

Radiation Polymerization of Acrylonitrile in a Viscous System with Styrene

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ABSTRACT: Radiation polymerization of acrylonitrile in a viscous system with styrene was performed at ambient temperature by using γ -rays. It is found that the overall rate of polymerization was accelerated after critical conversion due to the gel effect. As the molar fraction of styrene in monomer feed (f_{St}) is increased, both the total polymer conversion and molar fraction of acrylonitrile in the copolymer feed (F_{AN}) were decreased. The monomer reactivity ratios for acrylonitrile and styrene were determined to be r_1 (AN) = 0.25 and r_2 (St) = 2.0, respectively. The copolymers obtained were characterized by Fourier transformed infrared spectra (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), ¹H-NMR, and pyrolysis mass spectrometry (PMS). It was found that the slight addition of styrene to acrylonitrile strongly changes crystallinity, morphology, and thermal decomposition of the resulting polymer. ¹H-NMR measurement of AN/St copolymer showed the appearance of aromatic proton signals and shifted the resonance of the methylene proton to lower chemical shifts. The mass spectra of AN/St copolymers showed fragments of pyrolysates corresponding to oligonitriles with styrene end groups. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 268–275, 2002; DOI 10.1002/app.10324

Key words: polymerization; acrylonitrile; styrene; radiation

INTRODUCTION

Chelating resins based on acrylonitrile copolymers have been widely used for the adsorption of heavy metals.^{1–10} In previous works, the acrylonitrile–cellulose copolymer^{10–12} and acrylonitrile homopolymer granules¹³ were prepared by a radiation polymerization technique, followed by amidoximation for the purpose of adsorption of uranium. The advantages of using a radiation

polymerization technique: (1) ionizing radiation initiates radical polymerization at ambient temperature in the absence of chemical initiators;¹⁴ (2) the initiation step of radiation polymerization is temperature independent, and the overall activation energies are much smaller than in the chemically initiated process;^{13,15–17} (3) the resulting polymer is homogenous and free from any impurities, and the molecular weight can be controlled by varying doses and dose rate;¹⁸ and (4) the degree of crosslinking and solubility of the resulting polymer can be controlled by adjusting the radiation conditions.^{19,20}

Kinetic of radiation-induced polymerization of acrylonitrile was studied in detail in our previous work.¹³ The homopolymerization of acrylonitrile

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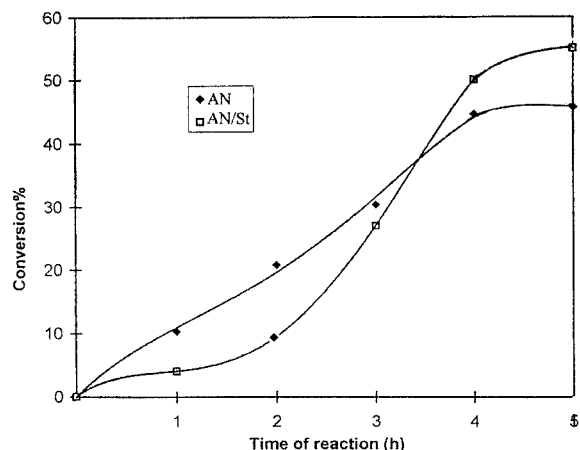


Figure 1 Conversion % vs. time of reaction (h) at $f_{St} = \text{zero}$ and $f_{St} = 0.06$, and constant radiation dose rate of 2 kGy/h.

monomer proceeds in a heterogeneous medium that produced homopolymer precipitating in the monomer solution. The aim of the present work is the study of polymerization of acrylonitrile in a viscous system employing different techniques. The effect of a styrene ratio on the percent conversion and the determination of reactivity ratios were investigated. Characterization of the produced acrylonitrile copolymers was spectroscopically studied by XRD, SEM, DPMS, NMR, and FTIR.

EXPERIMENTAL

Polymerization

Radiation-induced polymerization was carried out in a Pyrex tube containing monomer solutions in DMF, and exposed to Cobalt-60 rays, at the National Center of Radiation Research and Technology (NCRRT) Cairo, under air atmosphere and ambient temperature. The resulting 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 monomers and the initial monomers, respectively.

Measurements

Elemental analysis based on N determinations was measured by a Heraeus N-rapid analyzer. FTIR spectra were measured for the samples in the form of a KBr disk using a Shimadzu-8201 FTIR Spectrometer.

