Regulation of the Thermal Reactions of Polyacrylonitrile by γ-Irradiation

Wenwei Zhao,* Yukio Yamamoto, and Seiichi Tagawa

The Institute of Scientific and Industrial Research, Osaka University,
8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

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Thermal treatment of γ-irradiated polyacrylonitrile was performed to investigate the radiation effects on the thermally activated reactions. It was found that the exothermic reaction and the discoloration of the irradiated samples occurred at much lower temperatures than for nonirradiated ones, and the reactions can be regulated by the preirradiation dose. The structures formed by the thermally activated reactions of the irradiated samples consisted of C═N and/or C═C conjugation sequences having broad electronic absorption bands up to 500 nm and an emission band at green-blue light region. The preirradiation caused an increase in absorption intensity with no shift in wavelength of the absorption peaks. A spectral shift was observed for the emission of the preirradiated samples, demonstrating an occurrence of the energy transfer among the conjugated unsaturation sequences. Free radical identification by ESR indicated that the radiation effect was not due directly to trapped radicals but caused by the functional groups generated during irradiation, which contributed to the initiation of the thermal reactions. The differential scanning calorimetric and thermogravimetric analyses confirmed that the preirradiation lowered the onset temperature of the reactions and alleviated the heat evolution process.

Introduction

The thermally induced reactions of polyacrilonitrile (PAN) have been the subject of a number of investigations for the last half century.[1−12] Thermal treatment of PAN at temperatures above 200 °C leads to changes in physical properties which are of great practical importance. For example, the electrical property of PAN can be altered from an insulator to a semiconductor and, eventually, to a conductor, depending on the heat treatment conditions.[13−16] Another important application of this thermal treatment of PAN is found when the polymer is used as a precursor to produce high-quality carbon fibers.[5,8−11] The production process for PAN-based fibers involves two main stages: (1) an oxidation at moderate temperatures (200−250 °C) in air that stabilizes the fiber and (2) carbonization under vacuum or an inert atmosphere at high temperatures (1000−3000 °C).

The primary stages of the thermally induced conductivity change in PAN films as well as of the thermally induced stabilization of PAN-based carbon fiber precursors generally consisted of thermally activated reactions of the nitrile groups. Although various reaction schemes have been proposed, it seems to be widely accepted that the intramolecular reaction leads to a ladder structure containing conjugated C═N sequences.[10] The reaction is highly exothermic ($\Delta H \sim 1300$ J/g) and causes the degradation of the polymer backbone. Therefore, a process that could regulate the exothermic process would be very useful. Incorporation of a small amount of nucleophilic reagents such as carboxylic acids has been found to be effective in reducing the exothermic effect and is widely used in the process of producing carbon fibers from PAN precursors.[4,6,8,10] Alternatively, we postulate that the reactions can be regulated by ionizing irradiation.

The effect of γ-irradiation on the thermal reactions of PAN was recently reported by Tarakanov.[17] The author has found that the irradiated samples are oxidized much more rapidly than the unirradiated ones. This result may imply that the irradiation accelerates the conjugated ladder structure formation, because the earlier studies have indicated that the formation of the ladder structure is the prerequisite to the oxidation process.[6] However, no direct evidence has yet been obtained.

