

# Processes Involved During Radiation Grafting of *N*-Vinyl Pyrrolidone onto Poly(ethylene terephthalate) Fabric

E. H. El-Gendy,<sup>1</sup> N. M. Ali,<sup>1</sup> I. A. El-Shanshoury<sup>2</sup>

<sup>1</sup>National Centre for Radiation Research and Technology, Atomic Energy Authority, Nasr City, Cairo 11731, Egypt

<sup>2</sup>National Centre for Nuclear Safety and Radiation Control, Atomic Energy Authority, Nasr City, Cairo 11731, Egypt

Received 24 September 2005; accepted 26 October 2005

DOI 10.1002/app.23655

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Kinetics of radiation grafting of *N*-vinyl pyrrolidone (NVP) onto poly(ethylene terephthalate) (PET) fabric revealed the existence of four different processes. These are as follows: the grafting, the homopolymerization, the degradation, and the diffusion. The grafting process was followed by the increase in weight with the increase in irradiation time ( $t$ ), while the homopolymerization and the degradation processes were evaluated from changes in the square root of the specific viscosity of the irradiated monomer solution ( $\sqrt{\eta_{sp}}$ ) with the increase in  $t$ . All processes were carried out at different NVP concentrations, different irradiation temperatures ( $T$ ), and a dose rate  $1.31 \text{ Gy s}^{-1}$ . All processes followed first-order kinetics except the degradation process that followed a 0.6-order. The rate ( $R$ ) and rate constant ( $k$ ) of grafting and diffusion processes were found

to increase with the increase in  $T$ , while the homopolymerization and degradation processes showed negative temperature dependence. The sum of  $R$  of the four processes was proportional to the initial NVP concentration, while  $k$  of the four processes was independent of  $T$  and has a value of  $0.674 \text{ min}^{-1}$ . The respective apparent activation energies of 24.0, 6.24, 6.84, and  $2.5 \text{ kJ mol}^{-1}$  were calculated for the four processes. The NVP molecules participated in each process and their energies were evaluated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3009–3022, 2006

**Key words:** *N*-vinyl pyrrolidone; poly(ethylene terephthalate); kinetics; grafting; homopolymerization; degradation; diffusion

## INTRODUCTION

Improvements of natural and synthetic polymers imparting more desirable properties are extremely useful for different areas of applications. The grafting of vinyl monomers onto synthetic fibers has received considerable attention by various workers<sup>1–9</sup> to improve their properties, in particular the dyeability, reduction of static charge, and moisture absorption. Vlagie and Stannett<sup>10</sup> studied the kinetics of radiation-induced graft copolymerization of styrene onto poly(ethylene terephthalate) (PET) fibers and found overall activation energy for grafting to be  $13.7 \text{ kcal mol}^{-1}$ . The reaction was carried out in nonaqueous phase, and the presence of water in the reaction mixture was found to decrease the activation energy to a certain extent. Sakurada and coworkers<sup>11–13</sup> carried out radiation-induced graft copolymerization of PET using methacrylic acid (MAA) and acrylic acid (AA) as monomers and copper sulfate and Mohr salt as inhibitors. They found that in the presence of ethylene dichloride, the activation energy for AA was  $8.0 \text{ kcal mol}^{-1}$  in the temperature range  $18^\circ\text{C}$ – $40^\circ\text{C}$  and  $8.77$

$\text{kcal mol}^{-1}$  in the range  $15^\circ\text{C}$ – $20^\circ\text{C}$ . In the absence of ethylene dichloride the activation energies were considerably higher.

Aggour<sup>14</sup> carried out graft copolymerization of poly(vinyl alcohol) using 2-acrylamide-2-methyl-1-propanesulfonic acid as radical initiator. He found that the initial rate and the final percentage of grafting were increased by an increase in reaction temperature. The kinetics was studied to determine the rate constants of the first-order reaction. An activation energy  $16.3 \text{ kJ mol}^{-1}$  was found for the grafting reaction.

Recently, we have studied the modification, the dyeing kinetics of PET fabric via radiation grafting with MAA,<sup>9,15</sup> and the kinetic parameters of the graft copolymerization of AA onto PET.<sup>16</sup> Preswelling of the fabric in chloroform was carried out before irradiating the samples in the monomer solution. Optimum conditions for grafting indicated that the best conditions were achieved when using methanol-to-water ratio of 25%:75% by weight and a fabric-to-liquor ratio of 1:40 for both MAA and AA monomers. The reaction rates and rate constants were determined. It was found that the reaction rate increased with the increase in AA concentration and increase in irradiation temperature. In the presence of Mohr salt as inhibitor and in the temperature range 277–303 K, an activation energy  $22.5 \text{ kJ mol}^{-1}$  was found for the grafting AA onto PET.

Correspondence to: E. H. El-Gendy (egendy@gawab.com).

In this article, attention was paid to broaden the study of the kinetics of grafting *N*-vinyl pyrrolidone (NVP) onto PET fabric to cover the various processes involved during grafting, in particular the homopolymerization and the degradation processes. The grafting process was carried out in solutions containing methanol–water solvent at a ratio of 25% : 75% and a fabric-to-liquor ratio of 1 : 20 by weight. The effects of NVP concentration, irradiation time, and temperature on the reaction rate, rate constant, reaction order, activation energy, and pre-exponential rate constant for the different processes involved during grafting were studied and evaluation of the number of molecules and their energies participating in each process was carried out.

## EXPERIMENTAL

### Materials

Thermally stabilized, heat treated at 493 K for 1.5 min, low density PET fabric, product of Hankook Synthetic, Korea, is mill-scoured in a solution containing 0.01 g L<sup>-1</sup> Data scour WS-100 and sodium carbonate (0.5 g L<sup>-1</sup>) at the boil for 1 h. The fabric was thoroughly washed with hot water, dried at ambient temperature, and then used for grafting.

*N*-vinyl pyrrolidone (NVP) monomer (product of Aldrich, Germany), pure chloroform for analysis (product of El-Nasr chemical and pharmaceutical, Egypt), HPLC methanol (product of Aldrich, Germany), and nonionic Sandozin NIT liquid detergent (produced by Sandoz, Switzerland) were used as received.

### Radiation grafting

Grafting was carried out by the direct irradiation method in a <sup>60</sup>Co gamma source of 1.31 Gy s<sup>-1</sup> dose rate for different periods, NVP concentrations, and temperatures to achieve a wide range of graft yield. Dry weighed PET samples were impregnated overnight in chloroform, as a swelling agent, before the introduction into wide mouth tubes provided with ground joint stoppers containing the solvent and the monomer. About 1 g sample was then added to the grafting solution and deaerated with bubbling nitrogen for 5 min. The grafted fabrics were removed from the reaction tube after irradiation to the desired dose. The homopolymer (HP) was extracted from the grafted fabrics with boiling water. The samples were then dried at 313 K in a vacuum oven to a constant weight. The graft yield or degree of grafting (GY) was determined as the percentage increase in weight as follows:<sup>7</sup>

$$\text{Graft yield (\%)} = 100[(W_G - W_0)/W_0]$$

where  $W_0$  and  $W_G$  are the weights of the initial and final grafted samples, respectively.

Low irradiation temperatures were achieved by irradiating the tubes containing the sample solution in ice–water mixture. The lower the temperature is the higher the ratio of ice-to-water. Irradiation intervals of 15 min were used. Irradiation was carried out in the temperature range 278–315 K. The temperature inside the grafting solution increased 1–2 K, depending on the initial irradiation temperature.

### Viscosity measurements

The apparent viscosity of irradiated and unirradiated solutions is measured by a cone-plate type digital rheometer, model LV, Brookfield Engineering Laboratories, using CP40 spindle. The coefficient of viscosity ( $\eta$ ) is calculated from the slope of the shear stress–shear rate linear relationship. Its unit is cent Poise (cP). Viscosity measurements were carried out at a constant temperature of 298 K.

The specific viscosity ( $\eta_{sp}$ ) of the solution is calculated from the apparent viscosity as follows:

$$\eta_{sp} = [(\eta_{irr}/\eta_{unirr}) - 1] \quad (1)$$

where  $\eta_{sp}$ ,  $\eta_{irr}$ , and  $\eta_{unirr}$  are the specific viscosity, viscosity coefficient of irradiated and unirradiated monomer solutions, respectively. The value of ( $\eta_{irr}/\eta_{unirr}$ ) represents the relative viscosity ( $\eta_{rel}$ ).