X-ray diffraction of the samples were recorded within the angle range of $2\theta = 5-50^\circ$ on a Shimadzu XRD-610 diffractometer using $\text{Cu K}\alpha$ radiation. The operating voltage and current were 30 kV and 20 mA, respectively.

The samples were photographed by using a scanning electron micrograph (SEM) (JEOL 5400) after coating under vacuum with a thin layer of gold.

The $^1\text{H-NMR}$ spectra were recorded in DMSO-d_6 on a Varian 300-MHz spectrometer. Mass spectra are obtained using a Shimadzu GCMS-QP1000EX quadrupole mass spectrometer. The samples were heated on the direct insert probe for solid materials until the complete decomposition of the polymer sample at a heating rate of $20^\circ\text{C}/\text{min}$, ionization energy of 60 eV, ionization current of 60 mA, and vacuum of 10^{-6} Torr.

RESULTS AND DISCUSSION

Radiation-Induced Polymerization

The kinetics of radiation-induced polymerization of acrylonitrile in precipitating media was studied

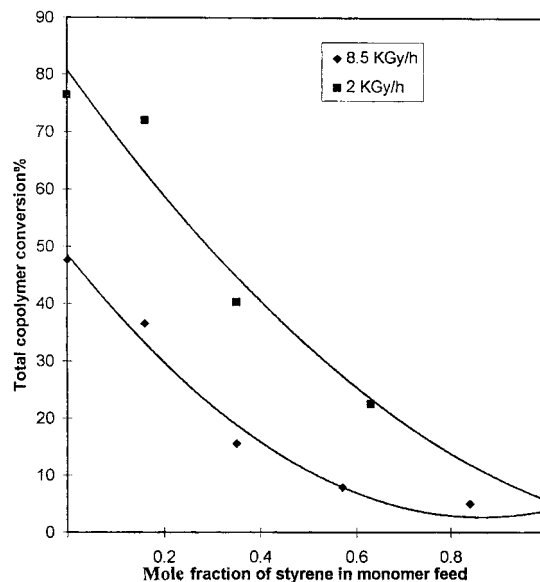


Figure 2 Conversion % against mol fraction of styrene in the monomer feed (f_{St}) at radiation dose rates of 2 and 8.5 kGy/h.

Table I Effect of Styrene Ratio (f_{St}) on Both the Total Copolymer Yield % and the Mol Fraction of Acrylonitrile in the Copolymer (F_{St}) at Dose Rate of 2 kGy/h

Mole fraction of styrene in monomer feed (f_{St})	0.0	0.03	0.16	0.35	0.57	0.84	1.0
Total copolymer conversion %	47.6	—	36.5	15.6	7.9	5.0	2.5
Mole fraction of acrylonitrile in the copolymer (F_{St})	1.0	0.90	0.68	0.52	—	0.0	0.0

in our previous work.¹³ The solubility parameters of acrylonitrile and polyacrylonitrile (PAN) are different, and there is no interaction between the acrylonitrile monomer and acrylonitrile polymer; therefore, the polymer does not dissolve in its monomer solution, resulting in polymer precipitate in the reacting medium, and separate as a fine powder. In addition, the intermolecular forces of PAN are strong so that the cohesion energy is high (1000 J/cm³), molecular chains are not flexible, and the polymer cannot be easily distorted under the action of external forces.²¹

A small amount of styrene monomer added to acrylonitrile dissolves the resulting polymer and performs the polymerization in a viscous system. The intermolecular attractive forces of polystyrene are weak so that cohesion energy is low (312 J/cm³) and the molecular chains become flexible enough. Figure 1 shows the conversions % vs. time curves for the polymerization of acrylonitrile monomer in precipitating media ($f_{St} = \text{zero}$) and viscous media ($f_{St} = 0.06$) at total monomer concentration of 35 vol%, where f_{St} is the mol fraction of styrene in monomer feed. It can be seen that the polymerization of acrylonitrile in a heterogeneous medium, at $f_{St} = \text{zero}$, increases smoothly with the reaction time, whereas the polymerization of acrylonitrile in viscous system, at $f_{St} = 0.06$, proceeded slowly at the initial stages of reaction until conversion of 10% and then the overall rate suddenly increases when the reaction mixture converted into a highly viscous gel-like phase. This process in which acceleration in the overall rate of reaction at critical conversion has been reached is referred as the "gel effect."

