Chelating Polymer Granules Prepared by Radiation-Induced Homopolymerization. I—Kinetic Study of Radiation Polymerization Process

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ABSTRACT: Chelating polymer granules containing amidoxime chelating groups were synthesized by radiation-induced homopolymerization of acrylonitrile monomer. The chemical reactive intermediate polyacrylonitrile was treated with hydroxylamine solution to convert the chemical active cyano groups into the amidoxime groups. Kinetic study of the effects of monomer concentration, radiation dose, dose rate, and temperature on the polymerization process was investigated. It was found that at low monomer concentration, the rate of polymerization is roughly independent on the initial monomer concentration, while at high monomer concentration, 35–65%, a marked acceleration on the rate was observed. The order of the dependence of the initial rate of polymerization on the dose rate is 0.77, which deviates from the classical square-root law due to the precipitation of the formed polymer. The conversion percent and molecular weight of the produced polymer are inversely proportional to dose rate at constant radiation dose. The activation energy was found to be 2.7 kcal/mol, and the rate constant of initiation is independent of temperature. The effect of type of solvent on the polymerization was studied. DMF solvent of the closest solubility parameter to the solubility parameter of polyacrylonitrile is the best solvent for the polymerization process. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1405–1412, 2000

Key words: chelating polymer granules; radiation-induced homopolymerization

INTRODUCTION

Chelating polymers containing amidoxime groups have attracted much attention for the adsorption of uranium. A number of chelating resins containing amidoxime groups have been prepared by reacting the acrylonitrile–divenylbenzene copolymer with hydroxylamine.[1–4] Several research groups have continued this line of work, developing and testing the various kinds of adsorbents containing amidoxime groups.[5–10] In our previous work,[10,11] radiation-induced graft polymerization has been used with high efficiency to synthesize chelating filter paper with amidoxime groups. Irradiation by ionizing radiation is able to initiate radical polymerization at ambient temperature in the absence of chemical radical initiators.[12] 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] The advantage of using radiation-induced polymerization is that the resulting polymer is homogeneous and free from any impurities, and the molecular weight can be controlled by varying doses and dose rate.[16] Another important advantage is that the degree of crosslinking and solubility of the resulting polymer can be controlled by adjusting the radiation conditions. The formation of crosslinking polymer by radiation polymerization can be developed

without using a crosslinking agent. The use of high-energy radiation in the synthesis of chelating resins has a dual effect; crosslinking process usually accompanies radiation-induced polymerization of crosslinkable polymers at high doses.[17,18] In the present work, radiation-induced homopolymerization was used to prepare chelating polymer granules containing amidoxime groups. Effects of monomer concentration, radiation dose, dose rate, temperature, and type of solvent on the kinetic of radiation polymerization were investigated.

EXPERIMENTAL

Polymerization

Radiation-induced homopolymerization was carried out in a Pyrex tube containing monomer solution in DMF and exposed to Cobalt-60-rays, located at the National Center of Radiation Research and Technology (NCRRT) Cairo, under air atmosphere. The resulting polymer yield was separated from the unreacted monomer by precipitation in distilled water, washed several times by water, then filtered and dried at 70°C for 6 h. 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. Effect of different concentrations, 15–65 (vol %), was investigated for 1, 2, 3, 4, and 5 h duration, at a constant dose rate of 2 KGy/h. The effect of different dose rates of 0.5, 1, and 2 KGy/h was investigated at an initial monomer concentration of 45%.

Activation energy was calculated from the Arrhenius equation by adjusting the monomer solution at various temperature degrees of 10, 25, and 70°C, and then rapidly irradiated for 10–50 min at a constant dose rate of 8.5 KGy/h.

Viscosity—Average Molecular Weight Determination

Viscosity measurements were carried out in DMF at 298 K by a Ubbelohde Viscometer. $\bar{M}_v$ was calculated from the Mark-Houwink formula taking values for K and α.[19]

$$[\eta] = K \cdot \bar{M}_v^{\alpha}$$

where $K = 39 \times 10^{-3}$ dm^3/g and $\alpha = 0.75$.