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(1) Burlant, W. J.; Parsons, J. L. *J. Polym. Sci.* **1956**, *22*, 249.
(2) Schurz, J. *J. Polym. Sci.* **1958**, *28*, 438.
(3) Grassie, N.; Hay, J. N.; McNeill, I. C. *J. Polym. Sci.* **1958**, *31*, 205.
(4) Grassie, N.; Hay, J. N. *J. Polym. Sci.* **1962**, *56*, 189.
(5) Bailey, J. E.; Clarke, A. J. *Nature* **1971**, *234*, 529.
(6) Watt, W.; Johnson, W. *Nature* **1975**, *257*, 210.
(7) Coleman, M. M.; Petcavich, R. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 821.
(8) Peebles, Jr. L. H.; Peyser, P.; Snow, A. W.; Peters, W. C. *Carbon* **1990**, *20*, 707.
(9) Peebles, Jr. L. H.; Peyser, P.; Snow, A. W.; Peters, W. C. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 2069.
(10) Bashir, Z. *Carbon* **1991**, 29, 1081.
(11) Kakida, H.; Tashiro, K.; Kobayashi, M. *Polym. J.* **1996**, *28*, 30.
(12) Xue, T. J.; McKinney, M. A.; Wilkie, C. A. *Polym. Degrad. Stab.* **1997**, *58*, 193.
(13) Teoh, H.; Metz, P. D.; Wilhelm, W. G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 297.
(14) Ritsko, J. J.; Crecelius, G.; Fink, J. *Phys. Rev. B* **1983**, *27*, 2612.
(15) Chung, T. C.; Schlesinger, Y.; Etemad, S.; Macdiarmid, A. G.; Heeger, A. J. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1239.
(16) Chatterjee, N.; Palit, S. K.; Maiti, M. M. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 2875.
(17) Tarakaov, B. M. *Fiber Chem.* **1995**, *27*, 150.

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We have studied the effects of γ-irradiation on the conjugated structures formation in poly(vinyl aclohol) and poly(vinyl chloride) and found that the pendant side groups in these polymers could be more readily eliminated when irradiation is performed either prior to or in situ of the thermal treatment, resulting in the formation of conjugated sequences.[18,19] These studies tend to offer a facile way to prepare conjugated polymers in addition to understand the initiation mechanisms of the elimination reactions. In this paper, we report γ-irradiation effects on the conjugated ladder structure formation in the thermal treatment of PAN. Direct evidence of radiation enhancement of the conjugation sequence formation was obtained by the UV−visible and FTIR absorption spectroscopies for PAN films.

Experimental Section

PAN was obtained from Aldrich ($M_w = 86\ 200$; $M_n = 22\ 600$). The film of PAN was prepared by spin coating a 3 wt % solution of PAN in dimethyl sulfoxide onto a silicon wafer. The film was dried under 0.1 Torr first at 50 °C for 1 day and then at 100 °C for another day. Then, the film was removed from the substrate and cut into 10 × 30 mm slices. FTIR measurement indicated that the solvent was completely removed. The film thickness was measured to be about 6 μm. The films were then transferred into flat quartz cells with a Pyrex neck and sealed under vacuum (10^{-4} Torr) prior to irradiation.

Irradiation was performed at room temperature with γ-rays (^{60}Co source) at a dose rate within the range of 1.0−3.5 kGy/h. Postirradiation thermal treatment was carried out by isothermal heating as well as progressive heating.

Isothermal heat treatment was performed by putting the quartz cell containing thin film sample of PAN into a tube furnace which was previously heated to a given temperature. The temperature was automatically controlled with a variation of less than 2 °C. Electronic absorption spectra of isothermally heated films were measured at various heating time intervals using a Shimadzu UV-3100PC scanning spectrophotometer. FTIR spectra and emission spectra were obtained on Perkin-Elemer Spectrum 2000 FTIR spectrometer and LS50B luminescene spectrometer, respectively.

Progressive heating was done on differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) devices from Shimadzu Co. Ltd. with a heating rate of 10 °C/min under N_2 atmosphere (20 mL/min). Electron spin resonance (ESR) measurements were carried out using a Varian E-line spectrometer.

Results and Discussion

The main change in chemical structures caused by the thermal treatment of PAN at a moderate temperature is the formation of conjugated carbon−nitrogen double bonds with the consumption of the pendant nitrile groups.[1−3] As a result, the electronic absorption behaviors of the materials will be modified, although the absorption spectra have rarely been reported.[15] Electronic absorption spectra of the heated PAN films with and without preirradiation are shown in Figure 1. For the samples without preirradiation (Figure 1a), the absorbance developed very slowly at the heating temperature of 170 °C, in agreement with the early studies, which have indicated that almost no changes can be observed in the infrared spectra and no reactive intermediate is identified by ESR measurements when the heating temperature is lower than 180 °C.[10,20] In contrast, for the samples irradiated prior to the thermal treatment, the absorbance increased more rapidly when heated at the same temperature (Figure 1b−d). The spectra show two broad absorption bands with maxima at 270 and 360 nm. The absorption intensities increased with heating time or preirradiation dose with no significant change in peak positions. The correlation between the absorbance at 360 nm and heating time is illustrated in Figure 2. It can be seen that in the early