The increase of the reaction rate is attributed to the acceleration of propagation or a reduction of termination rate in which the termination by mutual interaction of two high molecular weight growing chains becomes diffusion controlled in the highly viscous system. In polymerization reaction, once the reaction medium has reached a critical viscosity, the growing polymer chains are trapped in the gel-like phase and termination by interaction of two active chain-ends becomes

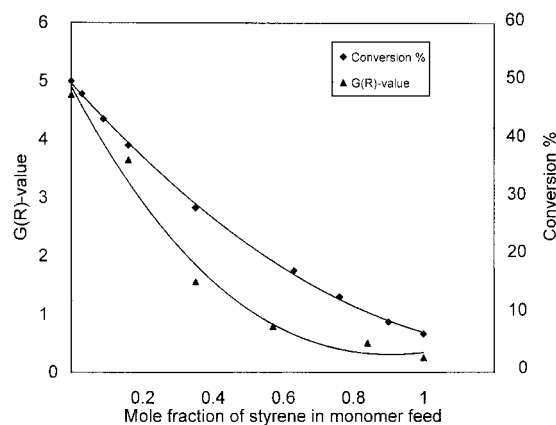
highly unlikely or even impossible, owing to the lack of mobility of the polymer chains.¹⁶

However, no considerable change in the total conversion percent is observed at low styrene ratio, but further addition of styrene comonomer retards the polymerization process and sharply decreases the total conversion percent. Figure 2 shows the total polymer conversion % of acrylonitrile–styrene comonomer against the mol fraction of styrene in monomer feed (f_{St}) at different radiation dose rates of 2 and 8.5 kGy/h and constant radiation dose of 20 kGy. It can be seen that the polymer yield decreases exponential with increasing of styrene ratio.

Table I shows that the increasing of styrene ratio is accompanied by a significant decreasing of both the total copolymer yield and the mol fraction of acrylonitrile in copolymer (F_{Ac}). Reactivity ratios for acrylonitrile and styrene were calculated using the Finemann and Ros equation:²²

$$\frac{f(1-F)}{F} = r_2 - \frac{f^2}{F} r_1$$

where $F = F_{Ac}/F_{St}$ and $f = f_{Ac}/f_{St}$, F_{Ac} and F_{St} are the mol fractions of acrylonitrile and styrene in

**Figure 3** $G(R^*)$ -value and conversion % as a function of the mol fraction of styrene in the monomer feed (f_{St}) at a constant radiation dose of 2 kGy/h.

