

Kinetics Study of Radiation-Grafting of Acrylic Acid, Acrylonitrile, and Their Mixture onto Wool Fabric

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ABSTRACT: The effect of monomer concentration, exposure time, irradiation temperature, and weaving direction on the kinetics of grafting acrylic acid (AA), acrylonitrile (AN), and their mixture onto wool fabric has been studied at the dose rate of 1.38 Gy/s. The degree of grafting is found to depend on the methanol-to-water solvent ratio and fabric-to-liquor ratio. The grafting rate and rate constant are dependent on irradiation temperature, type of grafted monomer, and weaving direction. The grafting rates increase with the increase in irradiation temperature (276–308 K). The calculated activation energy is nearly the same (16.4–17.2 kJ mol⁻¹)

and the preexponential rate constant is dependent on the type of grafted monomer. The grafting of AA, AN, and their mixture are confirmed from the dyeing affinity of grafted fabrics towards Sandocryl Blue (SB), a basic dye. The formation of wool grafts and structural changes resulting from grafting were verified by using FTIR spectrometry and X-ray diffraction analysis. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4328–4340, 2006

Key words: kinetics; radiation grafting; acrylic acid; acrylonitrile; wool

INTRODUCTION

Radiation grafting of vinyl monomers onto natural and synthetic polymeric substrates has been reported to improve the physical, chemical, electrical, and mechanical properties.^{1–8} Optimum grafting conditions are required to reach maximum yields with minimum monomer–solvent solutions. Different factors contribute to the grafting process. The irradiation time, monomer concentration, fabric-to-liquor ratio (FLR), and irradiation temperature play important role in controlling the grafting process.^{9–16} In previous investigations^{4,8} on the improvement of some properties of nylon-6 and polyester (PET) fabrics by mutual irradiation grafting with *N*-vinyl pyrrolidone (NVP), it has been proved that the methanol is the best solvent suitable for giving considerably high graft yields. The results were attributed to the increased swelling ability of the fabric. Swelling time is an important factor in increasing graft yields. Recently, in a study on the kinetics of grafting PET fabric with acrylic acid¹⁷ (AA), it has been found that the order of grafting process increases linearly with the increase in radiation temperature at a rate of 0.01/°C with a value of 1.32 at 0°C. Apparent activation energy 22.5 kJ mol⁻¹ is determined for the grafting process.

It is now quite obvious that the order of grafting and the activation energy depend on the radiation conditions, the monomer–polymer systems as well as the experimental grafting conditions. The present article reports studies on the kinetics of grafting AA, AN, and their mixture onto wool fabric. The effects of monomer concentration (*C*), irradiation time (*t*), FLR, and irradiation temperature (*T*) on the kinetic parameters [reaction rate *R*, reaction order (*n*), and rate constant *k*] were investigated. Activation energy (*Q*) and preexponential rate constant (*A*) from mutual irradiation grafting were also evaluated. The grafting is checked and the grafted fabrics characterized using FTIR spectral and X-ray diffraction analyses (XDA).

EXPERIMENTAL

Materials

Wool fabric was supplied from Misr Spinning and Weaving Co., Mehalla El-Kobra, Egypt. The plane weave fabric [25 picks (weft) and 25 ends (warp)] was scoured and bleached. The fabric was cut into samples of known weight (~ 0.7 g), washed in distilled water solution containing 0.5 g/L plexophore detergent at 333 K, followed by rinsing in distilled water, and dried in a vacuum oven at 333 K. Strips of 10 cm × 5 cm were used to study the effect of weaving directions (weft and warp) on the graft yield.

Reagent-grade AA and acrylonitrile monomers, obtained from Aldrich (Germany) and BDH (England),

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respectively, were used. All chemical reagents were used as-received.

Grafting procedure

Wool samples were radiation-grafted in solutions of different monomer concentrations using methanol-water solvent. Mutual irradiation grafting was carried out at different ambient temperatures using dose rate of 1.38 Gy/s with ^{60}Co γ -sources. The samples were immersed in the respective monomer solutions to achieve different FLRs. The samples were then de-aerated with bubbling nitrogen for 5 min and closed before being placed in the γ -cell. Tubes containing samples for radiation grafting were placed in 1 L water container and the water temperature was measured before and after irradiation. The temperature was usually measured in 15–30 min interval up to a maximum of 2 h. After each interval, the container was refilled with fresh water. The temperature of the grafting solution was ± 2 K and ± 1 K of that of water before and after radiation grafting for the high (308 K) and low (275 K) temperatures, respectively. Low irradiation temperatures were achieved by adding crushed ice into the container. The grafted fabric was then washed thoroughly with hot distilled water to extract the residual monomer and the homopolymer occluded in the fabric. The fabric was then dried in a vacuum oven at 333 K until a constant weight was obtained. At least two samples were irradiated for the same dose. The degree of grafting (GY) was determined by the percentage increase in weight using the following equation:

$$\text{Degree of grafting or graft yield (\%)} = 100[(W_G/W_0) - 1] \quad (1)$$

where, W_0 and W_G are the weights of ungrafted and grafted samples respectively. More than two samples were used for each test and variations of about ± 0.5 –2% of weight of sample, depending on the graft yield, is obtained.

Dyeing procedure

A 2% of weight of fabric (owf) dye is dissolved in distilled water at a FLR of 1 : 50. Sandocryl Blue (SB), a basic dye, is used to dye grafted and ungrafted fabrics. The pH of the dye bath was adjusted to that which gives maximum color strength. The dyeing process was carried out in the presence of 1% of weight of dye solution sodium sulfate and 0.1 g/L Sandozin NIT liquid as a wetting agent. The temperature of the dye bath was then raised to 363 K and kept constant for 45 min. After the dyeing, the sam-

ples were rinsed in hot water containing nonionic detergent and in tap water and were allowed to dry.

A computerized micro colorimeter unit made by Dr. Lange (Germany) was used for the color measurements.¹⁸ The L^* , a^* , and b^* system used was based on the Commission International de l'Eclairage (CIE) color triangle (CIE units X , Y , and Z). In this system, the L^* value represents the dark–white axis, a^* represents the green–red axis and b^* represents the blue–yellow axis. The L^* , a^* , and b^* values of ungrafted and grafted fabrics before dye sorption were measured and taken as references. The CD intensity of the grafted samples after dyeing was determined as follows:

$$\Delta E^*(\text{CD}) = \sqrt{[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]} \quad (2)$$

The percentage increase in CD due to grafting is calculated using the equation:

$$\text{Increase in CD (\%)} = 100[(\text{CD}_G/\text{CD}_0) - 1] \quad (3)$$

where, CD_G and CD_0 are the color differences of grafted and original fabrics, respectively.

FTIR measurements

FTIR measurements of original and grafted fabrics (KBr pellet) were carried out using an FTIR spectrometer (Mattson, Class IIa) in transmission mode in the frequency range 400–4000 cm^{-1} . The spectra of the fabrics were obtained through an ATR accessory equipped with a KRS5 crystal at face angle of 45°.

X-ray diffraction measurements

XDA was performed using a Shimadzu DP-DI with $\text{CuK}\alpha$ characteristic radiation.