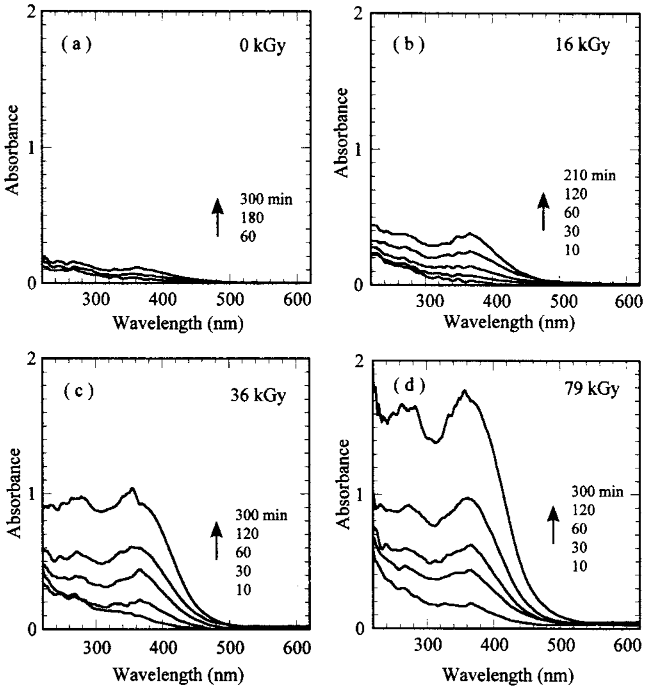

Figure 1. Electronic absorption spectra of thermal treated PAN films (170 °C) with a preirradiation dose of (a) 0 kGy, (b) 16 kGy, (c) 36 kGy, and (d) 79 kGy.

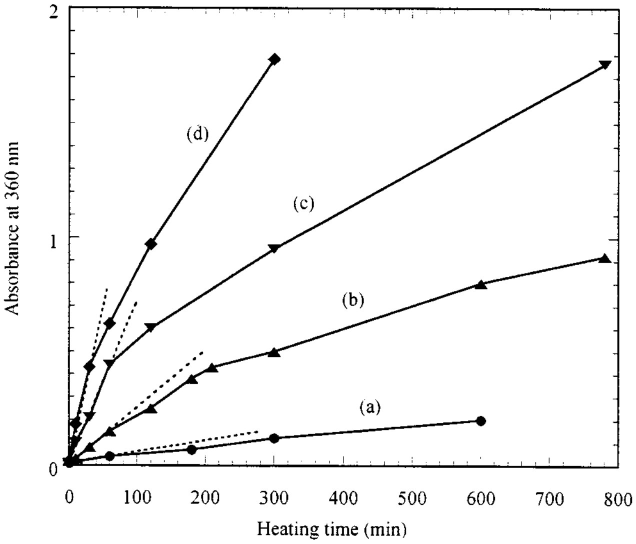

Figure 2. Dependence of the absorbance developed at 360 nm on the heating time at 170 °C. The preirradiation dose was (a) 0 kGy, (b) 16 kGy, (c) 36 kGy, and (d) 79 kGy.

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[18] Zhao, W.; Yamamoto, Y.; Seki, S.; Tagawa, S. *Chem. Lett.* **1997**, 183.

[19] Zhao, W.; Yamamoto, Y.; Tagawa, S. *J. Polym. Sci., Polym. Chem. Ed.* **1998**, 3089.

[20] Hasegawa, S.; Shimizu, T. *Jpn. J. Appl. Phys.* **1970**, *9*, 958.

