

Cross-Linked Polyacrylonitrile Prepared by Radiation-Induced Polymerization Technique

Sayed M. Badawy*,† and Ahmed M. Dessouki‡

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt, and National Center for Radiation Research and Technology, Cairo, Egypt

Received: March 9, 2003; In Final Form: July 5, 2003

Cross-linked polyacrylonitrile PAN granules were prepared at ambient temperature by γ -rays at a constant dose rate of 8.5 kGy/h. It was found that the rate of polymerization was linear with the radiation dose at the initial stage of polymerization, and then, at high conversion, it tends to level off above 35 kGy. Cross-linking of PAN is accompanied simultaneously with the polymerization process at high energy radiation. Characterizations of the cross-linked PAN prepared at different radiation doses were investigated by FT-IR, XRD, DSC, and TGA analysis. The appearance of an IR band at 1670 cm^{-1} confirmed the cross-linking of PAN via nitrile groups. The original crystal lattice and the entropy of melting ΔS_m did not change significantly at high radiation doses.

Introduction

Chelating polymers based on PAN have attracted much attention for application in the adsorption of heavy metals, in particular uranium.^{1–12} In our previous works,^{10–12} a radiation-induced polymerization technique has been used to synthesize a chelating polymer based on polyacrylonitrile. Radiation can promote cross-linking in a wide range of polymers and copolymers without additives during the polymerization process. The density of cross-linking can be controlled by the radiation dose.¹³ The chemical, physical, and mechanical properties can be improved to a great extent by cross-linking of polymers.¹⁴ The cross-linked structure of the polymer is essentially required for the packed column application. Moreover, the cross-linked polymer might form a more stable complex with metal ions due to its rigid network structures.¹⁵

In addition, the use of the radiation polymerization technique has the following advantages: (1) ionizing radiation initiates radical polymerization at ambient temperature in the absence of chemical initiators;^{11,16} (2) the initiation step of radiation polymerization is temperature-independent, and the overall activation energies are much smaller than in the chemically initiated process;^{11,17–19} and (3) the resulting polymer is homogeneous and free from any impurities, and the molecular weight can be controlled by varying doses and dose rate.^{11,20}

The aim of the present work is the synthesis of cross-linked PAN by high-energy radiation without additives and the study of its properties by FT-IR, XRD, DSC, and TGA analysis.

Experimental Section

Polymerization. Radiation-induced homopolymerization was carried out in a Pyrex tube containing acrylonitrile solution in DMF and exposed to ^{60}Co rays, at a dose rate of 8.5 kGy/h, under atmospheric air, at the National Center for Radiation Research and Technology (NCRRT)-Cairo. The resulting

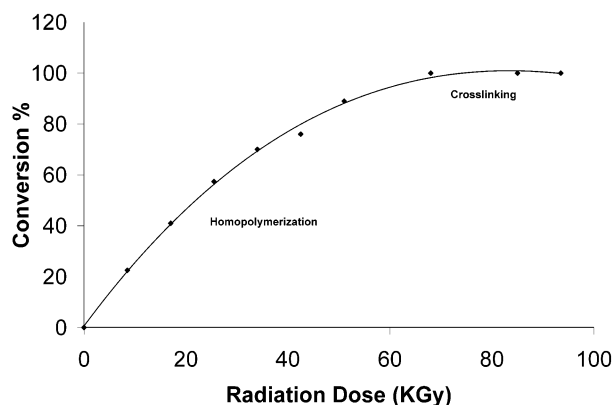


Figure 1. Conversion % vs radiation doses at monomer concentrated of 45% and dose rate of 8.5 kGy/h.

polymer yield was separated from the unreacted monomer by precipitation in distilled water, washed several times by water, then filtered, and dried. The conversion percent was determined by

$$\text{conversion \%} = \frac{M_o - M}{M_o} \times 100$$

where $(M_o - M)$ and M_o are the weights of the reacted monomer and the initial monomer, respectively.

Measurements. 1. *FTIR Spectra.* FTIR spectra were measured for the samples in the form of a KBr disk using a Shimadzu-8201 FTIR Spectrometer.

2. *Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).* Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a DSC-50 (Shimadzu) and a TGA-50 (Shimadzu), respectively, with a scan rate of $10\text{ }^{\circ}\text{C/min}$ in N_2 atmosphere.