RESULTS AND DISCUSSION

Optimum grafting conditions

Preliminary experiments to graft wool fabric have shown that AA yielded low GYs while AN showed considerably high yields. To enhance the grafting process, Mohr's salt was added to the monomer–solvent solution to inhibit the homopolymerization process. Figure 1 shows the dependence of the GY on the concentration of Mohr's salt for samples irradiated at a dose of 10 kGy and 10% of weight of solution (ows) AA. Maximum GY is found at inhibitor content of 0.75% of weight of monomer (owm). This concentration is used in the grafting solutions of AA and AA/AN comonomer (CM) mixture.

The effect of FLR on the graft yield (GY) of AA, AN, and their mixture is shown in Figure 2. The solvent

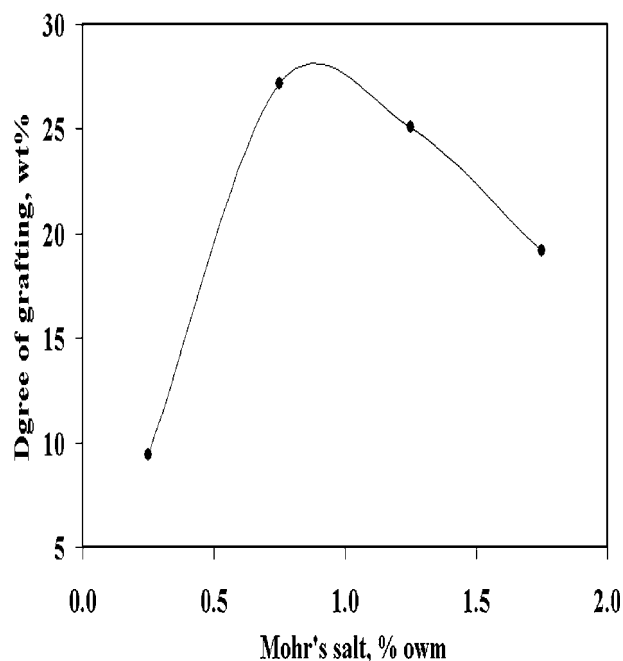


Figure 1 Effect of Mohr's salt on the grafting of AA onto wool fabric.

used is a mixture of water and methanol at a weight ratio of 75 : 25. The general feature of the curves is the same. The GY increases with the increase in FLR reaching a maximum followed by a relatively slow decrease at higher yields. The maximum GY was found to depend on the type of grafted monomer. The

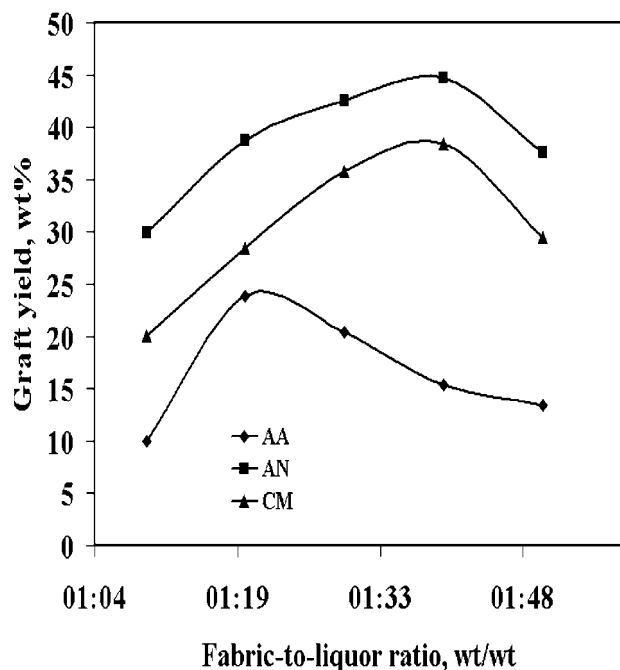


Figure 2 Effect of fabric-to-liquor ratio on the grafting of AA, AN, and their CM mixture onto wool fabric at similar irradiation conditions.

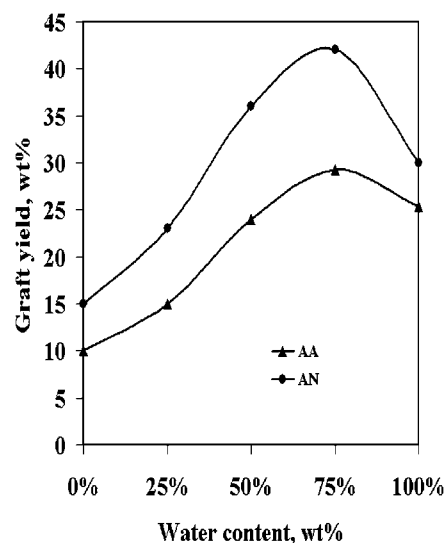


Figure 3 Effect of water-to-methanol ratio on the grafting of AA and AN onto wool fabric. FLR, 1 : 40; 20% ows monomer; dose, 10 kGy; temperature, 302 K.

value of FLR at maximum is 1 : 20, 1 : 40, and 1 : 40 for wool-graft-poly(AA), wool-graft-poly(AN), and wool-graft-poly(AA-co-AN), respectively. These ratios were kept throughout this study.

The effect of water-to-methanol solvent ratio (w/w) on grafting AA, AN, and their mixture onto wool is shown in Figure 3. The curves show maximum graft yields at water-to-methanol ratio of 75 : 25. This ratio is used through out this work.

The effect of AN in 20% ows CM mixture on grafting of wool fabric is shown in Figure 4. The GY increases with the increase in AN content, reaching a highest value of 26% around 50/50 w/w AA/AN mixture. No further increase in GY is noticed as the

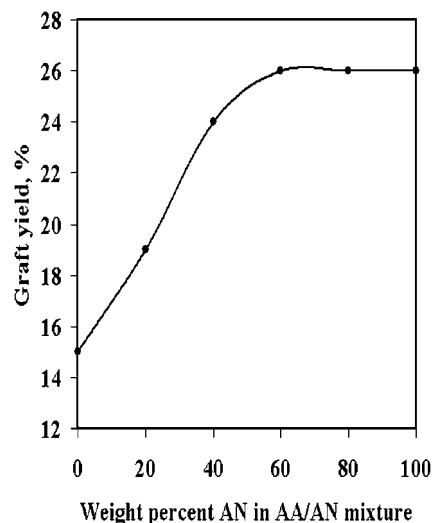


Figure 4 Effect of AN content on the grafting of AA/AN comonomer mixture onto wool fabric. Conditions as in Figure 3.