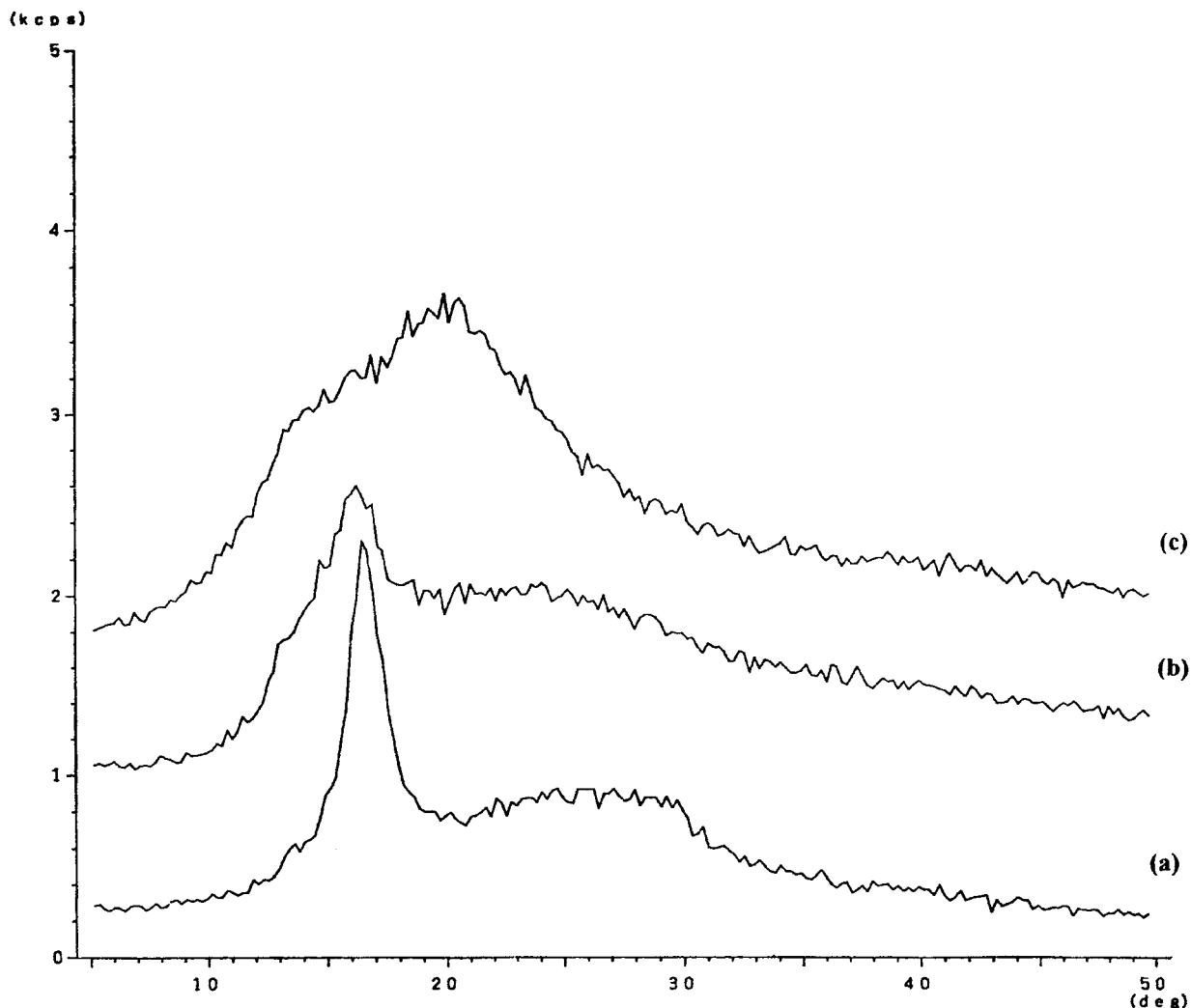


Figure 4 XRD spectra of (a) PAN, (b) AN/St copolymer at $f_{St} = 0.03$, and (c) AN/St copolymer at $f_{St} = 0.1$.

the copolymer, f_{Ac} and f_{St} are the mol fractions of acrylonitrile and styrene in the monomer feed, r_1 = the reactivity ratio of acrylonitrile, and r_2 = the reactivity ratio of styrene. A plot of $f(1 - F)/F$ against f^2/F is linear and yield a slope (r_1) of 0.25 and an intercept (r_2) of 2.0. The case where $0 < r_1 r_2 < 1$, the copolymerization is intermediate in structure between being alternating and being random in nature. The values of reactivity ratios suggest that the styrene monomer is more reactive, and enters the copolymers more frequently than acrylonitrile. This result is partially attributed to the electron-rich nature of the styrene double bond compared with the electron-deficient nature of the double bond in acrylonitrile.

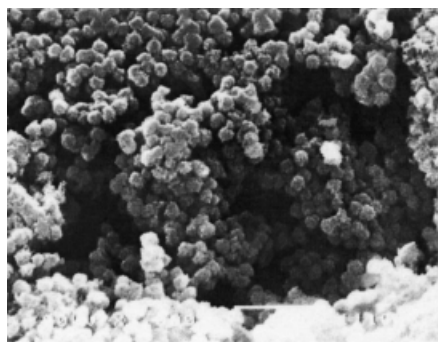
However, because the styrene has relatively unreactive radical whose resonance stabilization

is high (84 kJmol^{-1})²¹ the total copolymer yield was rapidly decreased with increasing the styrene ratio. At higher styrene ratio, $f_{St} > 0.35$, the resonance stabilization of the benzene ring suppresses the radical reactivity and completely inhibits the total polymerization processes.