Amidoximation

The resulting polyacrylonitrile was treated with a hydroxylamine–alcohol solution (pH = 7) at 80°C for 2 h under reflux. The prepared amidoxime polymer was washed with distilled water to remove excess hydroxylamine, and then dried at 70°C for 6 h. IR spectra were measured for the polyacrylonitrile and amidoxime polymer using a Perkin-Elmer 1650, FTIR Spectrophotometer.

RESULTS AND DISCUSSION

The polymerization of acrylonitrile proceeds in a heterogeneous medium. The acrylonitrile monomer does not dissolve the formed polyacrylonitrile, so it precipitated in monomer solution of a low solvent composition. In the radiation-induced polymerization, the rate of initiation is temperature independent and the polymerization process takes place in radiation cell temperature. The presence of additives such as solvent affects the initiation step due to its radiolysis to initiating free radicals.

The produced polymer is itself radiolyzed, and the radicals formed on adjacent polymer chains can react together to give a covalent bond, thereby linking the polymer molecules together, and a three-dimensional network structure is formed giving a crosslinked polymer structure. The use of high energy radiation in the synthesis of a chelating resin has a dual effect; the crosslinking process usually accompanies radiation-induced polymerization of crosslinkable polymers at high doses.[17,18]

The predominant variables that influence the radiation-induced polymerization includes: (a) radiation dose and dose rate, (b) monomer concentration, and (c) type of solvent.

Effect of Monomer Concentration

Figures 1 and 2 show the polymer yield and conversion percent vs. time curves, respectively, obtained at various monomer concentrations (vol %) in DMF solvent. It is observed for all monomer concentrations, 15–65%, that the polymer yield and conversion % increase with radiation time. At
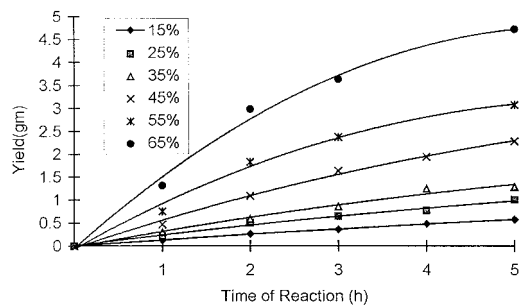
Figure 1   Polymer yield (g) vs. time of reaction (h) for various monomer concentrations, at dose rate of 2 KGy/h.

Figure 2   Conversion % vs. time of reaction (h) for various monomer concentrations, at dose rate of 2 KGy/h.

the lower monomer concentration the polymerization proceeds in soluble medium, and the rate of polymerization increases slowly with time. At high monomer concentration, 35–65%, the polymerization proceeds in precipitating medium, and the rate of polymerization is relatively fast and then slow down at high doses. The rate of polymerization or the rate of monomer disappearance is expressed by:

$$R_p = -\frac{d[M^\bullet]}{dt} = R_i^{0.5} \frac{K_p}{(2K_t)^{0.5}} [M] \qquad (1)$$

where K_p and K_t are constants of propagation and termination, $[M]$ is the monomer concentration at time t, and R_i is the rate of initiation.

Integration of eq. (1) at constant rate of initiation and constant dose rate, gives:

$$\ln\left(\frac{M_o}{M}\right) = Kt$$

where $[M_o]$ is the initial monomer concentration, $[M]$ is the monomer concentration at time t, and
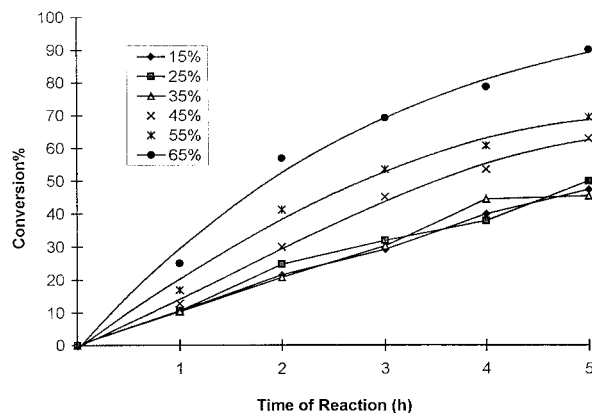
$$K = R_i^{0.5} \frac{K_p}{(2K_t)^{0.5}}.$$