3. *X-ray Diffraction.* X-ray diffraction studies of the samples were recorded within the angle range $2\theta = 5\text{--}50^{\circ}$ on a Shimadzu XRD-610 diffractometer using $\text{Cu K}\alpha$ radiation. The data were collected at a scan speed of 8 deg/min and 1.0 s at

* Corresponding author. E-mail: sayedbadawy@hotmail.com.

† Cairo University.

‡ National Center for Radiation Research and Technology.

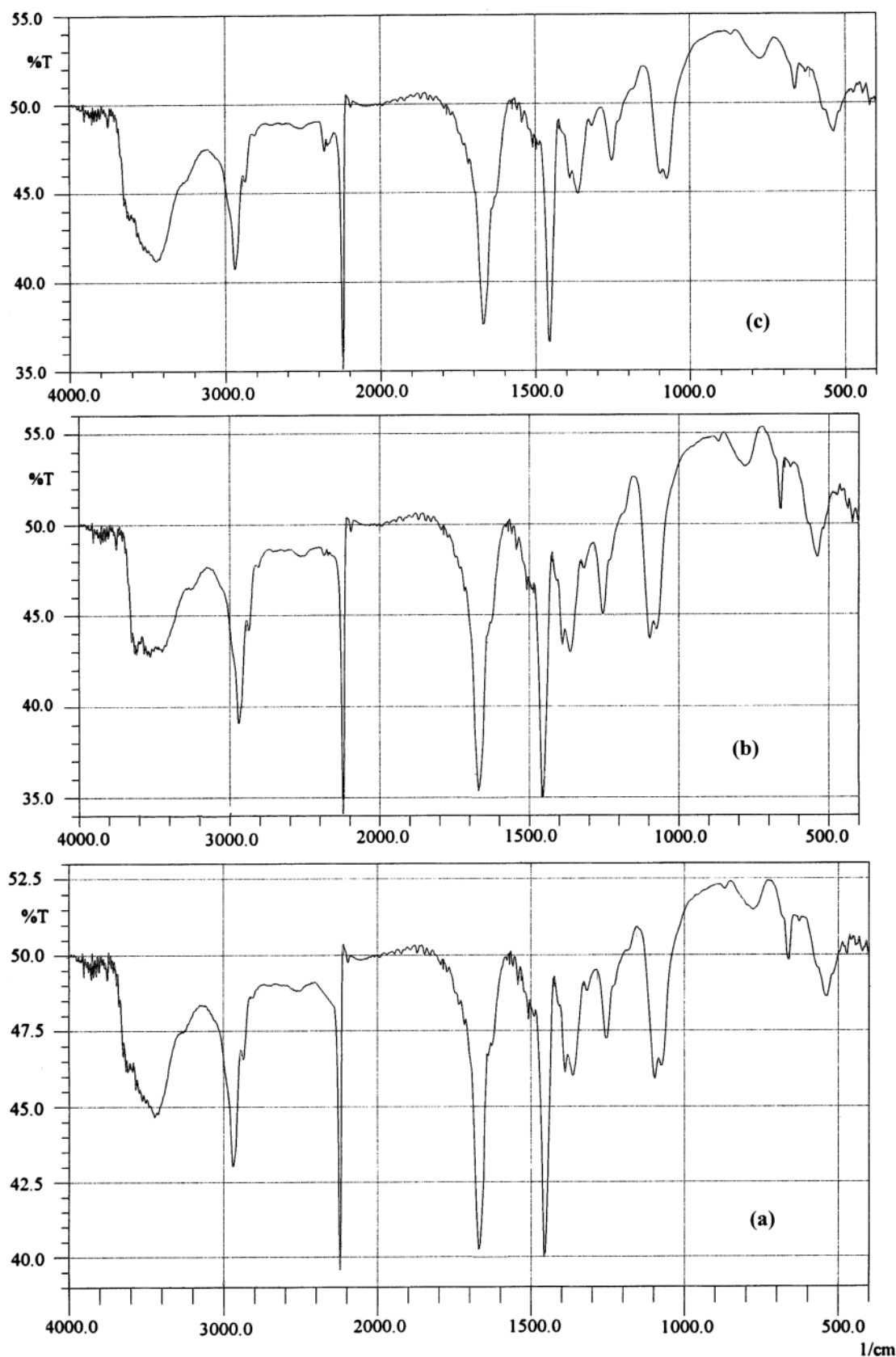


Figure 2. IR spectra of polyacrylonitrile at radiation doses of (a) 25.5, (b) 42.5, and (c) 59.5 kGy.