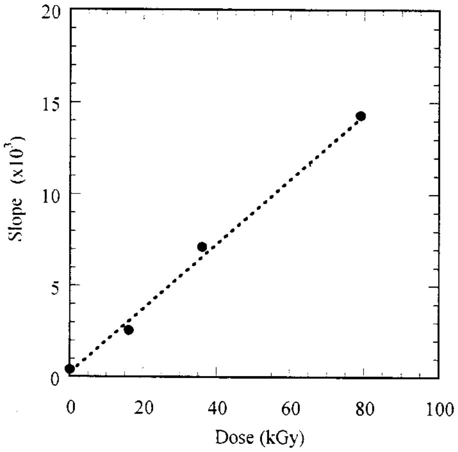


Figure 3. Plot for the dependence of the rate of absorption rise on the preirradiation dose. (The slopes were derived from the dotted lines shown in Figure 2.)

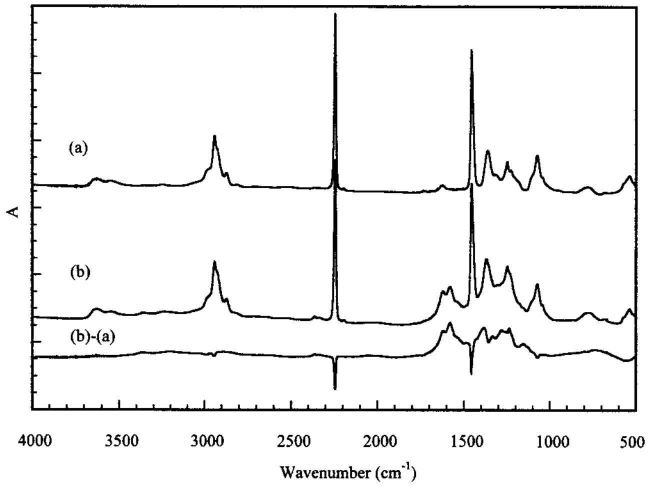


Figure 4. FTIR spectra of PAN: (a) original, (b) preirradiated to 79 kGy and then heated at 170 °C for 13 h, and (c) the subtracted spectra of panels b and a.

stages the aborbance increased linearly with heating time. The absorbance tended to flatten-off with the increase of heating time. A linear relationship was also found between the (absorbance/time) slopes in the early stage of the plots and the preirradiation doses, as is shown in Figure 3. Any radiolysis products, such as functional groups or radicals, contributed possibly to the formation of the conjugation structure. The formation rate was therefore proportional to the yields of the radiolysis products at low conversions in the early stage of the heat treatment. As the reaction progressed, PAN chains would begin forming a network (i.e. become less mobile) and the formation rate of the conjugation structures will decrease. This effect could cause such a flattening-off of the absorbance/time plots as seen in Figure 2.

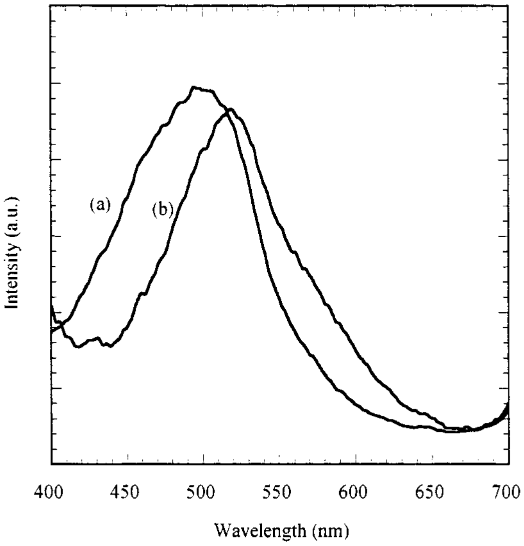


Figure 5. Emission spectra of PAN after irradiated to (a) 36 kGy and (b) 79 kGy, respectively, followed by heated at 170 °C for 13 h.