Plotting of $\ln(M_o/M)$ against irradiation time gives a slope equal to

$$K = R_i^{0.5} \frac{K_p}{(2K_t)^{0.5}}$$

as shown in Table I. It can be seen that for all monomer concentrations up to 35%, the rate of polymerization is roughly independent of the initial monomer concentration $[M_o]$. At higher initial monomer concentrations, the formed polymer precipitates in the monomer solution and a marked acceleration in the rate is observed, especially at an advanced stage of the polymerization. The values of propagation and termination constants for polymerization in the presence of polymer precipitants were measured for various system.[13–15] It was found that while K_p was little affected by the precipitation of the polymer, K_t noticeably decreased. The polymer is itself radi-

Table I   Effect of Monomer Concentration $[M_o]$ on the Rate Constant of Polymerization at Constant Rate of Initiation R_i Where, $K = R_i^{0.5} K_p/(2K_t)^{0.5}$

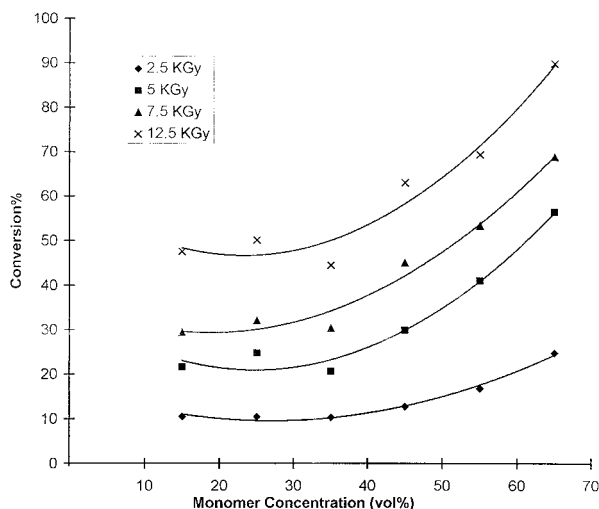| $[M_o]$	15%	25%	35%	45%	55%	65%
K h^{-1}	14×10^{-2}	16×10^{-2}	17×10^{-2}	20×10^{-2}	26×10^{-2}	40×10^{-2}
Polymer yield (g) at 2 KGy	0.30	0.50	0.60	1.0	1.8	3.0
Conversion % at 2 KGy	21.5	24.7	20.7	30	41.3	57

Figure 3 Conversion % vs. monomer concentration (vol %) for various radiation doses.

olized by radiation, and the polymeric free radicals contribute to the chain initiation. The unpolymerized monomer is then homografted onto the polymer precipitants, resulting in graft homopolymer.[13–15]

Figure 3 shows the plotting of initial monomer concentration against conversion % at various radiation doses of 2.5, 5, 7.5, and 12.5 KGy. The autoacceleration is obviously observed at higher monomer concentration above 35% similar to that observed in viscous system (gel effect). Autoacceleration in the rate of polymerization also occurs with monomers polymerized by chemical initiators.

Several theories have been suggested to interpret the mechanism of the autocatalytic effect observed in precipitating media[14]: (1) the monomer molecule containing a double bond may be stronger stabilized by resonance than the corresponding polymer, and accordingly, $G(R^\bullet)_P$ of the polymer may be larger than $G(R^\bullet)_M$ of the monomer, resulting in an increase in the rate of initiation, where $G(R^\bullet)$ is the number of radicals produced per 100 ev. This effect becomes very important at high conversion, when most of chains are initiated by radicals generated by the polymer. (2) The polymer formed could act as a cocatalyst in the reaction, by way of "immobilized" free radicals created by chain transfer on the surface of the polymer. (3) The acceleration was caused by a reduced rate of chain termination owing to the coiled state of the growing polymer chains, the active-end chain being efficiently shielded by the precipitated polymer, thus producing an effect of

steric hindrance, which should lower the general reactivity of the growing chain by a mechanism analogues to diffusion control. (4) The accessibility of the active end of a precipitated chain is further reduced as the growing chain coalesces with the precipitated dead polymer. This mode implies that both propagation and terminate rate constants steadily decrease with conversion.