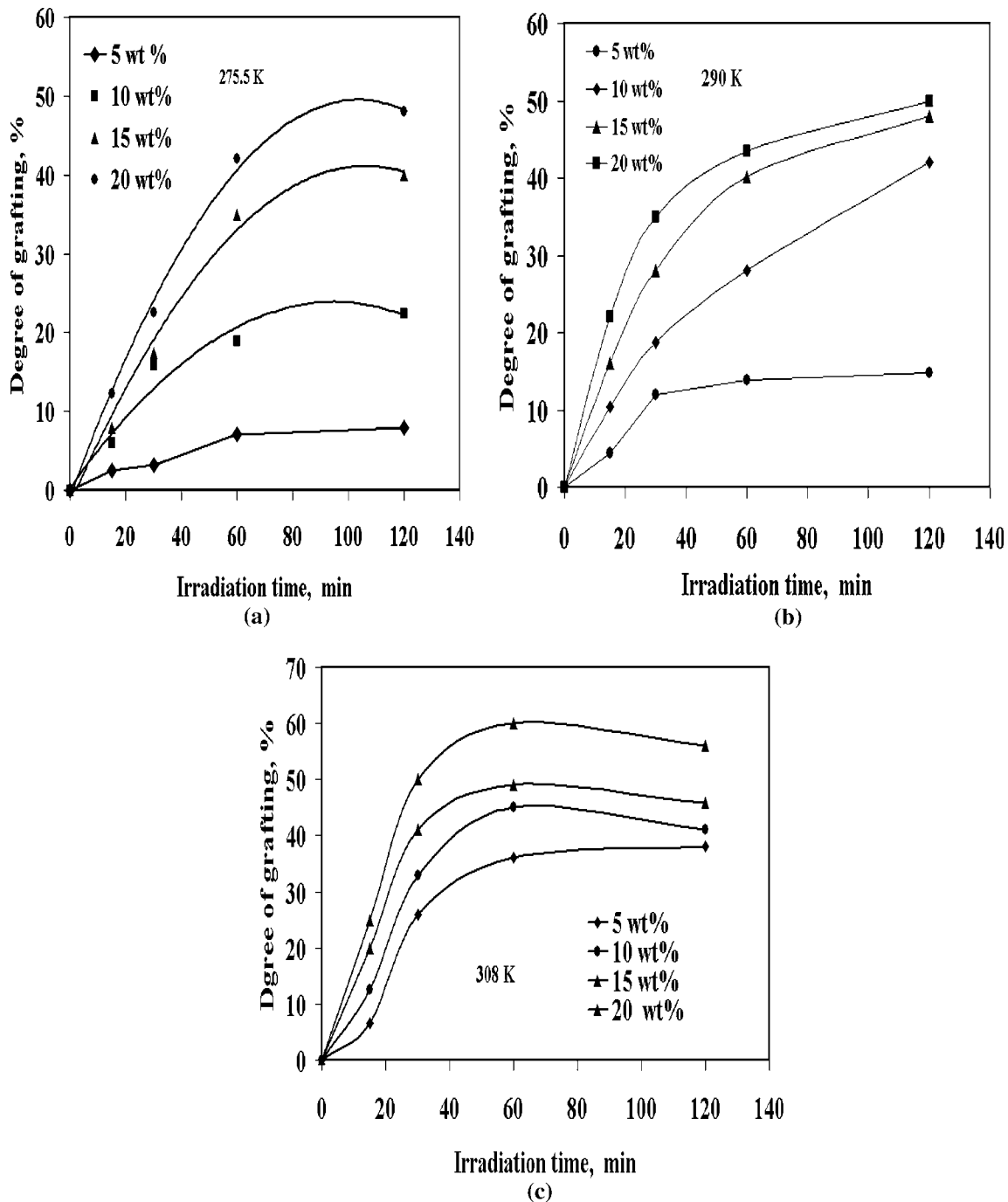


Figure 5 (a-c) Dependence of degree of grafting on irradiation time at different AA concentrations and different temperatures.

AN content passed the 50% in the mixture. It should be noted that 0.75% of weight of AA Mohr’s salt is added to all mixture solutions. The 50/50 ratio is used in all CM experiments.

Effect of monomer concentration

The reaction time and monomer concentration are important factors controlling the grafting. The GY of wool fabrics as a function of irradiation time (*t*) at

various monomer concentrations and different irradiation temperatures, for the corresponding optimum grafting conditions, is shown in Figures 5–7. The figures show typical GY–*t* curves. The GY increases with the increase in *t*, monomer concentration *C*, and irradiation temperature *T*. At high irradiation conditions, the curves show a tendency for a decrease in graft yields. This effect is attributed to the increased viscosity of the monomer solutions, resulting from the homopolymerization process.¹⁹

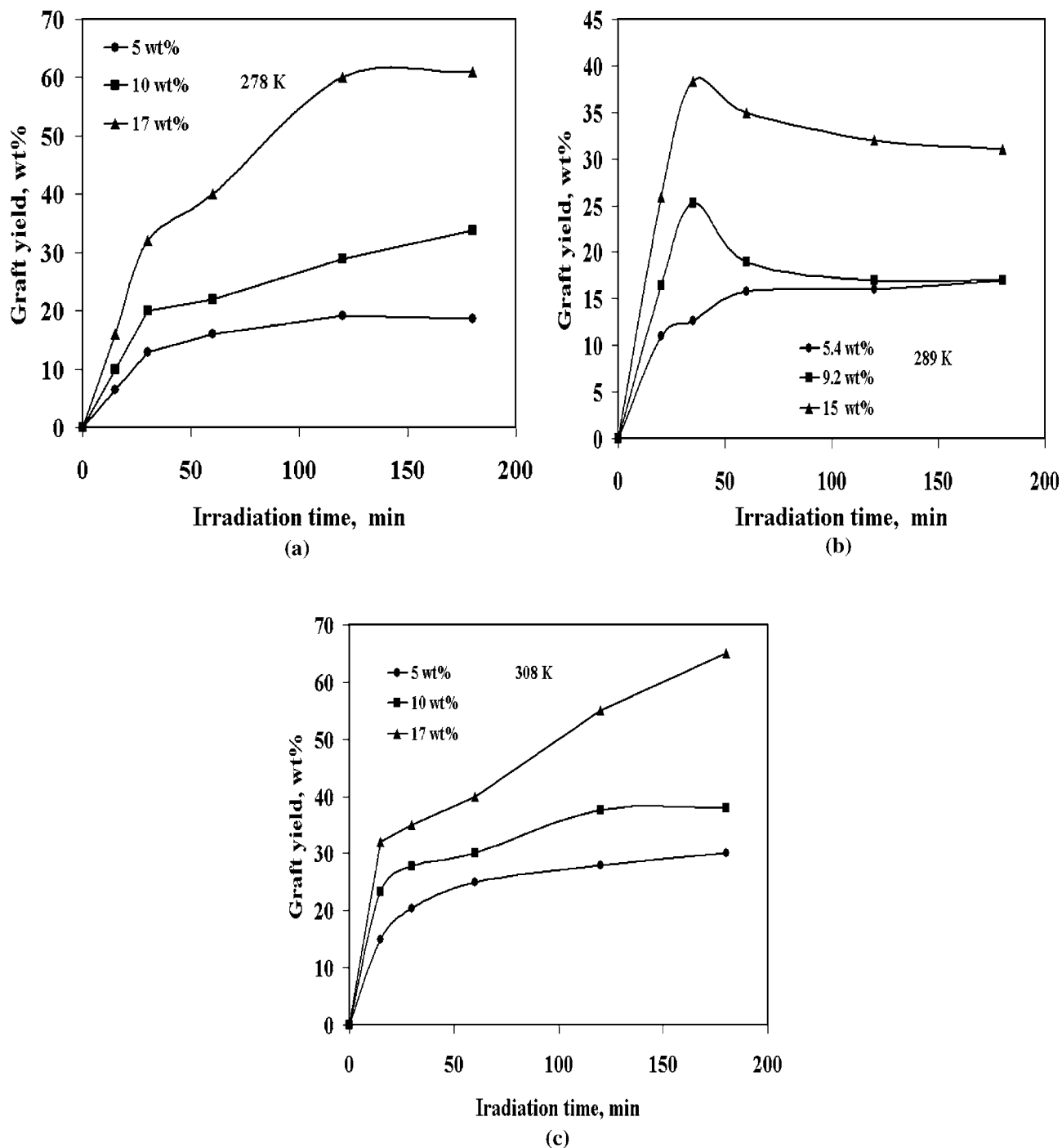


Figure 6 (a-c) Dependence of degree of grafting on irradiation time at different AN concentrations and different temperatures.