## RESULTS AND DISCUSSION

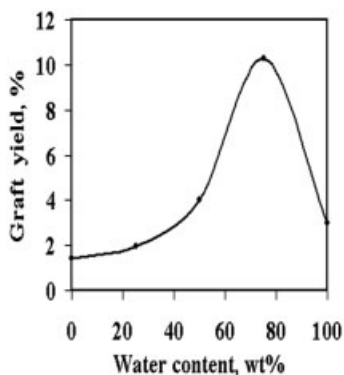
### Optimum grafting conditions

PET fiber is of hydrophobic nature. It is difficult to achieve reasonable degree of grafting with vinyl monomers without using the proper solvent and swelling agent. The best results were achieved by using water–methanol solvents. The effect of solvent on the grafting of NVP onto PET fabric is shown in Figure 1. The degree of grafting (GY) increases to 10.7% maximum at 25 : 75 by weight methanol-to-water ratio. Chloroform was used as the swelling agent. Impregnation overnight of the samples in chloroform gave the highest graft yield.<sup>9,15,16</sup>

In previous investigations<sup>4,5</sup> we have shown the important role of the fabric-to-liquor ratio LR in the grafting process. Figure 2 shows that the maximum graft yield occurs at LR of 1 : 20, by weight. Consequently, all samples were radiation grafted at 1.31 Gy s<sup>-1</sup> dose rate in a monomer solution containing methanol-to-water ratio of 25% : 75% and 1 : 20 fabric-to-liquor ratio.

### Effect of NVP concentration on the grafting rate

The dependence of the graft yield on irradiation time at different NVP concentrations and different irradiation



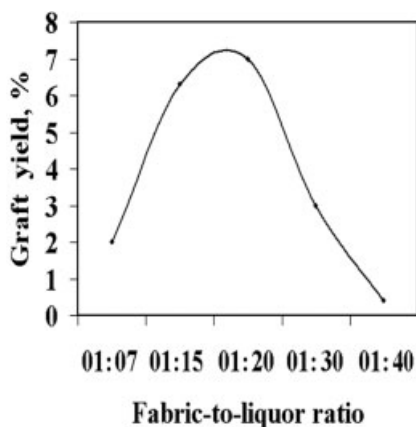
**Figure 1** Graft yield as a function of water-to-methanol content: 10%, NVP; 1 : 20, LR; 10 kGy, dose; 1.31 Gy s<sup>-1</sup>, dose rate; 301 K, temperature.

tion temperatures is shown in Figures 3–5. In general, the graft yield increases with the increase in irradiation time, NVP concentration, and irradiation temperature. It is obvious that an induction period (IP) appears before the start of the grafting process for samples grafted at the low temperature (278 K) and low monomer concentration (7.5% owf). The IP decreases with the increase in NVP concentration and irradiation temperature. Details on the factors affecting the IP are presented in separate investigations.<sup>5,15</sup>

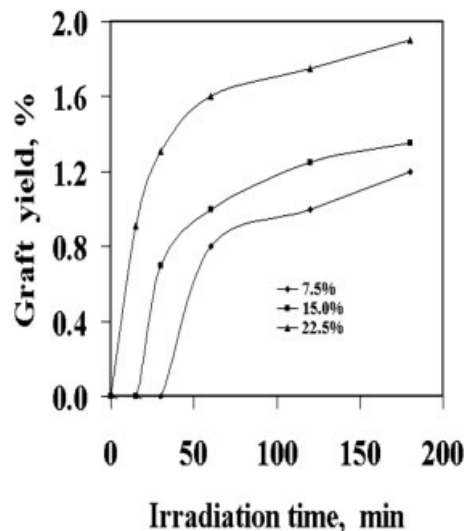
The initial rate of grafting ( $R_G$ ) is calculated at different NVP concentrations and irradiation temperatures. Table I shows the value of  $R_G$  at different NVP concentrations and different temperatures. The results show that  $R_G$  increases with the increase in NVP concentration and irradiation temperature.

### Order of the grafting process

It is known that the rate of grafting is related to the monomer concentration according to the equation:<sup>15,16</sup>



**Figure 2** Graft yield as a function of fabric-to-liquor ratio: 10% NVP; 75 : 25 water-to-methanol ratio; 10 kGy, dose; 1.31 Gy s<sup>-1</sup>, dose rate; 293 K, temperature.



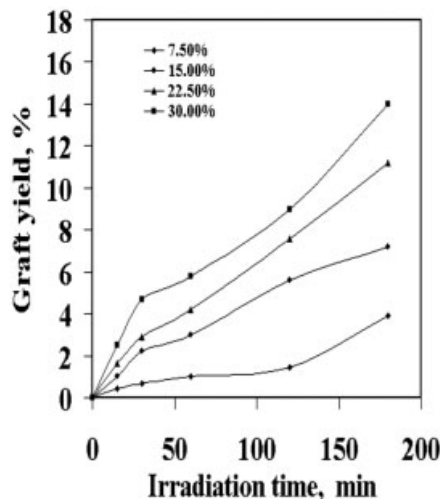
**Figure 3** Dependence of graft yield on irradiation time at different NVP concentrations: 1 : 20, LR; 75 : 25 water-to-methanol solvent; 1.31 Gy s<sup>-1</sup>, dose rate; 278 K, temperature.

$$R_G = k_G [C_{NVP}]^n \quad (2)$$

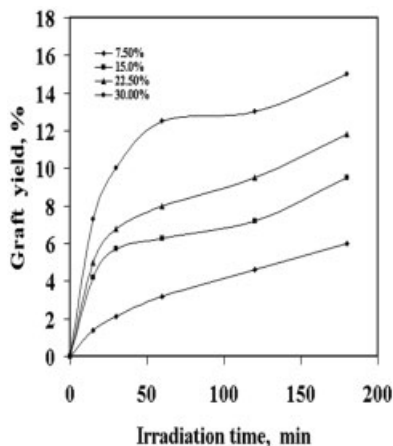
where  $R_G$ ,  $k_G$ ,  $C_{NVP}$ , and  $n$  are the rate of grafting, the rate constant, the monomer concentration, and the reaction order, respectively. Taking the logarithm of both sides, eq. (2) becomes

$$\log R_G = \log k_G + n \log C_{NVP} \quad (3)$$

The plot of  $\log R_G$  versus  $\log C_{NVP}$  gives a straight line the slope of which is the order  $n$  and the intercept is  $\log k_G$ . The value and unit of  $k$  is the same as that of  $R$  at  $\log C_{NVP}$  of zero, i.e. at  $C_{NVP}$  of 1%. Figure 6 shows logarithmic plots of  $R_G$  versus  $C_{NVP}$  at different



**Figure 4** Dependence of graft yield on irradiation time at different NVP concentrations: 1 : 20, LR; 75 : 25 water-to-methanol solvent; 1.31 Gy s<sup>-1</sup>, dose rate; 296 K, temperature.



**Figure 5** Dependence of graft yield on irradiation time at different NVP concentrations: 1 : 20, LR; 75 : 25 water-to-methanol solvent; 1.31 Gy s<sup>-1</sup>, dose rate; 315 K, temperature.

irradiation temperatures. The values of  $R_G$  and  $C_{NVP}$  are plotted as percent per hour and percent, respectively. The results displayed on the computer chart give the values of  $n$  and  $\log k$ . Table II shows the values of  $n_G$ ,  $\log k_G$ , and  $k_G$  at the corresponding irradiation temperatures. It is shown that  $k_G$  increases with the increase in temperature and the grafting process follows first-order kinetics and is independent of test temperature.

The increase in  $R_G$  and  $k_G$  with the increase in irradiation temperature necessitates the study of this dependence kinetically. Consequently, the activation energy and the pre-exponential rate constant are calculated.