Effect of Radiation Dose and Dose Rate

Figure 4 shows the polymerization % against time of irradiation for different dose rates. It was found that the rate of polymerization was linear with the radiation dose in the initial stage of polymerization, as a function of time of irradiation, from zero to 5 h, and then tends to level off above 5 h, i.e., the amount of initiating radicals formed by radiation increases linearly with radiation dose and then reaches a certain limiting values at a higher dose due to the consumption of the monomers, mostly in the former polymerization. It can be seen that the higher the irradiation dose rate, the higher the polymerization % obtained at constant time. In radiation polymerization, the rate of polymerization is given by the classical square-root law, whereas in the present work, the logarithmic plots of initial rate of polymerization vs. dose rate shows a deviation from square-root law. The order of the dependence of the rate of polymerization on the rate of initiation, dose rate, is 0.77, and the following relationship is obtained:

$$R = KI^{0.77}$$

This value is in agreement with values reported by others[14] when chemical initiators were
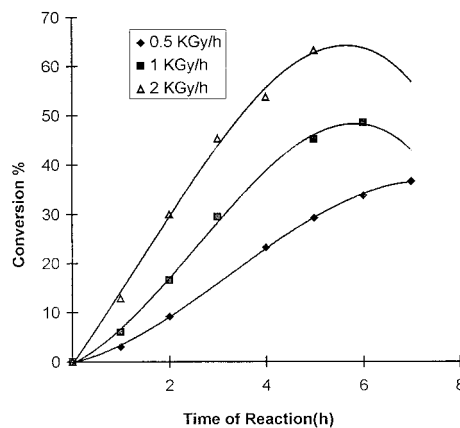

Figure 4 Conversion % vs. time of reaction (h) for different dose rates of 0.5, 1, and 2 KGy/h.
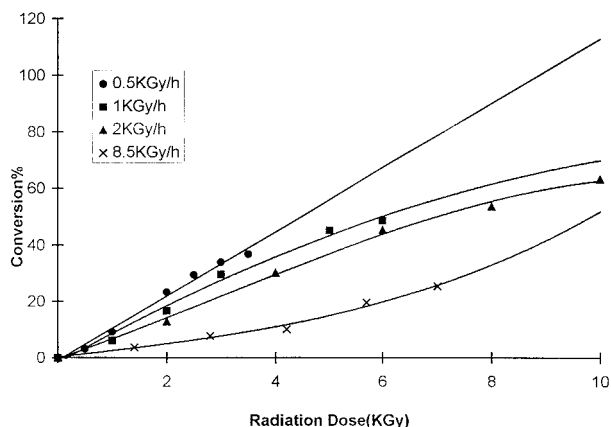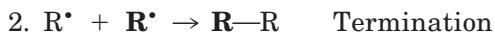
Figure 5 Effect of dose rate on the conversion % at constant radiation doses.

Figure 6 Effect of temperature on the conversion % at constant radiation conditions.

used for polymerization of acrylonitrile. Thus, the deviation from the classical square-root law is not due to any specific process involving the radiation initiation, but results from the subsequent chain propagation and termination steps that are affected by the precipitation of the growing polymer chains.[14]

On the other hand, Figure 5 shows the plotting of these data at constant dose, the polymerization % is inversely proportional to dose rate at a constant dose. As the rate of initiation R_i increased at constant radiation dose, the concentration of radicals increased, and some of the primary radicals escape captured by monomers to recombine with themselves or react with a growing polymer chain; thus, termination by primary radicals increased on the expense of propagation step:

1. $R^\bullet + M \rightarrow RM^\bullet$ Propagation

2. $R^\bullet + \mathbf{R}^\bullet \rightarrow \mathbf{R}$—R   Termination

(free radicals recombine with themselves)

Table II   Conversion %, Viscosity Number, and Molecular Weight at Constant Radiation Dose of 2 KGy

Dose Rate (KGy/h)	Conversion %	M_v (g mol^{-1})	$[\eta]$ dm^3 g^{-1}
0.5	23	10.8×10^4	0.15
1	16.5	6.24×10^4	0.1
2	12.8	3.9×10^4	0.07

3. $R^\bullet + RM_n^\bullet \rightarrow P$ Termination

(free radicals combine with growing chains)

where $RM_n^\bullet$ is a growing chain and P is the dead polymer molecule.