each step. The operating voltage and current were 30 kV and 20 mA, respectively. The average crystallite size (L_c) was determined from the broadening of the main diffraction peak centered around $2\theta \sim 17^\circ$. The full width at half-maximum (fwhm) B was measured in radians, and this was substituted

into the Scherrer equation, which gives the crystallite size:²¹

$$L_c = \frac{K\lambda}{B \cos \theta}$$

where K , the instrumental broadening factor, was determined

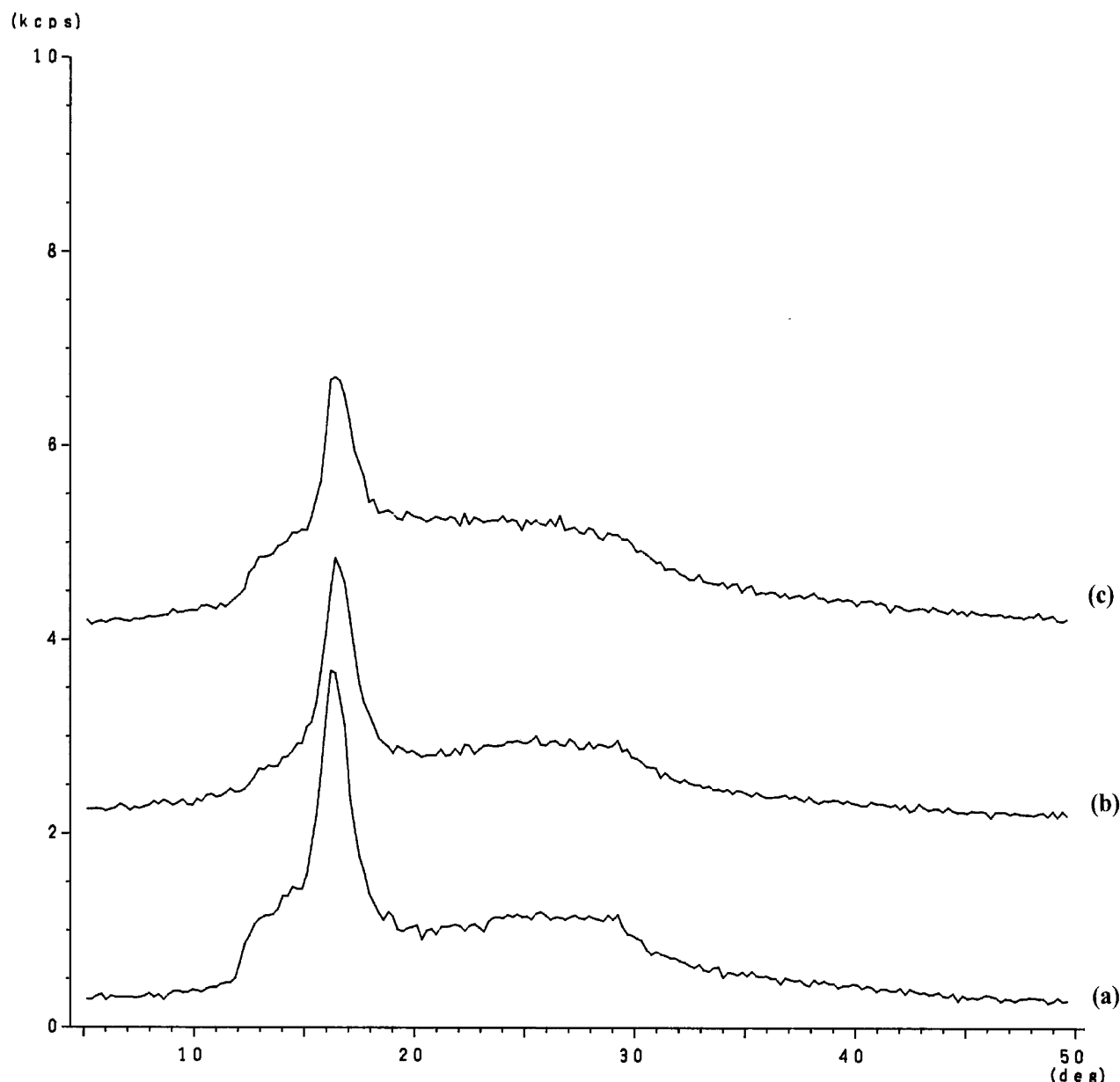


Figure 3. XRD spectra of polyacrylonitrile at radiation doses of (a) 8.5, (b) 42.5, and (c) 59.5 kGy.

and was assigned a value of 1.0 by using silicon as a standard; θ is the Bragg angle; and $\lambda = 1.54 \text{ \AA}$ is the wavelength of the X-rays.

Results and Discussion

The polymerization of PAN proceeds in a heterogeneous medium. The polymer does not dissolve in its monomer solution, resulting in formation of a polymer precipitate in the reacting medium, and separation as a fine powder. This may be attributed to the fact that the intermolecular attractive forces of PAN are strong, so the cohesion energy is high (1000 J/cm^3), molecular chains are not flexible, and the polymer cannot be easily distorted under the action of external forces. In addition, the solubility parameters of AN and PAN are different, 21.5 and $26.3 (\text{J/cm}^3)^{1/2}$, respectively, so there is no interaction between AN and PAN. The kinetics of radiation polymerization in homogeneous and heterogeneous mediums were studied in our previous works.^{11,22}

Figure 1 shows the polymerization % vs radiation dose at constant dose rate of 8.5 kGy/h. The rate of polymerization is

linear with the radiation dose at the initial stage of polymerization, and then tends to level off above 35 kGy. This is attributed to the amount of initiating radicals formed by radiation which increases linearly with radiation dose and then reaches a certain limiting value at a high dose due to the consumption of the monomers, mostly in the polymerization process. At high radiation doses above 34 kGy, the conversion reaches high values and with increasing radiation dose, the produced polymer in the polymerization system becomes reactivated. The process then involves the radiolysis of the polymer, leading to formation of branched polymer molecules, i.e., cross-linking. This cross-linking occurs when side chains or even hydrogen atoms are split off by radiation. The radicals formed on adjacent chains can react together to give a covalent bond, thereby linking the polymer molecules together and a three-dimensional network is formed.¹⁹ The use of high-energy radiation in the polymer synthesis has a dual effect; the cross-linking process usually accompanies radiation-induced polymerization of cross-linkable polymers at high doses.