### Activation energy of grafting

As seen from Table II,  $k_G$  increases with the increase in temperature. Applying Arrhenius equation

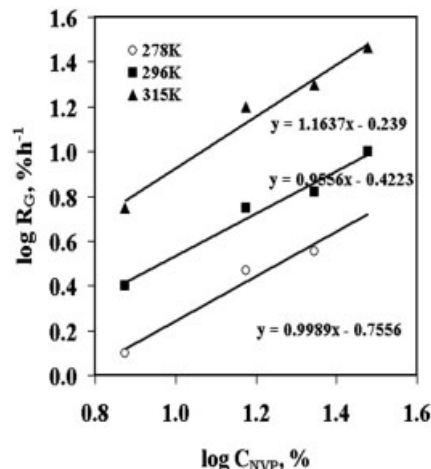
$$k = A e^{-Q/RT} \quad (4)$$

Taking the natural logarithm of both sides, then

$$\ln k_G = \ln A_G - Q_G/RT \quad (5)$$

**TABLE I**  
Dependence of Rate of Grafting on NVP Concentration and Irradiation Temperature

NVP concentration (wt %)	( $R_G$ ) <sub>278 K</sub> (% h <sup>-1</sup> )	( $R_G$ ) <sub>296 K</sub> (% h <sup>-1</sup> )	( $R_G$ ) <sub>315 K</sub> (% h <sup>-1</sup> )
7.5	1.60	1.72	5.64
15.0	2.80	4.0	16.8
22.5	3.64	6.6	19.98
30.0	—	10.00	29.20



**Figure 6** Logarithmic plots of grafting rate versus NVP concentration at different irradiation temperatures.

where  $k_G$ ,  $A_G$ ,  $Q_G$ ,  $R$ , and  $T$  are the rate constant, the pre-exponential rate constant, the overall activation energy of the grafting process, the universal gas constant, and the absolute value of the irradiation temperature, respectively. The plot of the natural logarithm of  $k_G$  ( $\ln k_G$ ) versus  $1/T$  gives a straight line the slope of which is  $Q/R$  and the intercept is  $\ln A$ . Figure 7 shows the linear relationship between  $\ln k_G$  and  $1000/T$  from which an overall activation energy of 23.3 kJ mol<sup>-1</sup> is calculated. The pre-exponential rate constant  $A$  is calculated from  $\ln A$  of 8.441. The calculated value of  $A$  is 4633% h<sup>-1</sup> (0.77 min<sup>-1</sup>). Consequently, eq. (4) becomes

$$k_G (\text{min}^{-1}) = 0.77 e^{-23,300 (\text{J/mol})/RT} \quad (6)$$

The overall activation energy for grafting NVP onto PET fabric falls within the acceptable range for the grafting process. The highest value for  $Q_G$  is 8.0 kcal mol<sup>-1</sup> (33.44 kJ mol<sup>-1</sup>) as reported by Chapiro.<sup>17</sup> Kaji et al.<sup>11</sup> and Shimano et al.<sup>18</sup> carried out radiation-induced graft copolymerization of PET using MAA and AA in the presence of ethylene dichloride. The reported activation energy for AA was 8.0 kcal mol<sup>-1</sup> in the range of 18°C–40°C and 8.77 kcal mol<sup>-1</sup> for MAA in the range of 15°C–20°C. Rao and Rao<sup>19</sup> reported a value of 10.7 kcal mol<sup>-1</sup> for  $Q$  of grafting by the catalytic method. A value 22.53 kJ mol<sup>-1</sup> was calculated in our previous investigation for grafting AA onto PET.<sup>16</sup> The calculated value of this work 23.3 kJ mol<sup>-1</sup> is very close to that of grafting AA onto PET fabric. The difference in the reported  $Q$  values can be attributed to differences in the form and treatment of PET, optimum grafting conditions, and type of monomers used.

### Homopolymerization of NVP

The radiation homopolymerization of NVP in its solution takes place in parallel to the grafting process. The

TABLE II  
Values of  $n$ ,  $\log k_G$ , and  $k_G$  at Different Irradiation Temperatures

Temperature (K)	Order	$\log k_G$ at 1% $C_{NVP}$	$k_G$ (% $h^{-1}$ ) at 1% $C_{NVP}$	$*k_G$ ( $10^{-5} \text{ min}^{-1}$ ) at 1% $C_{NVP}$
278	0.9989	-0.7556	0.1755	2.93
296	0.9556	-0.4223	0.3782	6.30
315	1.1637	-0.2390	0.5768	9.61

magnitude of the homopolymerization of NVP is followed by measuring the coefficient of viscosity  $\eta$  of irradiated and unirradiated solutions. The homopolymer concentration ( $C_H$ ) is considered to be proportional to the square root of the specific viscosity ( $\sqrt{\eta_{sp}}$ ) rather than  $\eta$  as shown from rearranging the following equation<sup>20</sup>:

$$\eta_{sp}/C_H = mC_H + [\eta_{sp}/C_H] \quad (7)$$

where  $\eta_{sp}/C_H$  is the reduced viscosity,  $C_H$  is the concentration of the HP,  $[\eta_{sp}/C_H]_{C \rightarrow 0}$  is the limiting viscosity number, or intrinsic viscosity at infinite dilution and  $m$  is the slope of the linear relationship. Since  $C_H$  is unknown and the initial concentration of the HP is expected to be directly proportional to the initial irradiation time  $t$ , then eq. (7), after rearrangement, becomes

$$\eta_{sp} = m(C_H)^2 + [\eta_{sp}] \quad (8)$$

This equation was applied in the calculation of the molecular weight of polymers soluble in their solvent by adding different polymer concentrations and measuring the corresponding  $\eta_{sp}$ . The intercept of eq. (8) is  $[\eta_{sp}]$ . In our case, the initial  $C_H$  at zero irradiation time is zero. Consequently,  $[\eta_{sp}]$  was considered zero and eq. (8) becomes

$$\eta_{sp} = m(C_H)^2$$

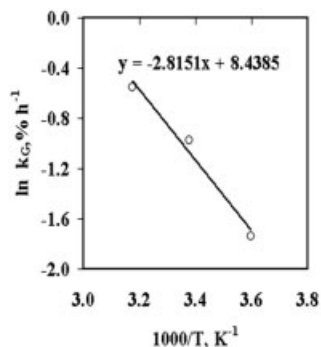


Figure 7 Arrhenius plot of the natural logarithm of the grafting rate constant versus the inverse of the absolute temperature.

$$\sqrt{\eta_{sp}} = a C_H$$

where  $a$  is the proportionality constant of the  $\sqrt{\eta_{sp}}-C_H$  relationship. The  $\sqrt{\eta_{sp}}$  was considered to represent the HP concentration adequately.

The dependence of  $\sqrt{\eta_{sp}}$  on irradiation time ( $t$ ) at different NVP concentrations is shown in Figures 8–10. The  $\sqrt{\eta_{sp}}$  increases with the increase in  $t$  reaching a maximum, followed by a steady and slow decrease in rate. The initial increase and decrease in rates is dependent on NVP concentrations and irradiation temperatures. The increase in  $\sqrt{\eta_{sp}}$  with increase in  $t$  represents the increase in the HP concentration with increase in irradiation time. The dependence of  $\sqrt{\eta_{sp}}$  on  $t$  at different NVP concentrations and different temperatures is studied in the following sections and the kinetic parameters were determined.

### Order of the homopolymerization process

The initial rate of the homopolymerization process  $R_H$  ( $\sqrt{\eta_{sp}}/t$ ) at the different irradiation temperatures  $T$  for the 7.5, 15, and 30% of weight of fabric (owf) NVP concentrations (Figs. 8–10) are shown in Table III. The order of the homopolymerization process  $n_H$  is calculated by plotting  $\log R_H$  versus  $\log C_{NVP}$  at the corre-

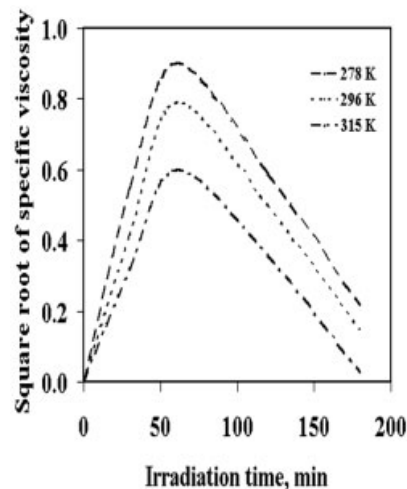
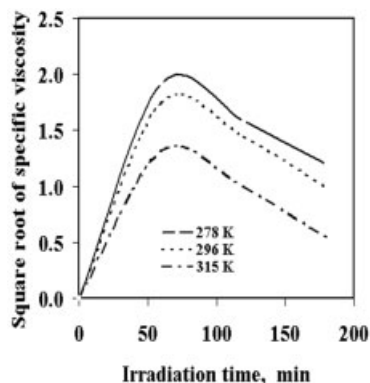


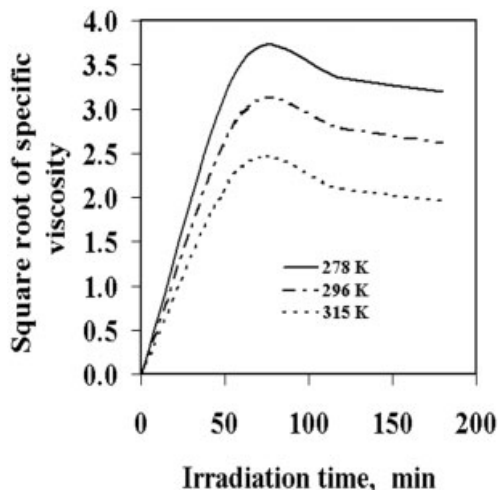
Figure 8 Dependence of the square root of specific viscosity on irradiation time for 7.5% NVP solution.