The initial rate of grafting (R) is related to the monomer concentration C according to the following equation:^{17,19,20}

$$R = k C^n \quad (4)$$

where, R , k , C , and n are the rate, rate constant, monomer concentration, and reaction order of the grafting process, respectively.

By taking the logarithm of both sides, eq. (4) becomes:

$$\log R = \log k + n \log C \quad (5)$$

The plot of $\log R$ versus $\log C$ yields a straight line with a slope of n and intercept of $\log k$. Figures 8–10 show logarithmic plots of R versus C for the different types of monomers at different irradiation temperatures

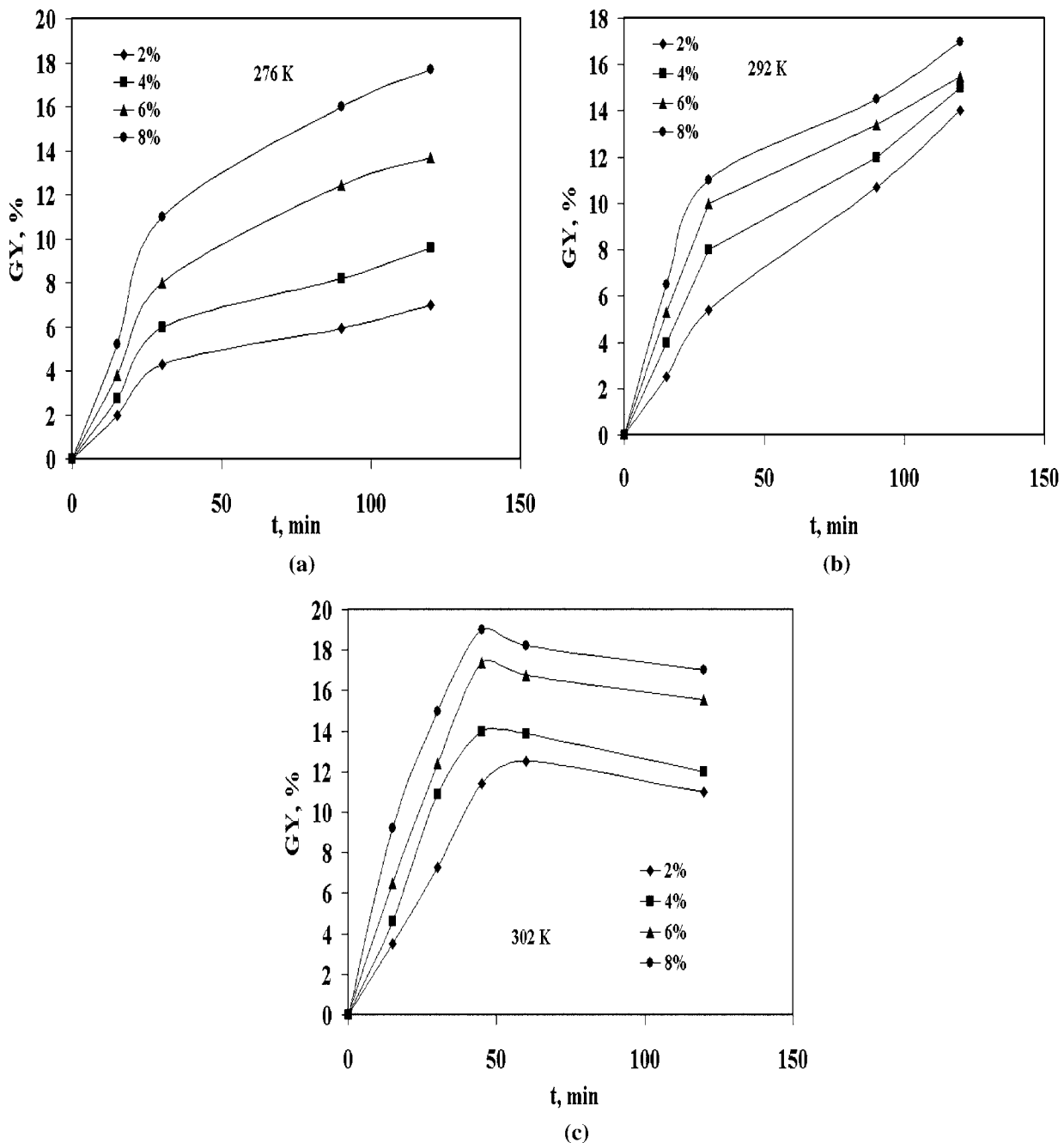


Figure 7 (a-c) Dependence of degree of grafting on irradiation time at different CM concentrations and different temperatures.

according to eq. (5). A linear relationship is obtained, the slope of which gives the reaction order n and the intercept ($\log R$ at $\log C$ of zero, i.e., at C of 1%) gives the value of $\log k$. The value of k (h^{-1}) is obtained by dividing that of R ($\%\text{h}^{-1}$) by 1%. The results of the $\log R$ - $\log C$ linear relationship for AA, AN, and their CM mixture are displayed on the curves using computer's best fit. Table I shows the values of n , $\log k$, and k at different irradiation temperatures. It is obvious from Table I that the reaction order of grafting AA, AN, and

their CM mixture onto wool is independent of irradiation temperature. However, the reaction order of grafting AA follows a first order kinetics while that for AN, and AA/AN mixture has average value for n of 0.73 and 0.65, respectively. Table I and Figures 8–10 also show that R and k increases with the increase in T for all grafted monomers. The magnitude of the value of R and k is dependent on the type of grafted monomer. Their values at constant T are the highest for AN grafts and the lowest for AA grafts.

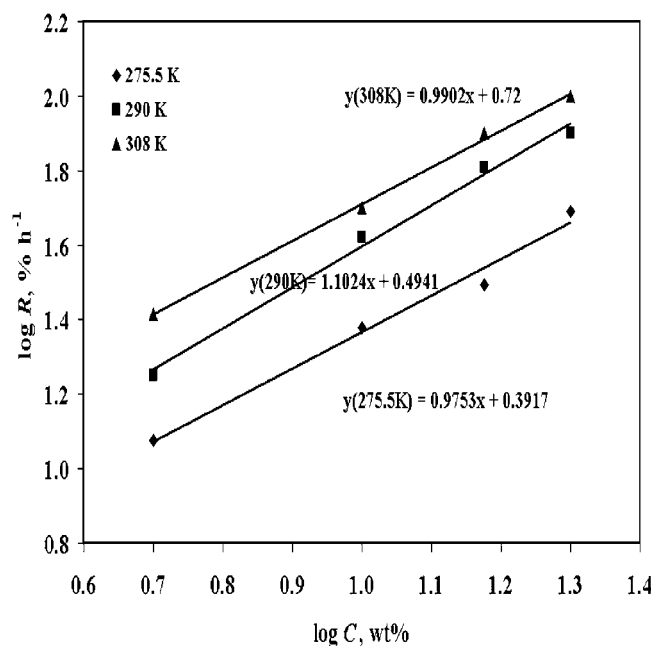


Figure 8 Logarithmic plots of grafting rates and AA concentrations at different irradiation temperatures.