Table II gives the values of the conversion % and the molecular weights at different dose rates, constant radiation dose, and constant initial monomer concentration of 45%. The increase in dose rate, at constant radiation dose, is accompanied by a significant decrease in the molecular weight. At a high dose rate, i.e., a high rate of formation of initiating radicals, the monomer radicals prefer to form short chains rather than to add to polymeric chains, so the degree of polymerization is inversely proportional to the dose rate as shown in Table II. The logarithmic plot of molecular weight $\bar{M}_v$ against dose rate shows that the order of the dependence of $\bar{M}_v$ on the dose rate is -0.6, i.e.:

$$\bar{M}_v = KI^{-0.6}$$

In theoretical approximation, the degree of polymerization of the resulting polymer decreases proportionally to the square root of the rate of initiation:

$$\overline{DP}_n = \frac{2K_p}{K_t^{0.5}} R_i^{-0.5} [M]$$

Table III   Effect of Temperature on the Conversion % and Rate of Polymerization

T °C	R_p (mol^{-1} s^{-1})	Conversion % at 2.8 KGy
15	3×10^{-4}	4.8
25	5×10^{-4}	7.7
70	6.6×10^{-4}	10.4

This value indicates little deviation from the value of the experimental results.

Effect of Temperature

Figure 6 shows the polymerization % at different temperatures (10, 25, and 70°C) and a constant dose rate. The polymerization increases slightly with the increase in temperature. Table III gives the values of rates of polymerization at different temperature degrees. It can be seen that the rate of polymerization is independent of temperature in comparison with radiation conditions.

The effect of temperature on polymerization can be represented by an Arrhenius equation from which the overall activation energy can be calculated:

$$\log R = \frac{E}{2.303RT} + \text{const.}$$

The overall activation energy E equals:

$$E = \tfrac{1}{2}E_i + E_p - \tfrac{1}{2}E_t$$

where E_i, E_p, and E_t are the partial activation energies for initiation, propagation, and termination steps, respectively. Plotting of $\log R$ vs. $1/T$ gives a slope corresponding to $E/2.303R$. From the slope, the overall activation energy E was calculated and found to be 2.7 kcal/mol. It is much smaller than in thermal polymerization. This value is close to the activation energy of the propagating step. This means that the activation energy of the initiation step E_i is not included in the resulting overall activation energy. The magnitude of E_i depends upon the type of initiation involved. For thermal or chemical means of initiation, E_i is usually of the order 25–30 kcal/mol, while for radiation-induced initiation, $E_i = 0$, so the rate of radiation polymerization rises more slowly with temperature than the rate of the thermal initiated reaction.[13–15] Thus, the overall activation energy E reduces only to the propagation and termination terms:

$$E = E_p - \tfrac{1}{2}E_t$$

and the Arrhenius equation becomes:

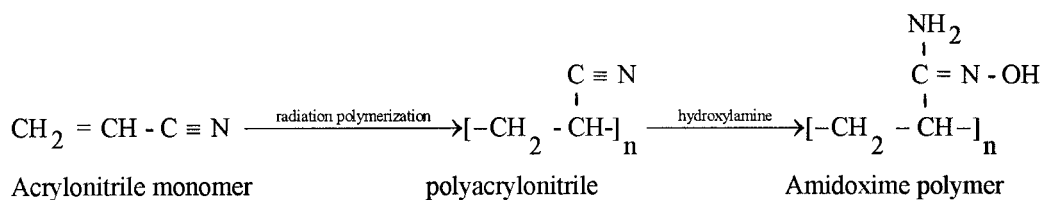$$\log R = \frac{E_p - \dfrac{1}{2}E_t}{2.303RT} + \text{const.}$$