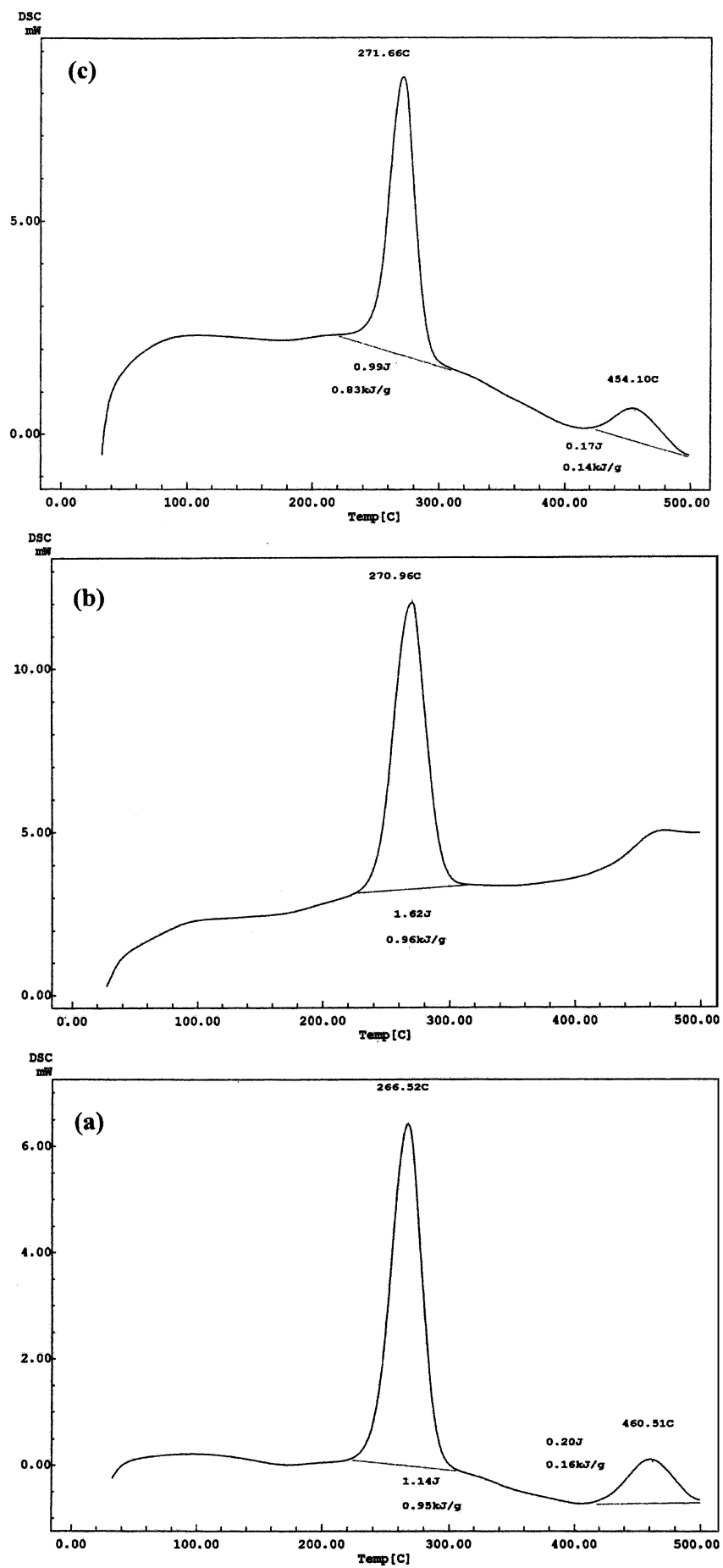


Figure 4. DSC of polyacrylonitrile at radiation doses of (a) 8.5, (b) 25.5, and (c) 59.5 kGy.

