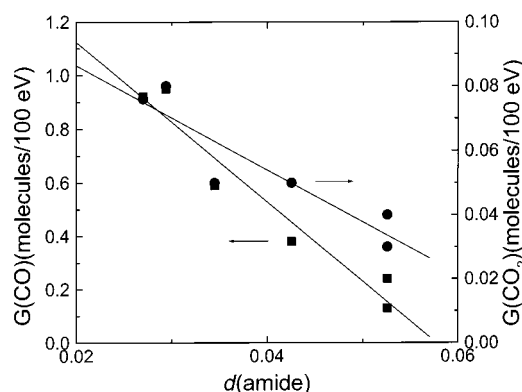
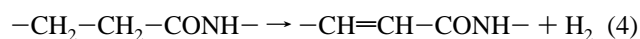
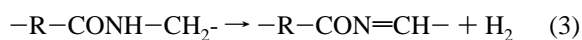
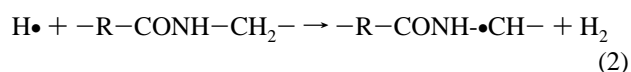
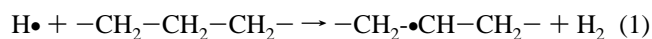
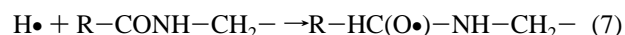
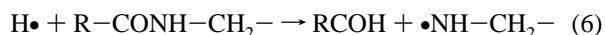
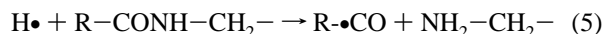


Figure 6. $G(\text{CO})$, (■), and $G(\text{CO}_2)$, (●), as a function of the relative number of amide groups in the monomer.

Reaction 1 was suggested by many studies on the radiolysis of polyolefines and polyamides.^{36–38} The secondary radical produced in reaction 2 is suggested to be the predominant radical in the degradation of nylons.^{14–18} Energetic arguments suggest that reaction 3 occurs to a lesser extent than reaction 2. Reaction 4 is responsible for the production of the carbon–carbon double bond conjugated to the carbonyl group, which was observed in the IR spectra of the radiolytic products as discussed above. The $\text{H}\cdot - \text{H}\cdot$ combination reaction is not considered important for H_2 production in the γ -radiolysis of solid polymers because the relative distance between H atoms is thought to be large.³⁹ In addition, the combination reaction is a second-order process and would not give the linear relationship shown in Figure 5.

(c) As previously discussed, the amide group may have a stabilizing effect on the production of H_2 in the radiolysis of nylons. Possible reactions are as follows:



Reactions 5 and 6 involve the scission of amide bond, which is the weakest bond in nylons.²⁷ Amine and aldehyde formation was observed in the IR spectra of irradiated nylons, as discussed above. Reaction 7 is proposed because the oxygen atom in the amide group has a high electron affinity. In addition, the radical $\text{R}-\text{HC}(\text{O}\cdot)\text{NHCH}_2-$ is considered to be one of the reactants leading to the production of CO_2 , which is discussed in the following section.

Production of CO and CO_2 Gases. It can be seen from the data in Table 2 that the radiolytic production of carbon monoxide and carbon dioxide decrease as the relative amount of the amide group in the nylon monomer units increases. For example, the $G(\text{CO})$ values are 0.88, 0.95, 0.59, 0.38, 0.24, and 0.17 molecules/100 eV for nylon 12, nylon 11, nylon 6/12, nylon 6/9, nylon 6/6, and nylon 6, respectively. The yields for CO and CO_2 decrease with an increase in relative amide number ($d(\text{amide})$), defined as the number of amide atoms (C,N,O) per total number of atoms in the monomer unit), as shown in Figure 6. The amide group is the only source of oxygen to give CO and CO_2 gases. Therefore, these results suggest that the scavenging effect of amide group is more effective than the processes for the production of CO and CO_2 in the radiolysis of nylons. Other studies show that chain cross-linking decreases and the chain scission increases with increasing content of the amide group in nylon. For example, the $G(x)$ values of the chain cross-linking, $G(x)$, in γ -radiolysis are 1.42,⁴⁰ 1.40,⁴¹ and 0.3⁷

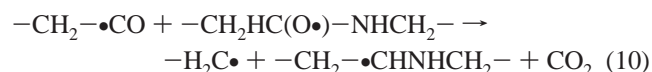
for LDPE, nylon 10/10, and nylon 6, respectively. The G values for chain scission, $G(s)$, in γ -radiolysis are 0.48, ~ 1.37 , and 2.6, respectively. This result suggests that the amide link in the polymer chain is weak and easy to rupture upon irradiation, but chain scission does not lead preferentially to CO and CO₂ formation. On the other hand, the aliphatic chain favors cross-linking more than scission in γ -radiolysis.