As a consequence, radiation-initiated polymerization is much easier to control than either the thermally or chemically initiated reactions.[15]

Effect of Solvent

The solubility parameters of acrylonitrile and polyacrylonitrile are 21.5 and 26.3 (J/cm^3)$^{1/2}$. Their solubility parameters are different, and there is no interaction between the acrylonitrile monomer and acrylonitrile polymer; therefore, the polymer does not dissolve in its monomer, resulting in polymer precipitate in the reacting medium, and separates as a fine powder. The

Table IV   Solubility Parameters of Solvents and Conversion % of Polymerization at 10 KGy and Dose Rate of 2 KGy/h

Type of Solvent	Solubility Parameter of Solvent (J/cm^3)$^{1/2}$	Conversion % at 10% [M_o]	Conversion % at 50% [M_o]
DMF	25	19	35.3
Diethylether	15.1	6.4	16.6
Acetone	20	Zero	2.5
Methanol	29.7	Zero	2
Chloroform	18.9	Zero	20.3
Acetonitrile	24.7	Zero	0.4

$$CH_2 = CH - C \equiv N \xrightarrow{\text{radiation polymerization}} [-CH_2 - CH-]_n \xrightarrow{\text{hydroxylamine}} [-CH_2 - CH-]_n$$

Acrylonitrile monomer   polyacrylonitrile   Amidoxime polymer

where the polyacrylonitrile unit bears $C \equiv N$ and the amidoxime polymer unit bears $C = N - OH$ with NH_2.

Scheme 1

intermolecular attractive forces of polyacrylonitrile are strong so that the cohesion energy is high (1000 J/cm^3),[20] molecular chains are not flexible, and the polymer cannot easily be distorted under the action of external forces.

The results of the radiation-induced polymerization of acrylonitrile monomer in various solvents are presented in Table IV, together with the solubility parameter of the solvents. From Table IV, the solubility parameter of DMF is the closest to the solubility parameter of polyacrylonitrile, so DMF is a good solvent for polyacrylonitrile, and leads to that the polymerization proceeds with high efficiency. The other solvents, with different solubility parameters cannot dissolve this polymer, and causes inhibition to the polymerization process. This is due to the small mobility of monomer, oligomer, and propagating radicals in the precipitating media. Polymerization did not proceed in solvents capable of accepting electrons
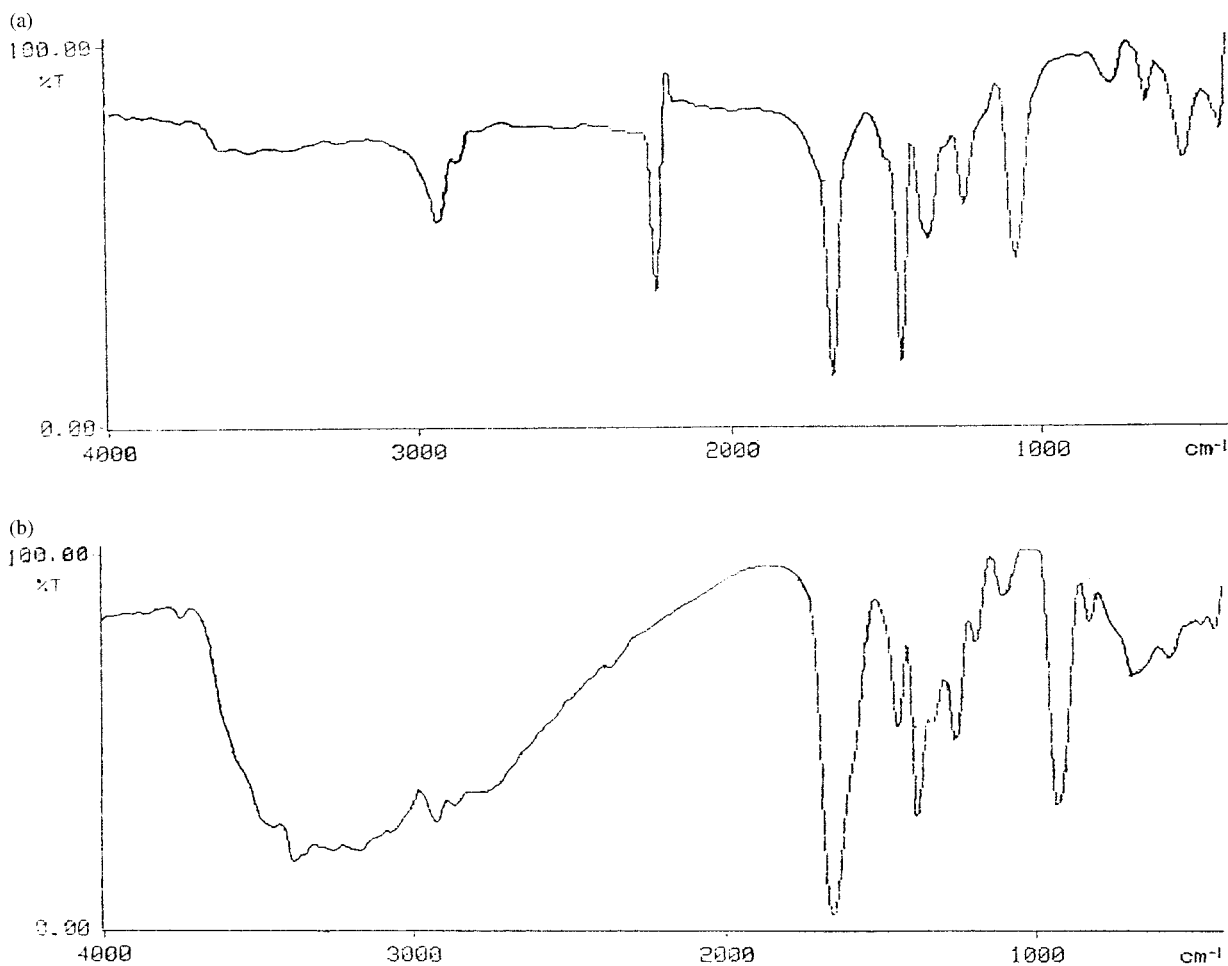