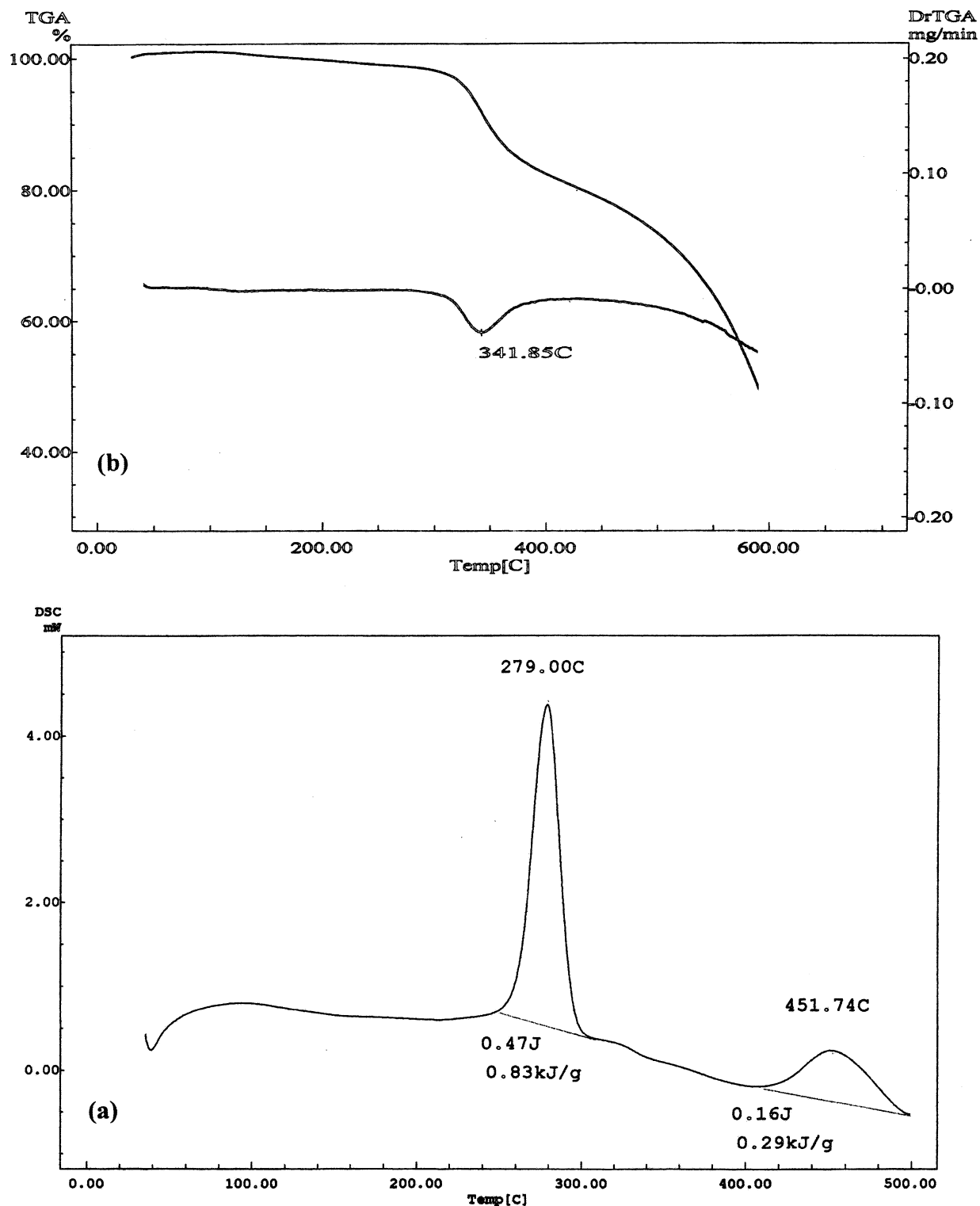


Figure 5. (a) DSC and (b) TGA of polyacrylonitrile

Figure 2 illustrates the FT-IR of PAN obtained at radiation doses of 25.5, 42.5, and 59.5 kGy. The bands at 3421, 2939, 2874, 2245, and 1458 cm^{-1} are assigned to $\nu_{\text{C}} = (\text{N}-\text{H})$, $\nu_{\text{as}}(\text{CH}_2)$, $\nu_{\text{s}}(\text{CH}_2)$, $\nu(\text{C}\equiv\text{N})$, and $\sigma(\text{CH}_2)$, respectively. The band at 1670 cm^{-1} is ascribed to the formation of $-\text{HC}=\text{N}-\text{N}=\text{CH}-$ conjugation across the polymeric chains (Scheme 1). The appearance of this band was attributed to the cross-linking of PAN via nitrile groups.²³

Figure 3 shows the XRD of PAN obtained at radiation doses of 8.5, 42.5, and 59.5 kGy. The XRD shows an intense peak (100) reflection located at $2\theta = 17^\circ$ and a weak peak at $2\theta = 29^\circ$ superimposed on an amorphous halo. The intense peak at $2\theta = 17^\circ$ corresponding to $d = 5.2 \text{ \AA}$ was interpreted as the (100) diffraction of hexagonal lattice formed by parallel close packing of molecule rods $\sim 6 \text{ \AA}$ in diameter. PAN has been described as adopting a stiff rodlike conformation due to the