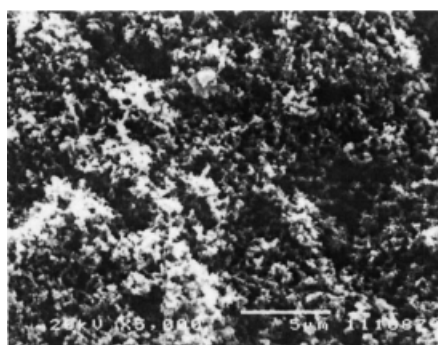
Figure 3 shows the plot of the calculated $G(R^*)$ value of acrylonitrile–styrene comonomers and the total polymer conversion % as a function of the mol fraction of styrene in the mixture. $G(R^*)$ of the comonomer mixtures is calculated by:²³

$$G(R^*)_{\text{comonomers}} = (G(R^*)_{\text{acrylonitrile}} \times W_{\text{acrylonitrile}}) + (G(R^*)_{\text{styrene}} \times W_{\text{styrene}})$$

where $G(R^*)$ is the number of radicals produced by 100 eV of absorbed energy and W is the weight



(a)



(b)

Figure 5 SEM of (a) PAN, (b) AN/St copolymer at $f_{St} = 0.03$.

fraction of the monomers. Because the rate of formation of initiating radicals is directly proportional to the $G(R^\bullet)$ value:²⁴

$$\frac{d[R^\bullet]}{dt} = \left[\frac{\varepsilon G(R^\bullet)}{100} \right] \times \frac{dQ}{dt}$$

where the rate of energy absorption per unit volume, dQ/dt , are related to the dose and dose rates, Figure 3 indicated the retardation due to the decrease in the rate of formation of initiating radicals with increasing of styrene ratio.

Previous studies¹⁶ on the kinetics of the gamma-ray initiated copolymerization of mixtures of similar system (MMA/St) found that no appreciable energy transfer took place in this mixture, and the apparent retardation is merely due to the kinetics of the propagation and termination steps in the binary mixture of monomers and not to any unusual drop in the rate of initiation.

Physical and Chemical Characterizations

Crystal Structure and Morphology

The X-ray diffraction (XRD) of AN/St copolymers at different molar fractions of styrene in the monomer feed (f_{St}) is shown in Figure 4. It is obvious that the crystallinity is strongly reduced with addition of styrene. The degree of crystallinity of PAN is 43%, calculated by dividing the area of the crystalline peak (d_{100}), at $2\theta = 17$, by the total diffraction area of the crystalline peak plus the amorphous halo. Inclusion of a little amount of styrene ($f_{St} = 0.03$) results in distortion and defect in the crystal lattice. The degree of crystallinity is reduced to 0.2%. Further addition of styrene ($f_{St} = 0.09$) changes the crystalline peak ($2\theta = 17$) to an amorphous hump. The crystal lattice disappeared and is replaced by the amorphous phase.

The morphology was confirmed by Scanning Electron Microscopy (SEM), as shown in Figure 5. SEM of pure PAN shows a microspheres particles with diameters $\sim 1.0 \mu\text{m}$. SEM of AN/St copolymer at $f_S = 0.03$, shows that the microspheres particles were replaced by an amorphous surface. The growth of the microspheres is attributed to that the growing polymer chains, after having reached a critical length, separate from the solution to form a second phase. Inclusion of styrene as a comonomer leads to form a soluble polymer in a viscous media that precipitates in water producing amorphous polymer.

FTIR Spectra

Figure 6(a) shows the IR spectrum of PAN with the prominent nitrile band at 2245 cm^{-1} . Inclusion of styrene results in a decrease in band intensities of nitrile group at 2245 cm^{-1} and the appearance of bands characteristic of styrene at 700 and 759 cm^{-1} (=CH out-of-plane bending vibration), bands at 1600 and 1459 cm^{-1} (C=C ring stretching vibration) and a band at 3028 cm^{-1} (=C—H stretching vibration).

¹H-NMR Spectroscopy

Figure 7 shows the ¹H-NMR spectra of AN/St copolymers at different molar fractions of styrene in monomer feed (f_{St}). The spectrum of PAN shows two signals for the resonance of methylene proton at 2.0 ppm and methine proton at 3.1 ppm.