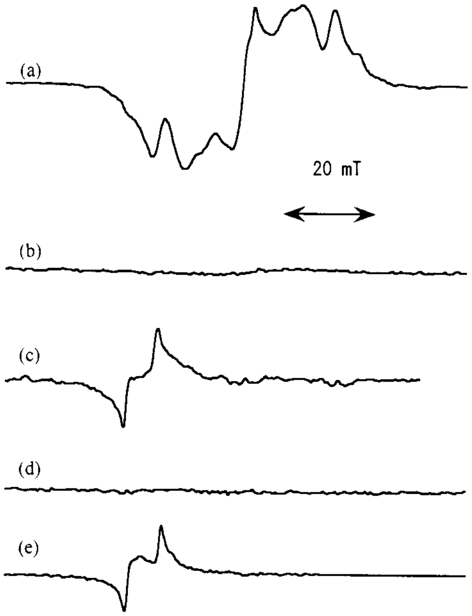
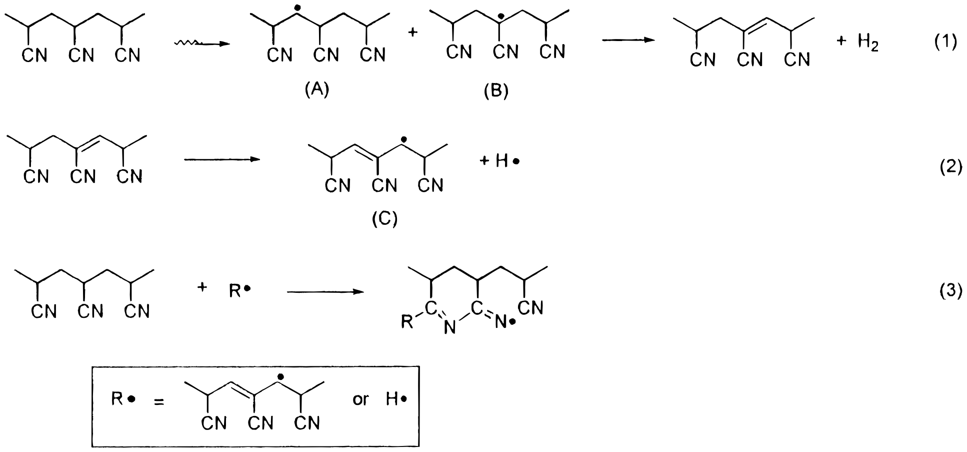


Figure 6. ESR spectra: PAN after irradiation by γ-rays to 10 kGy (a), then annealed at 50 °C for 10 min (b), further annealed at 140 °C for 30 min (c); nonirradiated PAN heated at 140 °C for 30 min (d); and PVC heated at 140 °C for 30 min (e).

Figure 4 shows the changes in FTIR spectra upon thermal treatment of the preirradiated films. The spectra confirmed that C=N bonds (~1600 cm^{-1}) were produced while the nitrile groups (2241 cm^{-1}) were consumed. At the same time, the C=C (~1600 cm^{-1}) groups might also be produced to some extent because a decrease in intensity of CH_2 (1450 cm^{-1}) resonances of the polymer backbone was also observed. From the above results, it can be concluded that the absorbance developed at the range of 220−500 nm in the preirradiated PAN films reflects the formation of C=N and C=C conjugated π-electron systems. The formation of the conjugated unsaturation structures in nonirradiated PAN was identified, but in that case, it required a much higher temperature to activate the reaction.

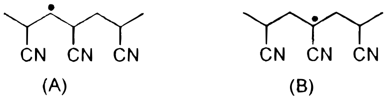
In addition, the preirradiated PAN films showed interesting emission properties after the thermal treatment. As can be seen from Figure 5, the emission maxima appeared at around 500 nm with a clear wavelength shift on preirradiation dose. This behavior is in contrast to that of the absorption spectra, which showed no significant wavelength shifts as a function of preirradiation dose or on heating time (Figure 1). The con-

Scheme 1



stant absorption pattern in Figure 1 suggests an invariable conjugation length distribution for the samples with different concentrations of the unsaturation sequences. It is reasonable to assume that the cyclization reaction to produce the conjugation groups is a chain reaction, and therefore, the change in preirradiation dose or in heating time alters only the conjugation structure concentration but not the conjugation length distribution. Accordingly, the shift of the emission spectra should be interpreted in terms of the increase in concentration of the conjugated moieties. Specifically, the higher concentration of the conjugated moieties enables the excited energy transfer and the emission through the longer conjugation sequences, while the transfer is limited at the lower concentrations. Further investigations are apparently required to elucidate the mechanism of the energy transfer among the conjugation sequences.