Figure 7 IR spectra of (a) polyacrylonitrile and (b) polyacryloamidoxime.

such as acetonitrile despite their slightly different solubility parameter. Chloroform solvent gives considerable polymerization % at high monomer concentration despite their far apart solubility parameter. As already stated, acrylonitrile does not polymerize cationically in the chlorinated solvents or others solvents.[15] The sensitization of acrylonitrile polymerization in chloroform may be due to the considerable chain transfer of chloroform.

The presence of solvents play another important role in the radiation-induced polymerization due to its radiolysis. The free radical yields of the solvent must be taken into account in the chain initiation in addition to the free radicals of the monomer; thus, the rate of formation of initiating radicals is described by[22]:

$$\frac{d[R]}{dt} = \left[\frac{\varepsilon_m G_m(R^\bullet)}{100} + \frac{\varepsilon_s G_s(R^\bullet)}{100} \right] \times \frac{dQ_A}{dt}$$

where ε_m and ε_s are electron fractions of the monomer and the solvent, G_m and G_s are G-values of the monomer and solvent, respectively. (dQ_A/dt) is the rate of energy absorbed per unit volume, which is related to the dose rate.

Amidoximation

The resulting homopolymer containing reactive intermediate cyano groups can be converted to a chelating polymer containing amidoxime groups by chemical treatment. It is known that the cyano group is easily converted into an amidoxime group by the reaction with hydroxyl amine solution. The synthetic scheme is shown in Scheme I.

The IR spectrum shown in Figure 7(a) and (b) shows that the band associated with the nitrile group at 2248 cm^{-1} disappears on treatment with hydroxylamine, and is replaced by the bands in the region of 3000–3500 cm^{-1} (broad, N—H and O—H stretching vibration), a band at 1650 cm^{-1} (C=N stretch vibration), and a third band at 920 cm^{-1} (N—O, stretch vibration). These peaks correspond to the amidoxime groups.

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