**Figure 9** Dependence of the square root of specific viscosity on irradiation time for 15% NVP solution.

sponding test temperature  $T$  according to eq. (3). Figure 11 shows that  $\log R_H$  increases linearly with the increase in  $\log C_{NVP}$  at the different test temperatures. The slope of the linear relationship is  $n_H$  and the intercept is the logarithm of the rate constant  $k_H$ . The slope of the linear relationship ( $n_H$ ) is almost constant and is independent of irradiation temperature and indicates first-order kinetics. The intercepts, the values of  $\log k_H$  displayed on the computer chart, are  $-0.6562$ ,  $-0.7042$ , and  $-0.7941$  for the temperatures 278, 296, and 315 K, respectively. The corresponding values of  $k_H$  are 0.2206, 0.1976, and 0.1606  $\text{min}^{-1}$ .

It is obvious that  $k_H$  decreases with the increase in  $T$ , showing negative temperature dependence. This phenomenon has been reported by Lokhande et al.<sup>3</sup> as well as in our previous work during grafting NVP onto nylon-6 fabric.<sup>15</sup> This behavior may be attributed to existence of rates other than that of grafting that increase considerably with the increase in  $T$  and consequently the rate of homopolymerization has to de-



**Figure 10** Dependence of the square root of specific viscosity on irradiation time for 30% NVP solution.

**TABLE III**  
Values of the Homopolymerization rate ( $R_H$ ) versus the  $\sqrt{m} \times a^2$  at Different Test Temperatures

$C_{NVP}$	T (K)	$R_H$ ( $\text{min}^{-1}$ )	$k_H$ ( $\text{min}^{-1}$ ) at 1% $C_{NVP}$
7.5%	278	0.018	0.221
	296	0.014	0.198
	315	0.010	0.161
15%	278	0.036	
	296	0.030	
	315	0.030	
30%	278	0.070	
	296	0.0594	
	315	0.046	

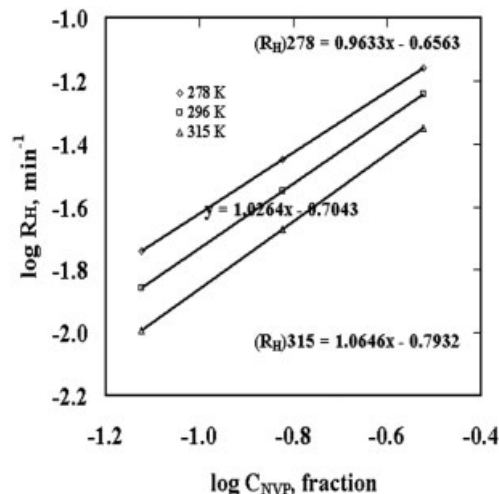
crease with increase in  $T$ . Therefore, the rate of decrease in  $k_H$  with the increase in  $T$  is used to calculate the activation energy of the homopolymerization of NVP.

#### Activation energy of homopolymerization

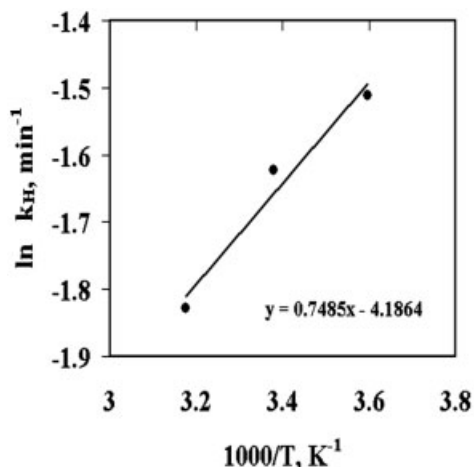
The dependence of  $k_H$  on  $T$  is plotted as shown in Figure 12. The linear relationship gives a value of 0.7856 for  $Q_H/R$ . The corresponding value of  $Q_H$  is 6.2  $\text{kJ mol}^{-1}$ . The value of the natural logarithm of the pre-exponential rate constant ( $\ln A$ ) is  $-4.1864$  and the corresponding  $A$  is 0.0152  $\text{min}^{-1}$ . The dependence of  $k_H$  on  $T$  is as follows:

$$k_H (\text{min}^{-1}) = 0.0152 e^{6200 (\text{J/mol})/RT} \quad (9)$$

The calculated value of  $Q_H$  is less than that reported by Bevington and Eaves<sup>21</sup> ( $2 \text{ kcal mol}^{-1} = 8.36 \text{ J mol}^{-1}$ ) for the polymerization of NVP in aqueous



**Figure 11** Logarithmic plots of homopolymerization rate versus NVP concentration at different irradiation temperatures.



**Figure 12** Arrhenius plot of the natural logarithm of the homopolymerization rate constant versus the inverse of the absolute temperature.

solutions. This could be explained on differences in the experimental conditions as well as on differences in solvents that affect considerably the results.

### The degradation process

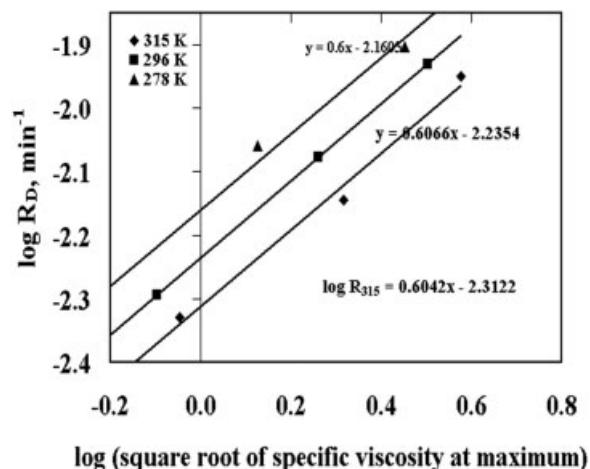
The results presented in Figures 8–10 for the dependence of  $\sqrt{\eta_{sp}}$  on irradiation time  $t$  show that as  $t$  increased deviation from linearity is noticed. The curves reach maximum values  $(\sqrt{\eta_{sp}})_{max}$ , followed by a continuous decrease in the concentration of HP ( $\sqrt{\eta_{sp}}$ ) in the solution. The deviation of  $\sqrt{\eta_{sp}}$  with the increase in  $t$  from linearity could be attributed to the decrease in the  $R_H$  with the decrease in NVP concentration because of its continuous depletion from its solution due to grafting and homopolymerization as well as the radiation degradation of the HP itself. The decrease in  $\sqrt{\eta_{sp}}$  at maximum with the increase in  $t$  is mainly due to radiation-induced degradation of the HP. Consequently, the decrease in  $\sqrt{\eta_{sp}}$  with the increase in  $t$  above  $t_{max}$  is followed kinetically and the different parameters were evaluated.

### The order and the activation energy of the degradation process

The initial slope of the decrease of  $\sqrt{\eta_{sp}}$  with the increase in  $t$  at  $t > t_{max}$  (about 75 min) is considered as

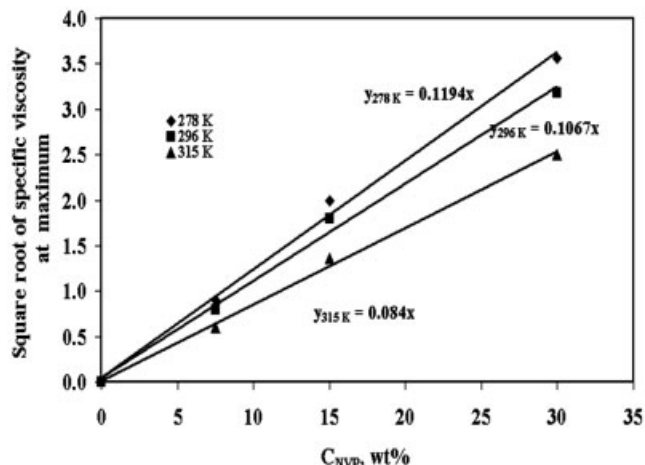
**TABLE IV**  
Values of the Degradation Rate  $R_D$  at Different Test Temperatures

$T$ (K)	$(R_D)_{7.5\%}$ ( $\text{min}^{-1}$ )	$(R_D)_{15\%}$ ( $\text{min}^{-1}$ )	$(R_D)_{30\%}$ ( $\text{min}^{-1}$ )	$k_D$ ( $10^{-3} \text{ min}^{-1}$ ) at 1% $C_{NVP}$
278	0.0057	0.0091	0.0125	6.910
296	0.00508	0.0088	0.0110	5.8134
315	0.0041	0.0079	0.0098	4.783