Effect of irradiation temperature

It is known that the influence of reaction temperature on the kinetics of graft copolymerization is extremely complex and no general rule can be formulated for this.¹ A change in temperature will affect strongly the various characteristic processes, which occur in grafting systems.^{17,18,21}

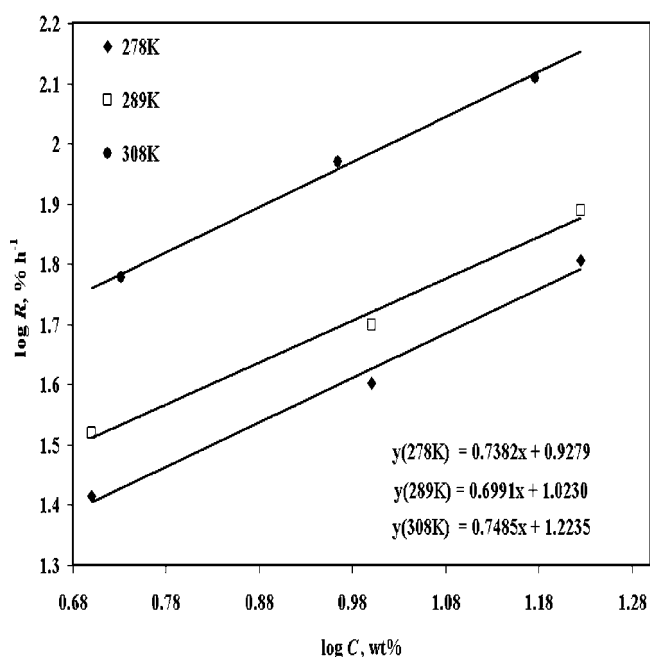


Figure 9 Logarithmic plots of grafting rates and AN concentrations at different irradiation temperatures.

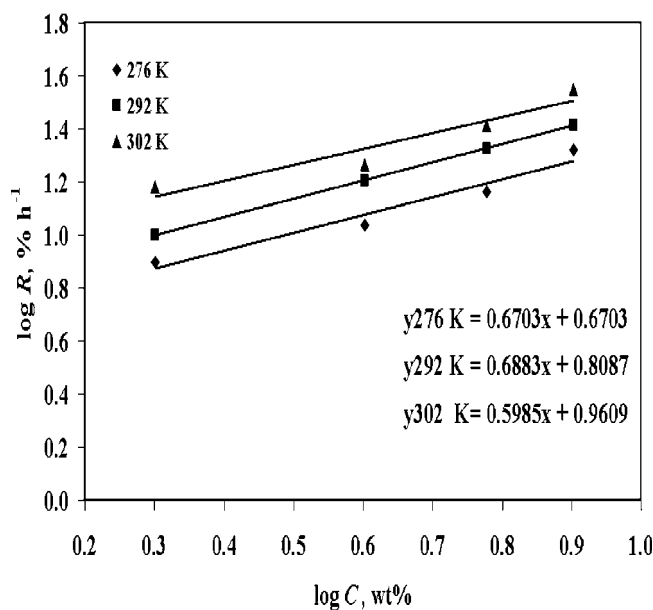


Figure 10 Logarithmic plots of grafting rates and CM concentrations at different irradiation temperatures.

The dependence of R and k on T as given in Table I and Figures 8–10, shows that the values of R and k increase with the increase in T and their magnitude is dependent on the type of grafted monomer. The value of k for AA graft increases from 2.46 to 5.25 h^{-1} as T increased from 275.5 to 308 K while the value of k for AN copolymer graft increases from 8.47 to 16.73 h^{-1} as T increased from 278 to 308 K. The wool-graft-poly (AA-co-AN) samples show intermediate values for R and k . The value of k for CM mixture graft increases from 4.68 to 9.14 h^{-1} as T increases from 276 to 302 K. The ratio $k_{\text{AN}} : k_{\text{AA}}$ is constant and independent of T (about 3.31). These results emphasize that the rate of grafting AN onto wool is higher than that of AA. To explain the differences in k for the different monomers and to understand the mechanism of the grafting process, the activation energy (Q) and the preexponential rate constant (A) should be calculated.

Activation energy determination

The dependence of k on T for grafting the different monomers onto wool is presented using Arrhenius-type equation:

$$k = A e^{-Q/RT}$$

where, k , A , Q , R , and T are the grafting rate constant, the preexponential rate constant, the activation energy, the Universal gas constant, and the absolute temperature, respectively. Figure 11 shows the plot of $\ln k$ versus $1000/T$ for the three monomer systems. The relationship is linear and indicates that $\ln k$ decreases linearly with increase in inverse of T . The slope of the

TABLE I
Kinetic Parameters for Grafting AA, AN, and Comonomer (CM) Mixture onto Wool Fabric

Monomer	T (K)	<i>n</i>	log <i>k</i>	<i>k</i> (h ⁻¹)	Q (kJ mol ⁻¹)	A (h ⁻¹)
AA	275.5	0.9753	0.3917	2.4643	16.4	3.185 × 10 ³
	290	1.1024	0.4941	3.1196		
	308	0.9902	0.72	5.2481		
AN	278	0.74	0.9279	8.47	16.5	1.08 × 10 ⁴
	289	0.70	1.0230	10.54		
	308	0.75	1.2235	16.73		
CM	276	0.67	0.6703	4.68	17.2	8.61 × 10 ³
	292	0.69	0.8087	6.44		
	302	0.60	0.9609	9.14		

linear equation gives the value of Q/R and the intercept gives the natural logarithm of the preexponential rate constant A . The displayed equations on the curves are as follows:

$$\ln k_{AA} = -1.9861 (1000/T) + 8.0661 \quad (6)$$

$$\ln k_{AN} = -1.9948 (1000/T) + 9.2874 \quad (7)$$

$$\ln k_{CM} = -2.0821 (1000/T) + 9.0602 \quad (8)$$

The corresponding values of Q and A are shown in Table I. The values of Q are 16.4, 16.5, and 17.2 kJ mol⁻¹ for grafting AA, AN, and their CM mixture, respectively. The value of Q for grafting wool fabric with AA, AN, and their mixture is almost constant. The corresponding A values are 3185, 10,801, and 8606 h⁻¹ respectively. The values of the frequency factor A for grafting AN, and CM mixture onto wool fabric are 3.4 and 2.7 times higher than that of AA. These results can be presented as follows:

$$k_{AA}(\text{s}^{-1}) = 0.89 e^{-16400 \text{ J/mol}/RT} \quad (9)$$

$$k_{AN}(\text{s}^{-1}) = 3.00 e^{-16500 \text{ J/mol}/RT} \quad (10)$$

$$k_{CM}(\text{s}^{-1}) = 2.40 e^{-17200 \text{ J/mol}/RT} \quad (11)$$

Since the Q value for the three grafted monomers is almost the same, the parameter that controls the grafting rate constant k is the frequency factor A and not the activation energy. Consequently, for a CM mixture of equal monomer concentration (50%/50%), one expects that the corresponding A_{CM} will be in between that of AA and AN, at the ratio 0.89 : 3.000 (1 : 3.37). The expected A_{CM} is [(0.89 × 1/4.37) + (3.000 × 3.37/4.37)] 2.5 s⁻¹. This value is very close to that experimentally obtained (2.4 s⁻¹), and supports the constancy of the Q value for the grafted monomers. The constancy in Q indicates that the mechanism of grafting AA, AN, and their CM mixture is the same. Moreover, the results indicate that the grafting affinity of wool fabric toward AN and