The spectra of AN/St copolymers show the appearance of multiplet resonance at 6.8–7.4 ppm

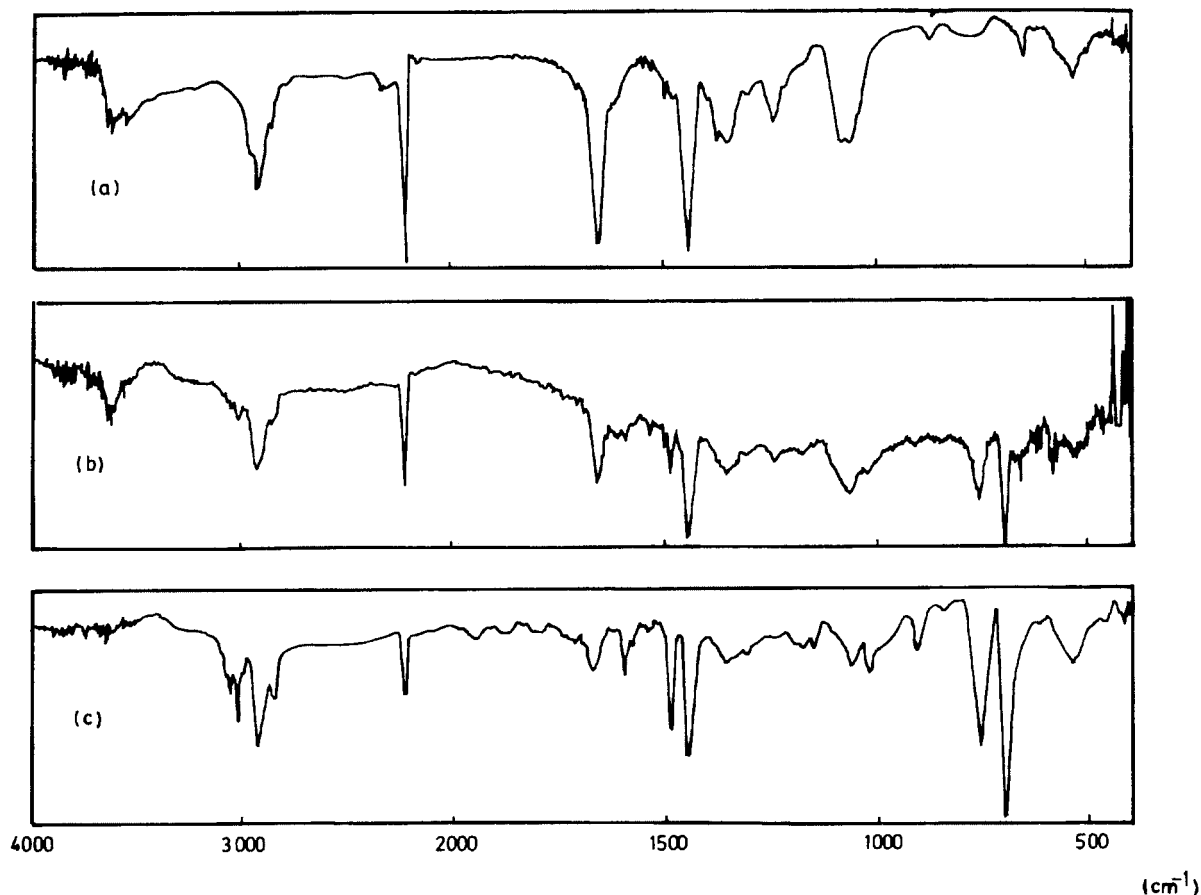


Figure 6 IR spectra of (a) PAN, (b) AN/St copolymer at $f_{St} = 0.16$, and (c) AN/St copolymer at $f_{St} = 0.35$.

corresponding to the aromatic protons of styrene. The increasing of the styrene ratio is accompanied by increasing in the intensities of the aromatic protons signals. In addition, the resonance of methylene proton at 2.0 ppm moves to lower chemical shifts with increasing the styrene ratio. The overlapping of the methylene protons signals complicates determination of the monomer sequence distribution. The signal at 2.0 ppm is assigned to AAA. The signals at 1.8 ppm, which appeared with decreasing acrylonitrile content and then disappeared with increasing styrene content, is assigned to AAS, whereas the signal at 1.5 ppm, which appeared with further increasing styrene content, is assigned to SSA, where A and S are referred to acrylonitrile and styrene structural units, respectively.