The formation of radical species following irradiation as well as heating was examined using ESR spectroscopy in order to clarify the root cause of the radiation-induced effect. Figure 6a shows the ESR spectrum of PAN measured at room temperature immediately after irradiation. The spectrum contained a hyperfine structure consisting of a triplet of doublets and a singlet central line. The hyperfine structure has been assigned by several authors to the following radicals A and B:[20,21]


(A) (B)

These radicals resulted from the abstraction of H atom from the main chain carbon atoms. However, these radicals were not stable and were annealed out on exposure to slightly elevated temperatures (Figure 6b). Interestingly, when the temperature was further increased, new ESR signals were observed in the preirradiated sample. As shown in Figure 6c, radicals with a singlet line were produced. However, an annealing temperature of 140 °C was apparently too low to generate radical intermediates in the nonirradiated sample (Figure 6d).

It has been claimed that no radical species could be detected when PAN is treated at a temperature below 180 °C.[20] The radicals generated by heating of PAN at above 180 °C have been identified and assigned to be polyimine radical and/or polyene radical, depending on the atmosphere. Polyimine radical is exclusively produced when the treatment is performed in a vacuum. Under the present conditions, however, the radical generated in the preirradiated samples shown in Figure 6c may not be assigned to polyimine radicals but more reasonably to polyene radicals, although the experiments were performed under vacuum. The peak-to-peak width (ΔH_{pp}) of the radical in Figure 6c is about 0.7 mT, close to that of a polyene radical (ΔH_{pp} 0.7–0.8 mT) and distinctly lower than the width for a polyimine radical (ΔH_{pp} 1.9–2.5 mT).[21] In addition, this radical (Figure 6c) was remarkably similar to that produced in the thermal treatment of poly(vinyl chloride) (Figure 6e), which is well-known to produce polyene radicals. Therefore, the radical in Figure 6c was assigned to the radical structure C, which could be produced from the primary radicals A and B via eqs 1 and 2 of Scheme 1 with the evolution of hydrogen. This reaction scheme is in agreement with the fact that hydrogen is observed to be the main gaseous product from γ-irradiation of PAN.[22]

A hydrogen atom is generated simultaneously with the radical C. These reactive intermediates may initiate the cyclization reaction in the way shown in eq 3. The addition of a hydrogen atom to a nitrile group has been suggested by several researchers in studies with small molecular compounds containing nitrile functionality.[23,24]

From these results, it may be concluded that the radicals generated by irradiation do not contribute directly to the subsequent thermal treatment, but the allylic structures derived from the radicals are thermally unstable and serve as initiation sites for the thermal reactions.

The specific reaction occurring in the thermal treatment of PAN is known to be exothermic and ac-

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(21) Andreeva, O. A.; Tolparov, Yu, N.; Firsov, E. I. *Vysokomol. Soedin. B* **1986**, *28*, 111.

(22) Hill, D. J. T.; Lang, A. P.; O'Donnell, J. H.; Pomery, P. J. *Polym. Degrad. Stab.* **1992**, *38*, 193.

(23) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1962**, *36*, 1938.

(24) Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1970**, *74*, 3362.