AA/AN mixture is 3.4 and 2.7 folds of AA, respectively. This explains the low value of the calculated reaction order for AN and CM. The low rates of grafting AA onto wool can be explained as follows. For the initial irradiation period, grafting initially occurs at the swollen surfaces by AA solution, followed by continuous monomer diffusion through grafted layers to reach active sites to give homogeneous distribution of the grafted chains in the fabric. The homopolymerization of AA plays an important role at high AA concentrations and longer irradiation times (high doses). Poly(AA) is insoluble in its monomer and has poor solubility in the water-methanol solvent at test conditions and forms a gelatinous layer over the fabric surfaces. The homopolymer, depending on the initial AA concentration, retards

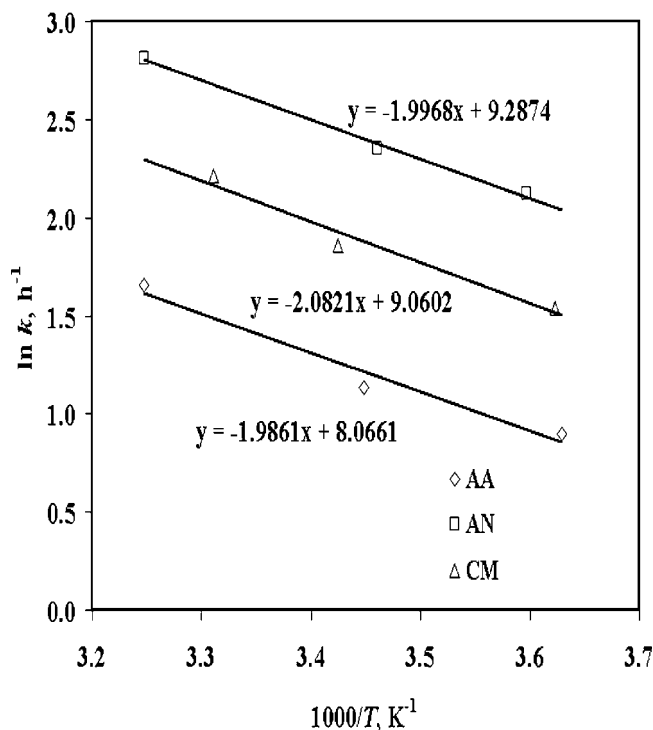
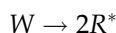


Figure 11 Arrhenius-type plot of the natural logarithm of the rate constant versus the inverse of the absolute temperature for AA, AN, and their CM mixture.

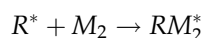
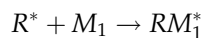
the monomer diffusion and hence slows the grafting process (Fig. 5). Moreover, the high rate of homopolymerization of AA over that of AN can be attributed to its higher G_R value (11 for AA and 5 for AN).^{6,22} The high G_R for AA decreases the effective monomer concentration to continue the grafting process, especially at high doses, and supports the idea that grafting rates are dependent not only on the amount of free radicals but also on the diffusivity of the monomer through the grafted layers. The molecular weight of AN (53), being smaller than that of AA (72), enhances its diffusion through the fiber matrix to reach active sites with the result of higher contribution in the copolymer formation. Consequently, Mohr's salt was added in all grafting experiments using AA or AA/AN mixture to reduce the homopolymerization and increases the grafting process.

The overall activation energy for grafting AA, AN, and their mixture onto wool fabric falls within the acceptable range for the grafting process. The highest value is 8 kcal mol⁻¹ (33.44 kJ mol⁻¹) as reported by Chapiro.¹ Kaji et al.²³ and Shimano et al.²⁴ carried out radiation-induced graft copolymerization of PET using methacrylic acid (MAA) and AA in the presence of ethylene chloride. The reported activation energy for AA was 8.0 kcal mol⁻¹ in the range 18–40°C and 8.77 kcal mol⁻¹ for MAA in the range 15–20°C. Rao and Rao²⁵ reported values 10.7 and 11.7 kcal mol⁻¹ for Q of grafting AA and vinyl acetate on PET fibers. Values of 22.53 and 23.3 kJ mol⁻¹ were calculated for grafting AA¹⁸ and NVP¹⁹ onto PET fabric. It is obvious that the differences in the reported and calculated values of Q can be attributed to the type of monomer, grafted substrate, and grafting conditions.

The similarity in Q values of the different monomers indicates that the mechanism controlling the grafting process is of the same nature. Moreover, the k values for AA are lower than those of AN. Consequently, it is expected that the mole fraction of poly (AA) in grafted CM mixture will be smaller than that of poly(AN). To explain the contribution of the different monomers in grafting wool fabric with 50%/50% CM mixture at a constant FLR, it is worth considering the mechanism of radiation grafting of the CM. The copolymerization process proceeds via wool free-radical (R^*) as follows:



The free radical formed can attack AA (M_1) or an (M_2) according to reactions



Two copolymer chains can thus be initiated, one carrying a free radical site on monomer unit M_1 and the other on monomer unit M_2 . After initiation, comes

the process of propagation. Hence, the chain carrying a free-radical site on M_1 can add either monomer M_1 or M_2 . Similarly, the chain carrying a free-radical site on M_2 can add either another M_2 or an M_1 , i.e.:



where, PR means propagation reaction. Assuming that all the four types of addition take place, the growing chains still end with M_1^* or M_2^* . The rates of these PRs are as follows:

$$R_{11} = k_{11} [RM_1^*] [M_1] \quad (12)$$

$$R_{12} = k_{12} [RM_1^*] [M_2] \quad (13)$$

$$R_{21} = k_{21} [RM_2^*] [M_1] \quad (14)$$

$$R_{22} = k_{22} [RM_2^*] [M_2] \quad (15)$$

At a steady state wherein the rate of particular chain end [say, M_1^*] disappearing is equal to the rate of formation of the same chain end, then

$$[m_1]/[m_2] = \{[M_1]/[M_2]\} \times \{(r_1[M_1] + [M_2])/(r_2[M_2] + [M_1])\} \quad (16)$$

where, $[m_1]/[m_2]$ gives the ratio of the monomers M_1 and M_2 entered into the copolymer formed. If the monomer components $[m_1]$ and $[m_2]$ are expressed in terms of mole fraction instead of molar concentration, the mole fraction of monomer M_1 in the copolymer can be given by

$$[m_1]/([m_1] + [m_2]) = n_1 = 1 - n_2$$

where, n_1 and n_2 are the mole fractions of monomers M_1 and M_2 , respectively, in the copolymer formed. Similarly, the mole fractions of the monomer M_1 in the monomer feed can be given by

$$[M_1]/([M_1] + [M_2]) = N_1 = 1 - N_2$$

where, N_1 and N_2 are the mole fractions of the monomers M_1 and M_2 , respectively, in the monomer feed.