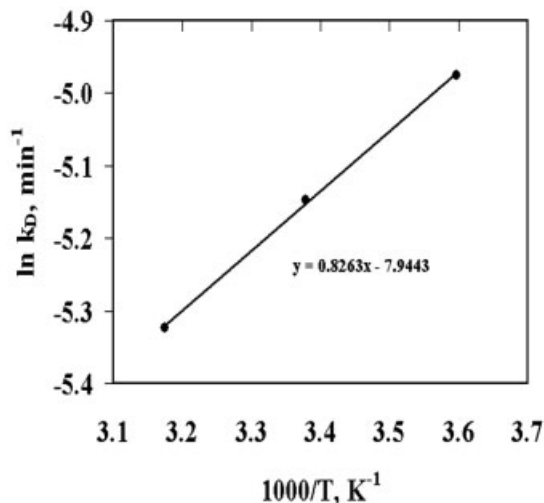


**Figure 13** Logarithmic plots of degradation rate versus the square root of specific viscosity at maximum at different irradiation temperatures.

a measure of the apparent degradation rate  $R_D$  (Table IV). It should be noticed that the values of  $(\sqrt{\eta_{sp}}/t)_H$  are positive, indicating a rate of increase in the HP concentration, while those for  $(\sqrt{\eta_{sp}}/t)_D$  are negative i.e. a rate of decrease. Logarithmic plots of  $R_D$  versus  $\sqrt{\eta_{sp}}$  at the maximum  $(\sqrt{\eta_{sp}})_{max}$  at different irradiation temperatures are shown in Figure 13. The value of  $(\sqrt{\eta_{sp}})_{max}$ , which represents the maximum concentration of the HP  $(C_H)_{max}$ , is expected to be directly proportional to  $C_{NVP}$ . To show this dependence a plot of  $(\sqrt{\eta_{sp}})_{max}$  versus  $C_{NVP}$  is made at different irradiation temperatures. Figure 14 shows that  $(\sqrt{\eta_{sp}})_{max}$  increases linearly with the increase in  $C_{NVP}$  at rates of 0.1194, 0.1067, and 0.084 per 1% of NVP concentration for  $T$  of 278, 296, and 315 K, respectively. Consequently, a plot of  $\log R_D$  versus  $\log (\sqrt{\eta_{sp}})_{max}$  rather than  $C_{NVP}$  is made and eq. (2) becomes



**Figure 14** Relationship between the specific viscosity at maximum and NVP concentration at different irradiation temperatures.



**Figure 15** Arrhenius plot of the natural logarithm of the degradation rate constant versus the inverse of the absolute temperature.

$$-dC/dt \text{ or } -d(\sqrt{\eta_{sp}})_{\max}/dt = k_D[(\sqrt{\eta_{sp}})_{\max}]^n \quad (10)$$

where  $C$  is the conversion and is the difference between  $(\sqrt{\eta_{sp}})_{\max}$  and  $(\sqrt{\eta_{sp}})$ , which is proportional to the concentration of the degraded HP at  $t > t_{\max}$ .

Figure 13 shows that the logarithmic relationship between  $R_D$  and  $(\sqrt{\eta_{sp}})_{\max}$  at different irradiation temperatures is linear with a slope indicating a 0.6-order kinetics, which is temperature independent. The values of the intercepts give  $\log k_D$  at the different test temperatures. The corresponding values of  $k_D$  at 278, 296, and 315 K are  $6.91 \times 10^{-3}$ ,  $5.8144 \times 10^{-3}$ , and  $4.873 \times 10^{-3} \text{ min}^{-1}$ , respectively. It is obvious that  $k_D$  decreases slightly with the increase in  $T$ , although the values of  $R_D$  increases with the increase in  $C_{\text{NVP}}$  (Table IV). The plot of the natural logarithm of  $k_D$  versus  $1000/T$  is shown in Figure 15. The linear relationship gives average activation energy of  $6.84 \text{ kJ mol}^{-1}$  and a pre-exponential rate constant of  $3.55 \times 10^{-4} \text{ min}^{-1}$  for the degradation of the HP. The Arrhenius rate equation becomes

$$k_D (\text{min}^{-1}) = 3.55 \times 10^{-4} e^{6840(\text{J/mol})/RT} \quad (11)$$

#### Kinetic parameters of the fourth process

It is obvious from the results that there are three significant processes involved during grafting NVP on to PET fabric. All these processes are concentration and temperature dependent in different ways such that

$$R_G + R_H + R_D = BC_{\text{NVP}} \quad (12)$$

where  $R_G$ ,  $R_H$ ,  $R_D$ ,  $C_{\text{NVP}}$ , and  $B$  are the rate of grafting, rate of homopolymerization, rate of degradation, NVP concentration, and proportionality constant, respectively. Differentiating eq. (12) with respect to  $C_{\text{NVP}}$  at a constant  $T$

$$dR_G/dC_{\text{NVP}} + dR_H/dC_{\text{NVP}} + dR_D/dC_{\text{NVP}} = B \quad (13)$$

Since  $dR/dC$  is the rate constant  $k$ , eq. (13) becomes

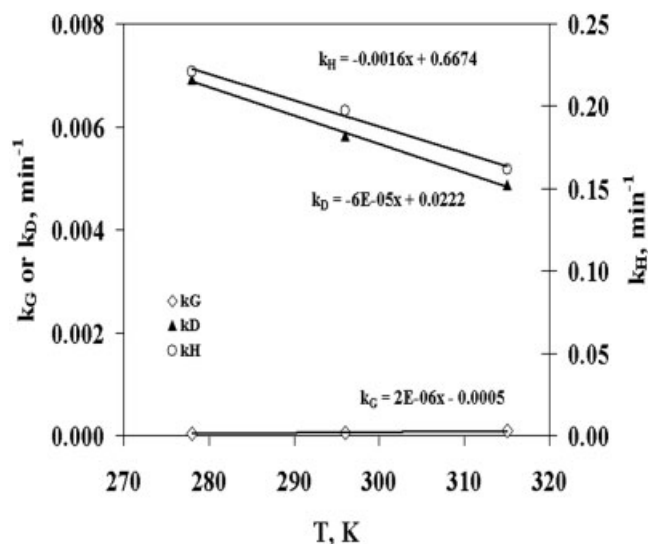
$$k_G + k_H + k_D = B \quad (14)$$

Differentiating eq. (14) with respect to  $T$

$$dk_G/dT + dk_H/dT + dk_D/dT = 0 \quad (15)$$

If this assumption is correct, then the algebraic sum of the  $dk/dT$  of the three processes should be zero.

The  $dk/dT$  is the slope of the dependence of  $k$  on  $T$ . Figure 16 shows linear dependence of  $k$  on  $T$  for the three processes within the 278–315 K temperature range. The slopes of the relationship ( $dk/dT$ ) is dependent on the process involved. The homopolymerization and degradation processes show a decrease in  $k$  with  $T$  while that of grafting showed an increase in  $k$  with  $T$ . The slopes for grafting, homopolymerization, and degradation processes, as displayed on the chart, are  $2 \times 10^{-6}$ ,  $-1.6 \times 10^{-3}$ , and  $-6 \times 10^{-5} \text{ min}^{-1} \text{ K}^{-1}$ , respectively. The algebraic sum of these values is negative and is not equal to zero and has a value of  $-1.60 \times 10^{-3} \text{ min}^{-1} \text{ K}^{-1}$ . This necessitates the existence of unidentified process with  $dk_u/dT$  of  $1.60 \times 10^{-3} \text{ min}^{-1} \text{ K}^{-1}$  such that the algebraic sum is zero. Consequently, eqs. (12)–(15) becomes



**Figure 16** Dependence of the rate constant on the absolute temperature for the grafting, homopolymerization, and degradation process.