Direct Pyrolysis Mass Spectrometry

In the temperature-controlled pyrolysis by mass spectrometer, the polymer normally de-

grades across a temperature range generating Total Ion Current (TIC) pyrogram and mass spectra of oligomers representative of the copolymer chain.²⁵

Figure 8 shows the TIC pyrogram of the PAN copolymers at $f_{St} =$ zero, 0.06, and 0.16. The pure PAN ($f_{St} =$ zero) rapidly degrades at 240°C, whereas the AN/St copolymer at $f_{St} = 0.06$ degrades at 286°C with maximum ions at 315°C. This indicated that the inclusion of a small amount of styrene increases thermal stability of the polymer. The TIC pyrogram of the AN/St copolymer at $f_{St} = 0.16$ shows that the increase of styrene ratio causes broadness in the TIC pyrogram, i.e., the decomposition distributes over a broader temperature range, and shifts the TIC peak to a high-temperature region. The broadening of TIC peak of AN/St copolymers may be due to a multidegradation process that occurs over a similar temperature range or to a wider range of volatilities of the pyrolysis products.

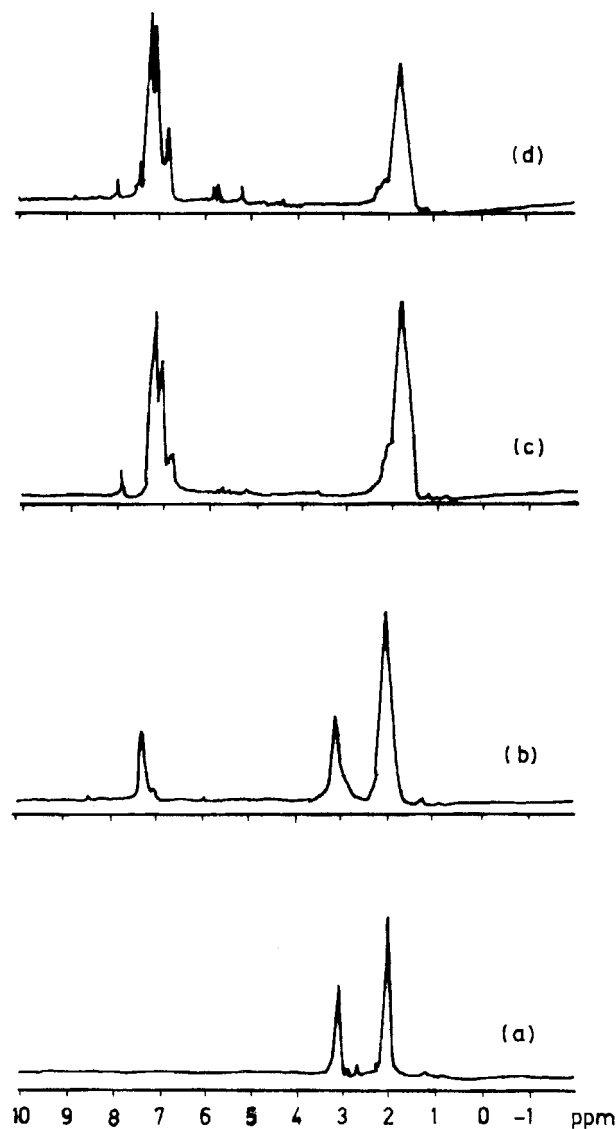


Figure 7 ¹H-NMR spectra of (a) PAN, (b) AN/St copolymer at $f_{St} = 0.03$, (c) AN/St copolymer at $f_{St} = 0.1$, and (d) AN/St copolymer at $f_{St} = 0.35$.

The mass spectra of pure PAN ($f_{St} = \text{zero}$) and AN/St copolymer ($f_{St} = 0.06$) are shown in Figure 9. The mass spectra of PAN were studied in previous work.²⁵ Peaks at 54, 107, 160, 213, 266, and 319 correspond to monomer, dimer, trimer, tetramer, pentamer, and hexamer of acrylonitrile [$54 + n53$] where n equal 0, 1, 2, 3, 4, 5, 6.

The mass spectra of the AN/St copolymer ($f_{St} = 0.06$) show that the styrene monomer (104 m/e) is detected in the pyrolysis products, and no styrene dimer or trimer are formed. The strong peaks at m/e 91 and 129 are due to the formation of tropylium ion and substituted tropylium ion, respectively, according to Scheme 1.