The copolymer eq. (16) can be expressed as²⁶

$$n_1 = [r_1 (N_1)^2 + N_1 N_2] / [r_1 (N_1)^2 + 2N_1 N_2 + r_2 (N_2)^2] \quad (17)$$

where, r_1 and r_2 are the terms k_{11}/k_{12} and k_{22}/k_{21} , respectively. The terms r_1 and r_2 are known as the reactivity ratios for a given pair of monomers M_1 and M_2 .

Substituting the proper values of N_1 and N_2 (0.5) and considering k_{11} and k_{22} to be proportional to k_{AA} and k_{AN} and k_{12} and k_{21} to be proportional to k_{CM} (Table I), the AA mole fraction (n_{AA}) around 276, 290, and 308 K are 0.35, 0.36, and 0.357 respectively, according to the reduced eq. (18):

$$n_{AA} = (r_{AA} + 1)/(r_{AA} + 2 + r_{AN}) \quad (18)$$

where, the calculated r_{AA} and r_{AN} are 0.53 and 1.81; 0.48 and 1.64; 0.574 and 1.83 respectively, at 276, 290, and 308 K, respectively. This indicates that 0.356 mole fraction (35.6%) AA is copolymerized with 0.644 mole fraction (64.4%) AN to form wool-graft-poly(AA-co-AN). Similar result for n_{AA} (0.38) is calculated from the values of r_{AA} and r_{AN} at 50°C (0.35 and 1.15) reported by Brandrup and Immergut.²⁷

To emphasize these results, dyeing experiments were carried out applying basic SB dye on grafted and ungrafted wool samples. The percentage increase in color difference (CD) is plotted as a function of graft yield (Fig. 12). The CD increases almost linearly with the increase in GY, followed by a tendency to level off with further increase in GY for AA and CM grafts. No improvement in the CD of AN grafts is observed. The CD-GY relationship of AA and AA/AN mixture grafts is similar to those obtained for dyeing cotton-graft-poly(AA),⁷ PET-graft-poly(AA),¹⁷ and PET-graft-poly(MAA).²¹ The improvement in the dye ability of the fabrics toward basic dyes is attributed to the introduction of the COOH groups in the fiber matrix as a result of grafting with AA and MAA. Consequently, the increase in CD with the increase in GY of AA and AA/AN mixture grafts is,

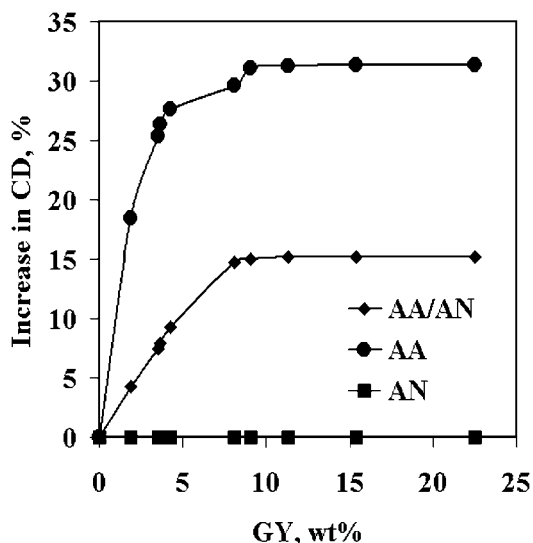


Figure 12 Increase in the color difference of Sandocryl Blue dye as a function of graft yield for AA, AN, and their CM mixture.

therefore, attributed to the presence of poly(AA) in the structure of wool fabrics. Comparison of the value of GY at a constant percentage increase in CD for wool-graft-poly(AA) and wool-graft-poly(AA-co-AN) indicates that wool-graft-poly(AA-co-AN) requires considerably high GY to reach that of wool-graft-poly(AA) samples. Since AN grafts have no influence on improving the CD of wool, the increase in the CD of wool-graft-poly(AA-co-AN) is attributed to the presence of poly(AA) in wool grafts. The ratio of the GY of wool-graft-poly(AA-co-AN) to that of wool-graft-poly(AA) samples, at a constant increase in CD(%), amounted to 3.4 : 1, respectively. This indicates that about 29% poly(AA) is present in wool-graft-poly(AA-co-AN) samples. Moreover, at GY higher than 10%, where leveling occurs, the ratio of the increase in CD for AA to that of AA/AN mixture is 15 : 31. This ratio also agrees well with the inverse ratio of the G_R values for AN : AA (5 : 11).^{6,22} It is obvious that the mole fraction of AA copolymerized with wool, depending on the overall graft yield of the two monomers, is about 0.29. This value is reasonably close to that calculated from the rate constants and the reactivity ratios.

The calculations of the kinetic parameters for the grafting of AA, AN, and their 50%/50% CM mixture onto wool fabric together with those of the reactivity ratios and the mole fractions of poly(AA) and poly(AN) in their copolymer, as supported by their dyeing affinity toward wool fabric, emphasize that the rate controlling process for grafting all monomers is of the same nature. The slowest process, which is the propagation of the chains, is the rate controlling. The calculated apparent activation energy and frequency factor are those of the propagation process. These results emphasize the importance of studying the kinetics of grafting of separate monomers and their binary mixtures.

Effect of weaving direction

The effect of weaving direction (weft and warp) on the grafting rates of AA and AN onto wool fabric is shown in Figure 13. Logarithmic plots of grafting rate and monomer concentration for the weft and warp directions gave straight lines, the slope of which is the reaction order n and the intercept is the logarithm of k . The equations relating $\log R$ to $\log C$ are displayed on the corresponding straight lines. Table II shows the values of n and k at 300 K. It is obvious from the results that the reaction order is independent of the weaving direction and only depends on the type of used monomer, and its value is similar to that in Table I. In general, for the same monomer, the value of k for the weft direction is higher than that of the warp direction. Moreover, the value of k for grafting AN onto wool in the weft (15.13 h^{-1}) and warp (7.27 h^{-1}) directions is much higher than that of AA

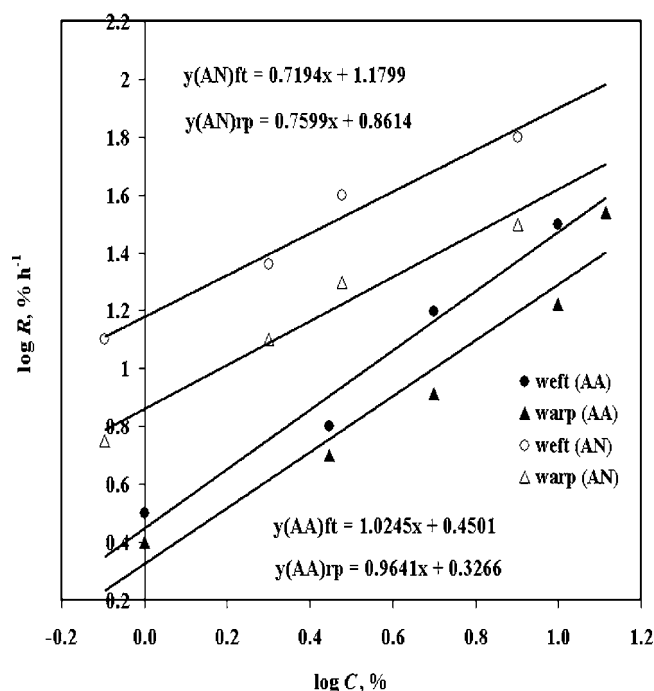


Figure 13 Effect of weaving direction on the logarithmic plots of the grafting rates versus AA and AN concentrations at 300 K.