The production of CO gas is thought to be due to the radicals that are formed in the cleavage of the amide group.^{21,27}



At the same time, the neighboring amide groups can prevent the carbonyl radicals from degrading to form CO gas. This scavenging effect increases with increasing amide concentration.

The mechanism for the production of CO₂ does not seem to be given in the literature. Table 2 shows that $G(\text{CO}_2)$ is only 10–20% of $G(\text{CO})$ for all the six nylons. CO₂ formation involves two amides and can be due to the following reaction:



where the radical $-\text{CH}_2\text{HC}(\text{O}\bullet)-\text{NHCH}_2-$ is formed by the reaction of $\text{H}\bullet$ and an amide group (as shown in reaction 7). As in the production of CO gas, neighboring amide groups can stabilize the radicals for the CO₂ production. It can be seen in Figure 6 that $G(\text{CO}_2)$ decreases linearly with increasing relative number of amide groups, $d(\text{amide})$. The similarity in $G(\text{CO})$ and $G(\text{CO}_2)$ suggests a common radical precursor, with CO₂ formation being less probable.

Post-Radiation Effects on Gas Evolution. The dynamic evolution of the gases from the bulk nylon polymers was investigated. In the first set of experiments, the irradiation time was set to 5 min and the gas evolution was continuously monitored for about 60 min. It was found that the dynamic profiles of only the H₂ gas could be monitored in this manner since the yields of CO and CO₂ gases were too low. The dynamic profiles for H₂ gas are characterized by a build-up during the radiation period followed by a prolonged decay tail. The immediate drop in the H₂ peak with the cessation of the radiation field suggests that its evolution is controlled by gas diffusion in polymer matrix and not due to post-irradiation effects. A number of numerical diffusion models developed from Fick's law of diffusion were used to model the dynamic profiles of H₂.⁴² The optimum diffusion coefficient D and gas yield $G(\text{H}_2)$ were simultaneously extracted from the best fit of the numerical simulation to the time profile data. The $G(\text{H}_2)$ values obtained in this manner were virtually the same as the values found in the isolation experiments (as given in Table 2). The D values extracted from the numerical simulation are listed in Table 3. It can be seen that the H₂ diffusion coefficients for all the six nylons vary in a relative narrow range, from 5.4×10^{-7} to 7.4×10^{-7} cm²/s. Panchev et al. reported diffusion coefficients of H₂ ranging from 2.7 to 3.0×10^{-7} cm²/s in the γ -radiolysis of polyamide P-54.⁴³ These values are 50% smaller than those obtained here and may be due to differences in the polymer sample or the sampling method.

To further investigate the time dependence of the gas evolution, the irradiations were performed with different isolation times following the irradiation to allow the gas to evolve from the bulk polymer without being flushed away by the carrier gas. The irradiation time was set to 10 min and the time used

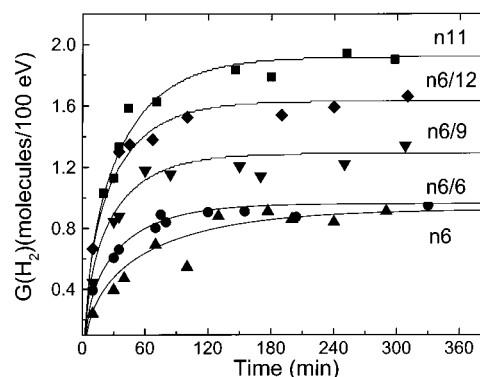


Figure 7. Profiles for H₂ evolution as a function of isolation time for nylons.

TABLE 3: Diffusion Coefficients Extracted from the Dynamic Profiles and the Isolation Profiles of the Nylons

polymer	D_{H_2} (10^{-6} cm ² /s)		D_{CO} (10^{-6} cm ² /s)	D_{CO_2} (10^{-6} cm ² /s)
	dynamic profile	isolation profile		
Nylon 12	0.70			
Nylon 11	0.74	0.55	0.3	0.04
Nylon 6/12	0.71	0.53	0.2	0.04
Nylon 6/9	0.66	0.46	0.2	0.02
Nylon 6	0.58	0.37	0.08	0.03
Nylon 6/6	0.54	0.23	0.07	0.02

to isolate the quartz cell ranged from 10 to 300 min. All three of the gases, H₂, CO, and CO₂, could be observed and were measured. The background accumulations of CO and CO₂ were subtracted using corresponding nonirradiation runs. Figure 7 shows the gas evolution as a function of isolation time for H₂ in all of the six nylons. Similar data were obtained for CO and CO₂. It can be seen that the gas yield increases gradually with isolation time until a plateau is reached. Note that the irradiation time in all these experiments is the same; the sample is isolated for varying times to allow that gas to diffuse out of the bulk. The time for the plateau to appear increases in the order of $\text{H}_2 < \text{CO} < \text{CO}_2$. For H₂, the plateaus appear around 120 min, depending on nylon type. For CO, the plateaus appear at about 240 min. However, for CO₂ gas, the plateaus could not be observed in the range of the measuring time.