TABLE V  
Kinetic Parameters of the Unidentified Process at  
Different NVP Concentrations and Test Temperatures

$T$ (K)	$k_U$ ( $\text{min}^{-1}$ ) at 1% $C_{\text{NVP}}$	$(R_U)_{7.5\%}$	$(R_U)_{15\%}$	$(R_U)_{30\%}$
278	0.4448	0.0334	0.0668	0.1354
296	0.4736	0.0355	0.071	0.142
315	0.504	0.038	0.076	0.152

$$R_G + R_H + R_D + R_U = BC_{\text{NVP}} \quad (16)$$

$$k_G + k_H + k_D + k_U = B \quad (17)$$

$$dk_G/dT + dk_H/dT + dk_D/dT + dk_U/dT = 0 \quad (18)$$

The kinetic parameters of the unidentified process is calculated from the value of  $dk_U/dT$ . The predicted values of  $k_U$  at different irradiation temperatures are calculated by multiplying  $1.6 \times 10^{-3} \text{ min}^{-1} \text{ K}^{-1}$  by the corresponding  $T$ . Table V shows the kinetic parameters of the unidentified process at different NVP concentrations and test temperatures. Figure 17 shows Arrhenius plot of  $\ln k_U$  versus  $1000/T$ . An apparent activation energy  $Q_U$  and pre-exponential rate constant  $A_U$  of  $2.53 \text{ kJ mol}^{-1}$  and  $1.33 \text{ min}^{-1}$ , respectively, are calculated from the slope of the straight line and the intercept, respectively. Moreover, the logarithmic plots of  $R_U$  versus  $C_{\text{NVP}}$  (Fig. 18) show that the unidentified process follows a first-order kinetics with intercepts that give values of  $k_U$  similar to those given in Table V.

The  $B$  of eq. (17) is evaluated by substituting the proper values of  $k_G$ ,  $k_H$ ,  $k_D$ , and  $k_U$  at the corresponding temperatures. It was found that  $B$  is independent of  $T$  and has a value of  $0.674 \text{ min}^{-1}$ .

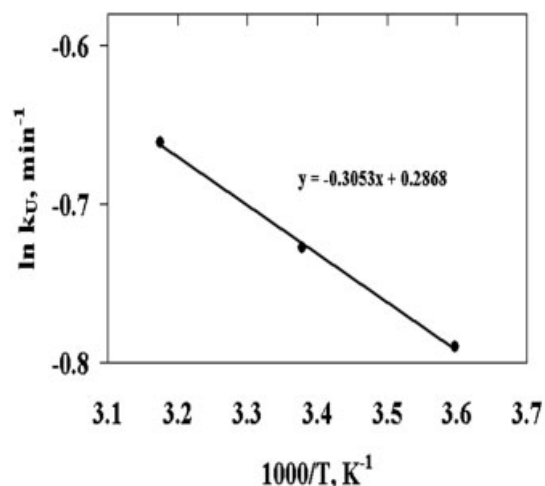


Figure 17 Arrhenius plot of the natural logarithm of the unidentified rate constant versus the inverse of the absolute temperature.

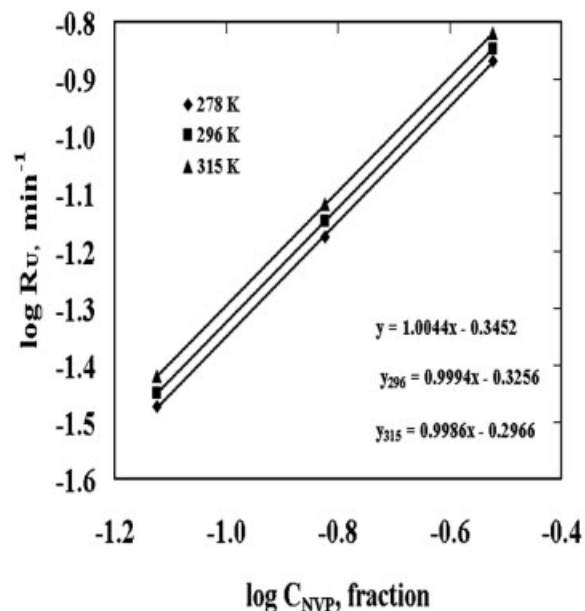


Figure 18 Logarithmic plots of the rate of the unidentified process versus NVP concentration at different irradiation temperatures.

To verify the results calculated according to eq. (18) one has to differentiate Arrhenius equation ( $k = A e^{-Q/RT}$ ) with respect to  $T$

$$dk/dT = A e^{-Q/RT}(Q/RT^2) \quad (19)$$

$$dk/dT = k(Q/RT^2) \quad (20)$$

Rearranging eq. (20) such that

$$Q = (dk/dT)/k \times RT^2 \quad (21)$$

Substituting the proper values of  $dk/dT$ ,  $k$ ,  $R$  ( $8.276 \text{ kJ mole}^{-1} \text{ K}^{-1}$ ), and  $T$  in eq. (21), the average value of the activation energy  $Q$  for the different processes calculated. Tables VI–IX show the calculations for the four different processes. Table X shows the experimentally obtained value of  $Q$  versus the calculated one for the different processes using eq. (21). The  $Q$  value is almost the same and emphasizes the existence of the unidentified process as well as the correct assumptions applied to verify the results.

It is obvious from the results that there are four processes involved during the radiation grafting of NVP onto PET fabric. These processes follow first-order kinetics, except that of the degradation that followed 0.6-order kinetics and all are monomer concentration and temperature dependent. This dependence, however, differs from one process to the other as shown by the values of  $dk/dT$ . Two processes, the grafting and the unidentified one, show an increase in  $k$  with the increase in  $T$ , while the other two processes,

TABLE VI  
Calculation of the Apparent Activation Energy of the Grafting Process

T (K)	$T^2$ ( $10^4 \text{ K}^2$ )	$k_G$ ( $10^{-5} \text{ min}^{-1}$ )	$(T^2/k)$ ( $10^9 \text{ K}^2 \text{ min}$ )	$(dk/dT)$ ( $10^{-6} \text{ min}^{-1} \text{ K}^{-1}$ )	$(dk/dT)R$ ( $10^{-5} \text{ J mol}^{-1} \text{ K}^{-2} \text{ min}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )
278	7.73	2.94	2.63	1.81	1.498	39.00
296	8.72	6.30	1.385	1.81	1.498	20.61
315	9.92	9.60	1.033	1.81	1.498	15.40

Average  $Q_G$  ( $\text{kJ mol}^{-1}$ ) = 25.

the homopolymerization and the degradation, show negative values for the slope  $dk/dT$ . An attempt to explain the different mechanisms of the four processes is as follows:

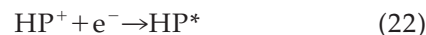
The initial rate of grafting increases with the increase in NVP concentration and irradiation temperature. In case of low monomer concentration and low irradiation temperature the grafting process is slow enough such that the presence of traces of impurities, e.g., oxygen, will delay the grafting process via peroxide radical formation and consequently an IP appears (Fig. 3 at 278 K).<sup>15,21</sup> At high monomer concentration and high temperature, the rate of production of free radicals increases and the amount of monomer available for grafting is high enough to start grafting without the appearance of IP (Fig. 5 at 315 K). Consequently, the rate of grafting increases with the increase in NVP concentration and irradiation temperature showing a positive  $dk_G/dT$  value.

The homopolymerization and the degradation processes compete with each other in opposite directions. The initial rate  $R_H$  increases with the increase in  $C_{\text{NVP}}$  (Fig. 11), while  $R_D$  increases with the increase in  $(C_H)_{\text{max}}$  which is proportional to  $C_{\text{NVP}}$  and  $(\sqrt{\eta_{\text{sp}}})_{\text{max}}$  (Fig. 13 and eq. (10)).

The effect of  $T$  on  $k_H$  and  $k_D$  is contradicting. The increase in  $T$  is expected to increase  $k_H$  in a way similar to that of grafting. However, both values decrease with increase in  $T$ . The decrease in  $k_H$  and  $k_D$  with increase in  $T$  is shown in Figure 16 and Tables III and IV. The slope,  $dk/dT$ , for the homopolymerization and degradation processes are  $-1.60 \times 10^{-3}$  and  $-6 \times 10^{-5} \text{ min}^{-1} \text{ K}^{-1}$ , respectively. Since both processes took place simultaneously from the initial stage of the homopolymerization and the rate of decrease of  $k_H$  with increase in  $T$  is faster than that of degradation,

then the net effect is the slow decrease in the value of the apparent  $R_H$  with the increase in  $T$  as shown in Figures 7–9. Moreover, the unidentified process, showing a positive and a high increase in  $k_U$  with increase in  $T$  ( $1.6 \times 10^{-3} \text{ min}^{-1}$ ), indicates a high consumption in the monomer concentration such that the amount of monomer available for the other processes decreases considerably and hence resulting in further decrease in their rates. The values of  $A$  for the different processes indicate that the grafting and the unidentified process are the main processes involved during the radiation grafting of NVP onto PET. The contribution of  $k$  of the grafting and the degradation to  $B$  is irrelevant.