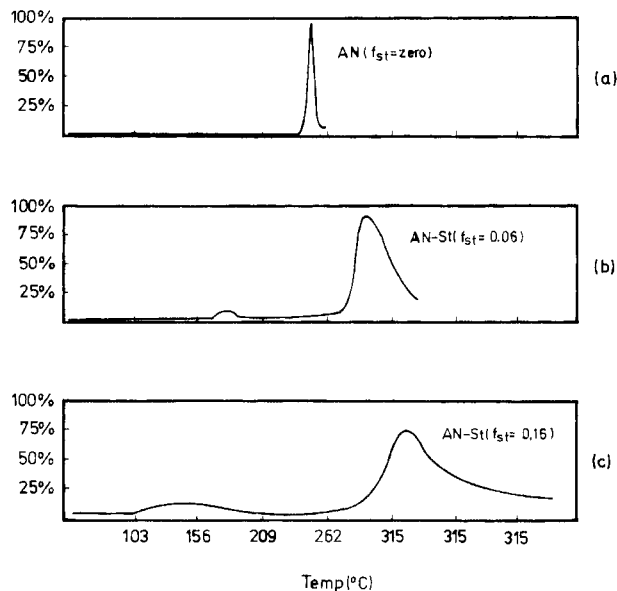


Figure 8 TIC of (a) PAN, (b) AN/St copolymer at $f_{St} = 0.06$, and (c) AN/St copolymer at $f_{St} = 0.16$.

Peaks at 157, 211, 264, and 317 correspond to the monomer, dimer, trimer, and tetramer of oligonitriles (R_n) with a styrene end group ($104 + n53$), where $n = 0, 1, 3, 4$.

The mass spectra showed that the relative abundances of styrene unit at 104 m/e and tropylium ion at 91 m/e increase with increasing of the styrene ratio, whereas the relative abundance (%) of the acrylonitrile unit at 54 m/e decreases.

CONCLUSION

The above investigations of radiation polymerization of acrylonitrile in a viscous system indicated that (1) the polymerization of acrylonitrile sud-

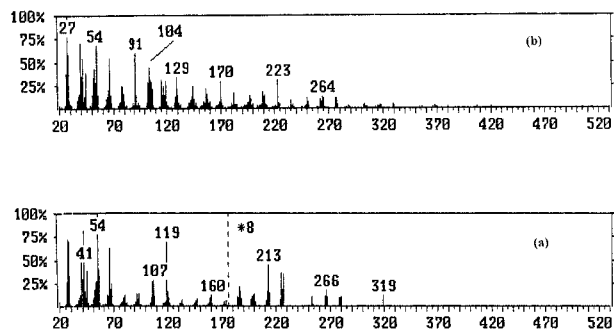
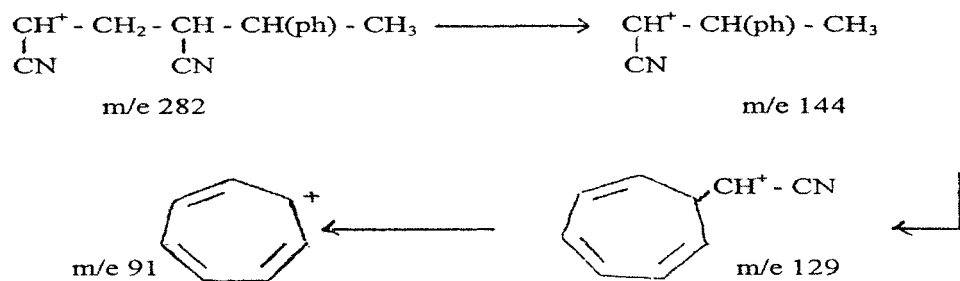


Figure 9 Mass spectra of (a) PAN and (b) AN/St copolymer at $f_{St} = 0.06$.



Scheme 1

denly increases at critical conversion in the homogeneous system with a styrene monomer due to the gel effect. As the molar fraction of styrene in the monomer feed (f_{St}) increased, the total polymer conversion was decreased because the styrene has relatively unreactive radical. The values of reactivity ratios suggested that the styrene monomer is more reactive, and enters the copolymers more frequently than acrylonitrile. (2) The presence of a small amount of styrene in the monomer feed strongly changes the physical and chemical properties of the resulting polymer. Inclusion of styrene ($f_{St} = 0.03$) results in distortion and defect in the crystal lattice. The addition of styrene is accompanied by increasing in the intensities of the aromatic protons signals in NMR spectra and shifting the resonance of the methylene proton to a lower value. The pyrolysis mass spectrometry analysis showed that the increase of the styrene ratio causes broadness in the TIC pyrogram due to the multidegradation process, which occurs over a similar temperature range and a wider range of volatilities of the pyrolysis products.

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