Model fitting of the isolation data can be performed if it is assumed that the gas evolution is completely controlled by the diffusion process. Because the experimental points are sparse and less accurate as compared with those in the dynamic profiles, it is impossible to extract both diffusion coefficients and yields simultaneously. Only the diffusion coefficients were extracted numerically using the previously obtained G values listed in Table 2. The results are listed in Table 3.

The diffusion coefficients for H₂ extracted from the isolation experiments are about 30% smaller than those obtained from the dynamic profiles. It can be also seen that the diffusion coefficients for CO₂ are $2\text{--}4 \times 10^{-8}$ cm²/s, which are 3 to 10 times smaller than those for CO. The estimated values of the diffusion coefficients should be within 10–20% so these differences are significant. Although there are no published values for the diffusion coefficients for nylons, the large difference between D_{CO} and D_{CO_2} seems abnormal. The diffusion coefficients for CO and CO₂ in solid polymers are usually close to each other, with the D_{CO_2} slightly larger than D_{CO} . For example, for natural rubber, $D_{\text{CO}} = 1.35 \times 10^{-6}$ cm²/s, $D_{\text{CO}_2} = 1.10 \times 10^{-6}$ cm²/s; for LDPE, $D_{\text{CO}} = 3.32 \times 10^{-7}$ cm²/s, $D_{\text{CO}_2} = 3.72 \times 10^{-7}$ cm²/s; and for 87/13 vinyl chloride-acetate, $D_{\text{CO}} = 8.6 \times 10^{-10}$ cm²/s, $D_{\text{CO}_2} = 1.3 \times 10^{-9}$ cm²/s.⁴⁴

Therefore, the data suggests that some post-radiation process is responsible for the formation of CO₂, resulting in an apparent slowing of its diffusion from the bulk polymer. Similar, but much smaller, effects may contribute to H₂ and CO, but the data is inclusive.

Li and Zhang⁴⁵ examined the changes in the physical properties of nylon 10/10 due to γ -radiolysis. The significant changes in gel fraction, crystallinity, etc., with the temperature of the post-irradiation heat treatment lead them to conclude that post-radiation effects occur in nylon. In addition, ESR studies¹⁴ show that the $-\text{CH}_2\text{CONH}-\bullet\text{CH}-$ radical is stable following the irradiation. It is not clear how this radical could contribute to the delayed production of CO₂ observed here.

Conclusions

The IR spectra of the radiolytic products for nylons 6 and 12 showed that $-\text{NH}-$, $-\text{CH}_2-$, and amide group decrease with irradiation. New species produced in the radiolysis were found. These include amines, aldehydes, and ketones, indicating that the amide group is ruptured in the γ -radiolysis. For nylon 12, the spectra show that amino end groups and carbonyl groups conjugated with carbon-carbon double bonds were formed. For nylon 6, the IR spectra show that various amines, aldehydes, and ketones are produced, suggesting that the decomposition is more complicated than nylon 12. The data indicates that the amide groups affect the decomposition mechanism significantly.

Analysis of the gases produced shows that the yields of the four major gas products in the radiolysis of the nylons are in the order $\text{H}_2 > \text{CO} > \text{CO}_2 > \text{CH}_4$. It was found that $G(\text{H}_2)$ increases linearly with $d(\text{H})$, the relative contribution of H atoms to the nylon monomer unit. The production of CO and CO₂ gases was attributed to the cleavage of amide group, but is found to decrease with increasing $d(\text{Amide})$, the relative number of amide atoms in the monomer unit. The stabilizing effect of the amide group on the production of CO and CO₂ gases is more effective than the processes responsible for their formation.

Gas evolution in the γ -radiolysis of the nylon samples was examined. Diffusion coefficients were determined from dynamic gas profiles and from isolate profiles for H₂. The results were similar with the isolation profiles giving values about 30% lower than the dynamic profiles. Isolation experiments of CO and CO₂ gas evolution show that the D_{CO_2} values are about 3–10 times smaller than D_{CO} when they are expected to be similar. These results suggested that post-radiation processes may be responsible for the production CO₂ and to a much less extent of H₂ and CO.

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