(2.82 and 2.12 h^{-1} respectively), while the ratio $k_{\text{weft}}/k_{\text{warp}}$ for AN is 1.56 fold of AA. This is in accordance to the results previously discussed.

The high rates of grafting in the weft direction can be attributed to the type of strings applied in both weaving directions and not to their number since the number in both directions is the same (25). The strings in the warp direction are more compact and highly twisted. This is checked by measuring the tensile strength (TS) and strain (ϵ) at break. The values of TS and ϵ for the warp and weft directions are $14.2 \times 10^6 \text{ Nm}^{-2}$ and 22%; $8.2 \times 10^6 \text{ Nm}^{-2}$ and 34%, respectively. These results support the idea that the diffusion of the monomer to reach active sites in the back bone of the fabric in the warp direction is slower than that in the weft direction, thus resulting in lower grafting rates.

Grafting confirmation

Grafting AA, AN, or 50%AA/50% AN CM mixture onto wool fabric was verified through IR spectra and

TABLE II
Effect of Weaving Direction on the Rate Constant for Grafting AA and AN onto Wool Fabric at 300 K

Monomer	Direction	n	$\log k$	$k (\text{h}^{-1})$
AA	Weft	1.0245	0.4501	2.82
	Warp	0.9641	0.3266	2.12
AN	Weft	0.7194	1.1799	15.13
	Warp	0.7599	0.8614	7.27

X-ray diffraction patterns. Structural changes in the wool fabrics resulted from grafting are shown in Figure 14 and Table III. Figure 14 shows typical FTIR-ATR spectra of original and grafted fabrics having almost the same AA and AN content (GY). Wool fabric, being of protein nature, has a complex structure. It contains different functional groups attached to the back bone. The most common groups are NH_2 , NH , SH , SS , CS , CO , OH and CH . The S-S , C-S , and C=S peaks for wool fabric are located between 500 and 1250 cm^{-1} . The S-H stretching peak is located at 2366 cm^{-1} . The strong absorption peaks at 1530, 1650, and 3400 cm^{-1} are assigned to stretching of the NH_2 , C=O , and NH groups. The peak at 3740 cm^{-1} is that for stretching the OH group [Fig. 14(a)].

The grafting of AA and AN onto wool introduces poly(AA) and poly(AN) in its structure; mainly CH_2 , CH , COOH (AA) and CN (AN), respectively. The absorption peak at 1966 cm^{-1} disappeared as a result of the introduction of poly(AA) and poly(AN) into wool. Additional weak peaks appeared at 2300 and 2380 cm^{-1} for wool-graft-poly(AA) [Fig. 14(b)], while a strong peak at 2250 cm^{-1} appeared due to the introduction of the CN groups for wool-graft-poly(AN) [Fig. 14(c)]. The peaks of wool-graft-poly(AA) and wool-graft-poly(AN) also appeared in the IR spectra of grafted copolymer [Fig. 14(d)].

The XRD patterns, Table III, show the three principal peaks of ungrafted and grafted samples located at different 2θ values. It is obvious from the table that grafting the fabric with AA, AN, and their CM mixture changed the position of the peaks of wool samples with the introduction of peaks characterizing the grafted monomer. Peaks at 2θ of 36.037° , 18.528° and

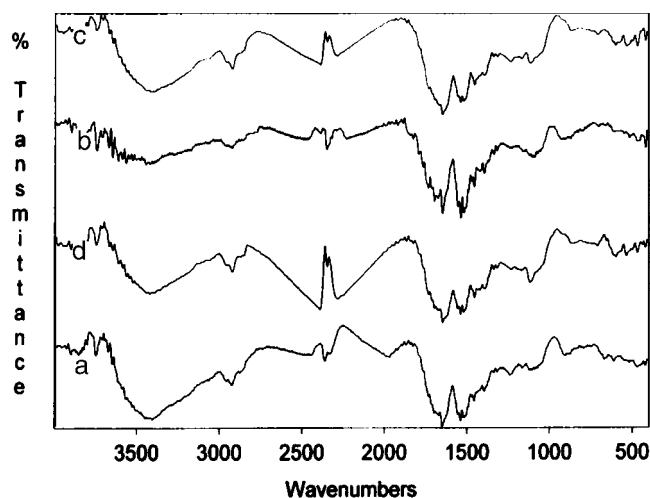


Figure 14 Typical FTIR-ATR spectra of (a) original wool sample; (b) 9.2% grafted AA; (c) 10.9% grafted AN; and (d) 20.1% grafted CM mixture.

TABLE III
X-ray Diffraction Parameters for Original and Grafted Wool Fabric

Material	Peak	2 θ (°)	<i>d</i> (Å)	Intensity (cps)
Wool	1	21.758	4.0813	170
	2	20.398	4.3502	160
	3	19.548	4.4374	160
Wool-graft-22% poly(AA)	1	23.288	3.8165	88
	2	24.138	3.680	82
	3	36.037	2.4900	75
Wool-graft-18% poly(AN)	1	19.888	4.4606	213
	2	24.138	3.6840	182
	3	18.528	4.7848	182
Wool-graft-18% poly(6.84% AA-co-11.16% AN)	1	17.848	4.9655	190
	2	7.989	11.0579	178
	3	23.454	3.7892	173

7.989° are characteristics of grafted AA, AN, and their CM respectively. Moreover, the CM peaks at 2 θ 17.848° and 23.454° are similar to those of AA and AN, respectively. The results also indicate that grafting decreases the lattice spacing between diffracting planes of wool fabric, with the exception of that of the CM at 2 θ 7.989°. From the results of FTIR and X-ray measurements, it can be concluded that AA, AN, and their CM were successfully grafted onto wool fabric.

CONCLUSIONS

The following conclusions are reached from the kinetics study of radiation-grafting of AA, acrylonitrile, and their mixture onto wool fabric:

1. The GY is dependent on the water-to-methanol solvent ratio and FLR.
2. The GY is dependent on irradiation time, monomer concentration, and irradiation temperature. The reaction rate increases with the increase in monomer concentration. The reaction order *n* of grafting AA, AN, and their CM mixture onto wool is independent of irradiation temperature. The AA grafting follows a first-order kinetics while AN and AA/AN mixture have average value for *n* of 0.73 and 0.65, respectively.
3. The reaction rate and rate constant increase exponentially with the increase in absolute temperature. The activation energy for grafting AA, AN, and their CM mixture is almost constant and varies from 16.4 to 17.2 kJ mol⁻¹.
4. The value of the frequency factor *A* for grafting AN and CM mixture onto wool fabric is 3.4 and 2.7 times higher than that for AA.
5. The mechanism for the copolymerization of 50%AA/50%AN onto wool shows that 0.356 mol fraction (35.6%) AA is copolymerized with 0.644 mol frac-

tion (64.4%) AN, to form wool-graft-poly (AA-co-AN).

6. The rate controlling process for grafting all monomers is the propagation of the chains initiated via free radicals. The calculated apparent activation energy and the rate constants are those of the propagation process.
7. The results emphasize the importance of the study of the kinetics of grafting of separate monomers and their binary mixtures.
8. The reaction order is independent of weaving directions and only depends on the type of used monomer. For the same monomer, the value of the rate constant *k* for the weft direction is higher than that of the warp direction.

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