SCHEME 1

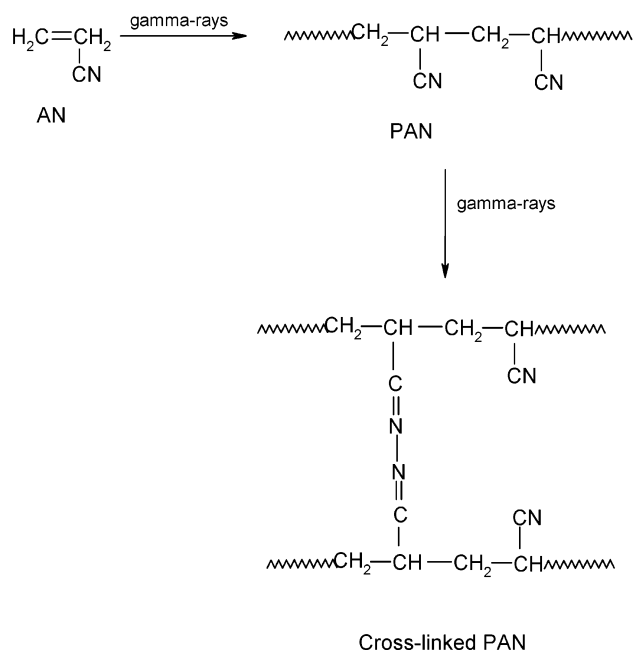


TABLE 1: T_m , ΔH_m , and ΔS_m Derived from DSC of Polyacrylonitrile at Radiation Doses of (a) 8.5, (b) 25.5, and (c) 59.5 KGy

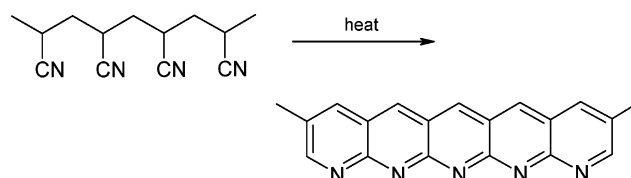
dose, kGy	T_m , °C	ΔH , J/g	ΔS_m , J/g/°C
8.5	266	950	3.6
25.5	270	960	3.5
59.5	271	830	3.1

intermolecular repulsion of the nitrile dipoles.^{21,24} The crystalline size estimated using a Scherrer equation is 57 Å. Owing to the very small crystallite size of PAN, the distinction between crystalline and amorphous regions is not sharply delineated as in a semicrystalline polymer such as polyethylene.²¹

It is obvious that the original crystal lattice was not distorted, and the oriented structure is still detected at high radiation doses. The slight decrease in the degree of crystallinity arises from the effect of high radiation doses which causes modification of the structure, such as branching and cross-linking structure. The destruction of crystallinity will be significant only at very high dose. It was previously found¹³ that the cross-linking occurs primarily in the amorphous regions, where chain flexibility allows adjacent chains to take up more readily the appropriate position needed to allow them to link together. In crystalline regions, links tend to occur preferentially near their surface.

Figure 4 shows the DSC of PAN obtained at radiation doses of 8.5, 25.5, and 59.5 kGy. A sharp exotherm appears in the temperature range 240–290 °C. A slight increase in melting temperature T_m is observed as the radiation dose increases. Table 1 shows that the difference in their T_m is similar to the difference in their ΔH_m . This means that the entropy of melting ΔS_m is similar at different radiation doses. The PAN has a low entropy of melting relative to its high melting point, because its strong intramolecular repulsive force stiffens the molecular chains, thereby reducing the conformational disordering.²⁵ It is known that the degradation of PAN in the temperature range 250–400 °C is explosive in nature. It was attributed to an inefficient removal of heat of polymerization of the nitrile groups which helps the interior temperature of the polymer to reach some critical value required for a number of secondary reactions to set in.²⁵

SCHEME 2



TG thermogram (Figure 5b), shows that the degradation of radiation-polymerized acrylonitrile starts at 315 °C which appeared as a single peak in DTG between 315 and 341 °C. Investigation of DSC and TGA (Figure 5) shows the appearance of sharp exotherm peak in the temperature range 240–290 °C without a weight-loss step, indicating a change in physical phase and/or chemical structure. The exotherm of PAN is attributed to the cyclization reaction and interchain polymerization of nitrile groups $-\text{C}\equiv\text{N}$ to conjugated polyimide $(-\text{C}=\text{N})_n$ by which PAN is characterized as shown in Scheme 2:

The formation of cyclic conjugated structure over 200 °C due to the linear polymerization of $\text{C}\equiv\text{N}$ was confirmed previously by FT-IR and (CP-MS) ¹³C NMR.²⁶

Conclusion

Cross-linked polyacrylonitrile PAN granules were prepared by a radiation-induced polymerization technique at different radiation doses and constant dose rate of 8.5 kGy/h. The rate of polymerization was linear with radiation dose in the initial stage of polymerization, and then tends to level off above 35 kGy. The use of high-energy radiation in the synthesis of PAN has a dual effect; the cross-linking process accompanies the radiation-induced polymerization. The IR band at 1670 cm^{-1} was ascribed to the formation of $-\text{HC}=\text{N}-\text{N}=\text{CH}-$ conjugation across the polymeric chains. With an increase of radiation doses, the degree of crystallinity slightly decreases, especially after a radiation dose of 59.5 kGy due to structure modification, whereas the original crystal lattice was not distorted. A strong exotherm peak in the temperature range 240–290 °C appeared without a weight loss step; this was attributed to the cyclization reaction and interchain polymerization of nitrile groups $-\text{C}\equiv\text{N}$ to conjugated polyimide $(-\text{C}=\text{N})_n$ preceding the mass loss.