The  $Q$  of the grafting, the homopolymerization, and the degradation processes is within the acceptable published values. However, the  $Q$  of the unidentified one ( $2.49 \text{ kJ mol}^{-1}$ ) is extremely low. To account for the  $Q$  value for the degradation of poly(NVP) one has to consider the mechanism of radiation degradation. When a thermal electron arrives in the vicinity of a positive ion, recombination occurs immediately and a highly excited molecule is produced as shown by the reaction:



where  $\text{HP}^+$  is an ionized HP molecule and  $\text{HP}^*$  is the excited state reached in this reaction. The  $\text{HP}^*$  has gained as much as 10–15 eV, the ionization potential, that almost certainly causes the molecule to undergo further dissociation. This will lead to a permanent chemical change according to the reaction



TABLE VII  
Calculation of the Apparent Activation Energy of the Homopolymerization Process

T (K)	$T^2$ ( $10^4 \text{ K}^2$ )	$k_H$ ( $\text{min}^{-1}$ )	$T^2/k$ ( $10^5 \text{ K}^2 \text{ min}$ )	$dk/dT$ ( $10^{-3} \text{ min}^{-1} \text{ K}^{-1}$ )	$(dk/dT)R$ ( $10^{-2} \text{ J mol}^{-1} \text{ K}^{-2} \text{ min}^{-1}$ )	$Q$ ( $\text{kJ/mol}$ )
278	7.73	0.2206	3.50	1.6	1.324	4.60
296	8.72	0.1976	4.48	1.6	1.324	5.92
315	9.92	0.1606	6.176	1.6	1.324	8.18

Average  $Q_H$  ( $\text{kJ/mol}$ ) = 6.23.

TABLE VIII  
Calculation of the Apparent Activation Energy of the Degradation Process

$T$ (K)	$T^2$ ( $10^4$ K $^2$ )	$k_D$ ( $10^{-3}$ min $^{-1}$ )	$T^2/k$ ( $10^7$ K $^2$ min)	$dk/dT$ ( $10^{-5}$ min $^{-1}$ K $^{-1}$ )	$(dk/dT)R$ ( $10^{-5}$ J mol $^{-1}$ K $^{-2}$ min $^{-1}$ )	$Q$ (kJ mol $^{-1}$ )
278	7.73	6.91	1.1187	6	4.966	5.55
296	8.72	5.814	1.500	6	4.966	7.44
315	9.92	5.651	2.035	6	4.966	10.10

Average  $Q_D$  (kJ/mol) = 7.7.

where  $C_1$  and  $D_1$  are saturated or unsaturated molecules.

Gamma rays ionize the HP molecules during radiation grafting of the samples with the result of the formation of ion–electron pairs. The recombination of the pairs according to reaction (22) will lead to reaction (23). Reaction (23), enhanced with the external thermal energy of 7.24 kJ mol $^{-1}$ , will lead to the dissociation of the HP molecule and a decrease in the viscosity of the solution as shown in Figures 7–9. The first-order kinetics, the very low overall activation energy of the unidentified process (2.52 kJ mol $^{-1}$ ), and its high value of  $dk/dT$  ( $1.6 \times 10^{-3}$  min $^{-1}$  K $^{-1}$ ) may indicate the contribution of ionic processes in the polymerization process. Very low temperature coefficients and activation energy, observed in radiation polymerization of acrylamide in aqueous solution, was reported by Collinson et al.<sup>22</sup>  $1.532 \pm 1.5$  kcal mol $^{-1}$ . Restaino et al.<sup>23</sup> reported extremely low  $Q$  value  $0.4 \pm 0.4$  kcal mol $^{-1}$ , during their studies on radiation polymerization of barium acrylate in the solid state. Activation energy as low as 1.5 kcal mol $^{-1}$  was also reported for the photopolymerization of AA in aqueous solution.<sup>24</sup> These results do not agree with the normal free radical polymerization kinetics, since they show an anomalous behavior from the point of view of conventional radical theory. Consequently, one may correlate the unidentified process to those in which the radiation initiated process proceeds by a long-chain reaction via ionic chain carriers. However, the irradiation temperature of this work (278–315 K) is high enough to assist ionic recombination and hence prevents ionic polymerization. This suggests that the unidentified process may be attributed to some other processes.

Two possible processes can play an important role during the grafting of NVP onto PET, particularly the chain transfer and the diffusion processes. Chain transfer of the growing polymer chain to the backbone polymer yields a ketene structure responsible for crosslinking.<sup>25–28</sup> This process requires activation energy close to that of grafting. The low value of  $Q_U$  and the extremely high value of the rate constant  $k_U$  of the unidentified process when compared with that of grafting, do not lead to accept the idea that chain transfer process is responsible for the unidentified process. Consequently, one has to consider seriously the role of the diffusion of NVP to be the rate controlling process for reaching the active sites in the copolymer and HP chains. Recall that the values of the logarithm of the rate constants of the different processes are calculated from the intercepts of the log  $R$ –log  $C_{NVP}$  relationship at log  $C_{NVP}$  of zero. This shows that all values of  $k$  are calculated at  $C_{NVP}$  of 1% owf. At this low value of NVP concentration, the rate of diffusion of the monomer molecules in the solvent should increase with the increase in  $C_{NVP}$  and irradiation temperature with a low value for the activation energy and a high frequency factor  $A$ . It is expected that the value of  $Q$  of the diffusion of NVP into the solvent till reaching reactive sites in poly(NVP) chains should be lower than that of the grafting and homopolymerization processes while that for  $A$  should be the highest. Table XI supports this idea and shows that  $Q_U$  is 0.1 and 0.4 times that of grafting and homopolymerization, respectively, while  $A_U$  is 1.73, 87.63, and 3752.0 times that of grafting, homopolymerization, and degradation processes, respectively. To assure that this assumption is correct the experiments for the different processes have to be repeated using solvent

TABLE IX  
Calculation of the Apparent Activation Energy of the Unidentified Process

$T$ (K)	$T^2$ ( $10^4$ K $^2$ )	$k_U$ (min $^{-1}$ )	$T^2/k$ ( $10^5$ K $^2$ min)	$dk/dT$ ( $10^{-3}$ min $^{-1}$ K $^{-1}$ )	$(dk/dT)R$ ( $10^{-2}$ J mol $^{-1}$ K $^{-2}$ min $^{-1}$ )	$Q$ (kJ mol $^{-1}$ )
278	7.73	0.445	1.76	1.6	1.324	2.33
296	8.72	0.4733	1.84	1.6	1.324	2.44
315	9.92	0.5037	1.97	1.6	1.324	2.61

Average  $Q_U$ , kJ/mole = 2.46

**TABLE X**  
**Experimental versus Calculated Activation Energy  $Q$  of the Four Processes**

Process	$Q_{\text{experimental}}$ (kJ mol <sup>-1</sup> )	$Q_{\text{calculated}}$ (kJ mol <sup>-1</sup> )	$Q_{\text{average}}$ (kJ mol <sup>-1</sup> )
Grafting	23.3	25.00	24.15
Homopolymerization	6.25	6.23	6.24
Degradation	6.84	7.7	7.27
Unidentified	2.53	2.46	2.49

solutions having different viscosity coefficients. Accordingly, it is expected that the higher the coefficient of viscosity of the solvent the higher the value of the activation energy of the diffusion process and the lower the value of its  $A_d$ .

#### Molecules and energies participating in the four processes

As stated before, the values of the rate constant  $k$  for the four processes are those of  $\log R$  versus  $\log C_{\text{NVP}}$  relationship at  $\log C_{\text{NVP}}$  of zero, i.e., at  $\log C_{\text{NVP}}$  of 1% owf. Similarly, the values of the pre-exponential rate constant  $A$  are those calculated from  $\ln k$  versus  $1/T$  relationship at  $1/T$  of zero, indicating that  $A$  is independent of monomer concentration or irradiation temperature.

At the 1% owf  $C_{\text{NVP}}$  and a fabric-to-liquor ratio of 1 : 20 wt/wt, the values of  $A$  for grafting, homopolymerization, degradation, and diffusion are  $1.2833 \times 10^{-2} \text{ s}^{-1}$ ,  $2.0833 \times 10^{-4} \text{ s}^{-1}$ ,  $5.917 \times 10^{-6} \text{ s}^{-1}$ , and  $2.22 \times 10^{-2} \text{ s}^{-1}$ , respectively (Table XI). The corresponding numbers of NVP molecules per second are  $3.3835 \times 10^{18}$ ,  $5.493 \times 10^{14}$ ,  $1.56 \times 10^{13}$ , and  $5.853 \times 10^{16}$ , respectively. These results indicate that about 98% of the monomer molecules ( $3.4431 \times 10^{18} \text{ s}^{-1}$ ) were grafted on the 1 g PET fabric, 0.02% of the monomer molecules were homopolymerized, 4.53%  $\times 10^{-4}$ % were degraded and 1.7% of NVP molecules were still in the solution. Moreover, about 2.83% of the HP molecules were degraded.