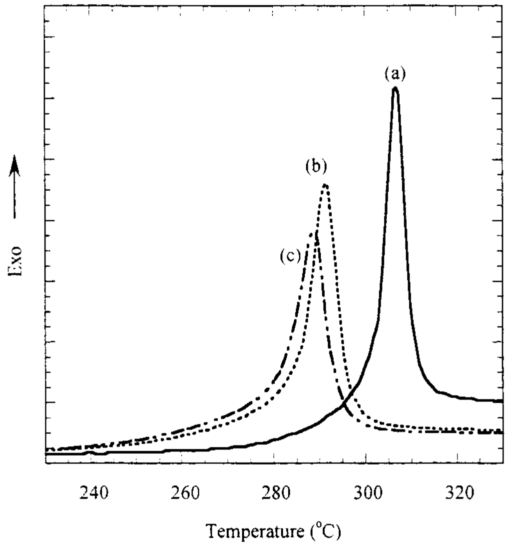

Figure 7. DSC curves of PAN with and without preirradiation; dose: (a) 0 kGy, (b) 53 kGy, and (c) 130 kGy.

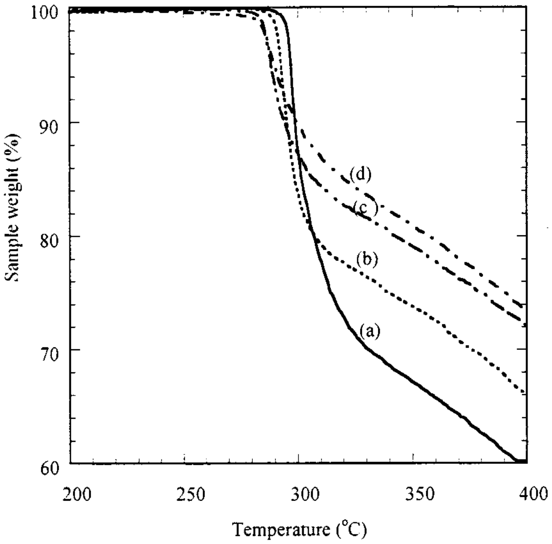

Figure 8. TGA curves of PAN with and without preirradiation; dose: (a) 0, (b) 24, (c) 92, and (d) 169 kGy.

companied with the loss of sample weight. Progressive thermal treatment was therefore performed using DSC and TGA apparatus to measure the evolution of heat and change of sample weight, respectively. Figure 7 shows typical DSC curves of the samples with and without irradiation. A sharp exothermic peak was found at 309 °C for the sample without irradiation, while the exothermic peaks of preirradiated samples shifted 20−30 °C to lower temperatures. There were no thermal transitions observed at lower temperatures of 170−200 °C, where considerable chemical structure changes were detected by other analytical techniques shown before. It should be noticed that the identifications of the chemical structure changes were performed after the samples were heated at a constant temperature for a certain period of time, while the thermal evolution in the DSC analyses were measured under a progressive heating condition. The thermal transitions at lower temperatures should also be observable by the DSC if the heating rate used was low enough. In addition, as seen from Figure 7, the peaks of preirradiated samples were broader with reduced intensities in comparison with those of the nonirradiated one, while the peak area was approximately constant. The results indicate that the kinetics of exothermic reaction, which is believed to be related to the cyclization of the nitrile groups, was significantly modified by prior irradiation treatment, but the difference seemed to be chiefly in the initiation step. Apparently the radiation products have initialized the cyclization reaction as already concluded from the ESR analysis. Decrease of the reaction temperature with attenuated heat evolution intensity is essential to protect the macromolecular backbone from decomposition during the cyclization reaction, which was confirmed by thermogravimetric analysis. As demonstrated by the results in Figure 8, the nonirradiated sample showed a weight loss of about 30% while the one preirradiated to 169 kGy showed the weight loss of less than 10% at the end of the exothermic reaction.

Summary

The γ-irradiation of PAN imparted considerable effects on the thermal reactions in the subsequent thermal treatment, including the reduction of the reaction temperature, the mediation of the exothermic process, and the acceleration of the formation of conjugation structures via the cyclization of the nitrile groups. The thermal reaction temperature or the reaction rate at a give temperature was a function of the preirradiation dose. As a result, the reaction could be regulated by the preirradiation treatment. The origin of the irradiation-induced effects was considered to be mainly due to the allylic structures from irradiation. The allylic structures were less stable to thermal treatment and decomposed to give reactive species, which then initiated the cyclization reaction.

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