References and Notes

- (1) Egawa, H.; Nakayama, M.; Nonaka, T.; Sugihara, A. *J. Appl. Polym. Sci.* **1987**, *33*, 1993.
- (2) Egawa, H.; Nakayama, M.; Nonaka, T.; Yamamoto, H.; Uemura, K. *J. Appl. Polym. Sci.* **1989**, *34*, 1557.
- (3) Nakayama, M.; Uemura, K.; Nonaka, T.; Egawa, H. *J. Appl. Polym. Sci.* **1988**, *36*, 1617.
- (4) Egawa, H.; Kabay, N.; Shuto, T.; Jyo, A. *J. Appl. Polym. Sci.* **1997**, *46*, 129.
- (5) Kabay, N.; Kataki, A.; Sugo, T.; Egawa, H. *J. Appl. Polym. Sci.* **1994**, *49*, 599.
- (6) Kubota, H.; Shigehisa, Y. *J. Appl. Polym. Sci.* **1995**, *56*, 147.
- (7) Okamoto, J.; Sugo, T.; Kataki, A.; Omichi, H. *Radiat. Phys. Chem.* **1985**, *25*, 333.
- (8) Okamoto, J.; Sugo, T.; Kataki, A.; Omichi, H. *J. Appl. Polym. Sci.* **1985**, *30*, 2967.
- (9) Saito, K.; Yamada, S.; Furusaki, S. *J. Membr. Sci.* **1987**, *34*, 307.
- (10) Dessouki, A. M.; El-Tahawy, M.; El-Boohy, H.; El-Mongy, S. A.; Badawy, S. M. *Radiat. Phys. Chem.* **1999**, *54*, 627.
- (11) Nizam El-Din, H. M.; Badawy, S. M.; Dessouki, A. M. *J. Appl. Polym. Sci.* **2000**, *77*, 1405.
- (12) Badawy, S. M. *Radiat. Phys. Chem.* **2003**, *66*, 67.
- (13) Charlesby, A. *Radiat. Phys. Chem.* **1977**, *9*, 17.
- (14) Tabata, Y. *Radiat. Phys. Chem.* **1979**, *14*, 235.
- (15) Kaneko, M.; Tsuchida, E. *Polym. Sci.: Macromolec. Rev.* **1981**, *16*, 397.
- (16) Naka, Y.; Kaetsu, I.; Yamamoto, Y.; Hayachi, K. *J. Polym. Sci.: Polym. Chem.* **1991**, *29*, 1197.

- (17) Chapiro, A. *Radiation Chemistry of Polymeric Systems*; Wiley-Interscience: New York, 1962.
- (18) *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons Inc.: New York, 1965; Vol. 1 and 11.
- (19) Chapiro, A. *Radiat. Phys. Chem.* **1979**, *14*, 101.
- (20) Siyam, T. *Handbook of Engineering Polymeric Materials*; Cheremisinoff, N. P., Ed.; Marcel Dekker: New York, 1997.
- (21) Bashir, Z. *Polymer* **1992**, *33*, 4304.
- (22) Badawy, S. M.; Dessouki, A. M. *J. Appl. Polym. Sci.* **2002**, *84*, 268.
- (23) Perhkar, S.; Dharmadhikari, J. A.; Athawale, A. A.; Aiyer, R. C.; Vijayamohanan, K. *J. Phys. Chem. B* **2001**, *105*, 5110.
- (24) Sokol, M.; Grobeiny, J.; Turska, E. *Polymer* **1987**, *28*, 843.
- (25) Kim, H. S. *J. Polym. Sci., B* **1996**, *34*, 1181–1186.
- (26) Surianaryanan, M.; Vijayaraghavan, R.; Raghavan, K. V. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 2503.