The number of NVP molecules participated in the different processes follows the order grafting > diffusion > homopolymerization > degradation.

A total of 1 g of the monomer solution and the fabric at 1% owf NVP and 1 : 20 LR requires that the irradi-

ated samples contain 0.04762 g fabric,  $4.762 \times 10^{-4} \text{ g}$  NVP, and 0.95274 g solvent. The reason for making the total weight of both the fabric and monomer solution 1 g will be seen from energy calculation. The weights of methanol and water solvent in the solution, according to their ratio of 1 : 3, are 0.23817 and 0.7147 g, respectively. The number of NVP, methanol, and water molecules in the solution is  $2.656 \times 10^{18}$ ,  $4.48 \times 10^{21}$ , and  $2.39 \times 10^{22}$ , respectively.

The rate of energy absorption per 1 g of solution and fabric is calculated from the applied dose rate  $1.31 \text{ Gy s}^{-1}$ . Since the energy absorbed from 1 Gy dose is  $6.25 \times 10^{15} \text{ eV}$ , the rate of energy absorption in 1 g at  $1.31 \text{ Gy s}^{-1}$  is  $8.1875 \times 10^{15} \text{ eV s}^{-1}$ . This energy is distributed between the PET and the monomer solution. Thus, the PET will absorb  $0.3869 \times 10^{15} \text{ eV s}^{-1}$  and the monomer solution will absorb  $7.8 \times 10^{15} \text{ eV s}^{-1}$ . The latter energy will be distributed between NVP, methanol, and water according to their molecular ratio in solution. The energy absorbed in NVP molecule, methanol, and water is  $3.87 \times 10^{12}$ ,  $1.95 \times 10^{15}$ , and  $5.85 \times 10^{15} \text{ eV s}^{-1}$ , respectively. The total energy absorbed by NVP molecules ( $3.87 \times 10^{12} \text{ eV s}^{-1}$ ) is shared by the four processes according to their molecular distribution. The energy absorbed by NVP molecules in grafting, homopolymerization, degradation, and diffusion is  $3.8 \times 10^{12}$ ,  $7.5 \times 10^8$ ,  $1.75 \times 10^7$ , and  $6.58 \times 10^{10} \text{ eV s}^{-1}$ , respectively. Dividing these values by corresponding number of NVP molecules per second shared in the four processes yielded a constant value of  $1.124 \times 10^{-6} \text{ eV}$  per NVP molecule. The energy per molecule is independent of the process in which the NVP molecule participated in. The velocity of NVP molecule at  $1.124 \times 10^{-6} \text{ eV}$  per NVP molecule is  $1.42 \text{ m s}^{-1}$ .

The results of the energy distribution indicated that the energy absorbed in PET is about 100 times that absorbed in NVP. Part of this energy will cause free radical production while the other part participates in the degradation of polymer chains.<sup>29</sup> Consequently, the number of free radicals produced in the fabric is expected to be higher than those formed in NVP with the result of higher rates of grafting than those of homopolymerization.

Recall that the activation energy for grafting, homopolymerization, and degradation is that energy required to graft, homopolymerize, and degrade 1 mol

**TABLE XI**  
**Values of  $Q$ ,  $A$  and their relative values with respect to that of the unidentified process**

Process	$Q$ (kJ mol <sup>-1</sup> )	$Q_U/Q$	$A$ (min <sup>-1</sup> )	$A$ (s <sup>-1</sup> )	$A_U/A$
Grafting	24.15	0.103	0.770	$1.283 \times 10^{-2}$	1.73
Homopolymerization	6.24	0.400	0.0152	$2.083 \times 10^{-4}$	87.63
Degradation	6.84	1.627	0.000355	$5.917 \times 10^{-6}$	3752
Unidentified	2.49	1	1.332	$2.22 \times 10^{-2}$	1

of poly(NVP) molecule, homopolymer molecule, and degraded HP molecule. The corresponding  $Q$  per polymolecular chain are  $2.5 \times 10^{-4}$ ,  $0.65 \times 10^{-4}$ , and  $0.696 \times 10^{-4}$  eV, respectively. Dividing the activation energy by the energy absorbed per NVP molecule ( $1.124 \times 10^{-6}$  eV) gives the number of NVP molecules in a poly(NVP) molecule. On the average, 222, 59, and 62 NVP molecules per poly(NVP) molecule are needed to form grafted, homopolymerized, and degraded chains, respectively, from the low concentration of 1% of NVP. The corresponding molecular weights are  $2.4 \times 10^4$ ,  $6.4 \times 10^3$ , and  $6.7 \times 10^3$ , respectively. Since the molecular weight is proportional to monomer concentration one expects higher molecular weights as the NVP concentration is increased.

The results given above show that the HP molecules and the degraded HP molecules have about 60 molecule per chain. This indicates that the decrease in the viscosity of the solution is due to the decrease in NVP chains in the solution and not due to the decrease in the chain length. This is in agreement with the results that show that only 2.8% of the homopolymer molecules were degraded. Moreover, the number of grafted chains are extremely higher than those of homopolymerization since 98.28% of NVP molecules shared in grafting while 0.016% participated in the formation of HP molecules.

## CONCLUSIONS

Four different processes have been found to work simultaneously during radiation grafting of NVP onto PET fabric. These processes are the grafting, the homopolymerization, the degradation, and the diffusion process. The kinetic parameters [ $R$ ,  $k$ ,  $n$ ,  $A$ , and  $Q$ ] for each process were evaluated from the  $\log R$  versus  $\log C_{\text{NVP}}$  and  $\ln k$  versus  $1/T$  relationships. The following observations can be made:

1. The grafting, the homopolymerization, and the diffusion processes followed first-order kinetics while the degradation process showed 0.6-order dependence.
2. The reaction rate and rate constant of the grafting and diffusion showed positive temperature dependence while those for the homopolymerization and the degradation indicated a negative temperature effect.
3. Activation energies of 24.15, 6.24, 6.86, and 2.49  $\text{kJ mol}^{-1}$  were determined for grafting, homopolymerization, degradation, and diffusion processes. The corresponding values for the pre-exponential rate constant are 0.770, 0.0152, 0.000355, and  $1.332 \text{ min}^{-1}$ , respectively.
4. About 98% of NVP molecules shared in grafting while 0.016% participated in the formation of HP molecules. Homopolymer molecules (2.8%) were

degraded during the radiation grafting process. The grafted chains are extremely higher than those of homopolymerization.

5. The sum of the reaction rates is directly proportional to NVP concentration. The proportionality constant, which is the sum of the rate constants, has a value of  $0.674 \text{ min}^{-1}$  and is independent of the irradiation temperature.
6. The rate of energy absorption by grafting, homopolymerization, degradation, and diffusion processes is  $3.8 \times 10^{12}$ ,  $7.5 \times 10^8$ ,  $1.75 \times 10^7$ , and  $6.58 \times 10^{10} \text{ eV s}^{-1}$ , respectively. Most of the energy is absorbed by the water-methanol solvent molecules.
7.  $1.124 \times 10^{-6}$  eV is absorbed per NVP molecule and is independent of the process it participated in. The corresponding velocity of NVP molecules in solution is  $1.42 \text{ m s}^{-1}$ .
8. The activation energy of the different processes and the energy absorbed per NVP molecule indicated that 222, 59, and 62 NVP molecules were added to form a poly(NVP) chain during the grafting, the homopolymerization, and the degradation processes, respectively.
9. The decrease in the viscosity of the solution is due to the decrease in NVP chains and not to the decrease in the chain length.

The authors thank Dr. O. M. Desouki for measuring the viscosity of the solutions.

## References

1. Rao, K. N.; Rao, M. H.; Moorthy, P. N.; Charlesby, A. *J Polym Sci Polym Lett Ed* 1972, 10, 893.
2. Kale, P. D.; Lokhande, H. T.; Rao, K. N.; Rao, M. N. *J Appl Polym Sci* 1975, 19, 19461.
3. Lokhande, H. T.; Mody, N. R.; Rao, K. N.; Rao, M. H. *J Appl Polym Sci* 1979, 23, 2139.
4. Zahran, A. H.; Hosamy, M. B.; El-Gendy, E. *Am Dyestuff Reporter* 1985, 75, 32.
5. El-Gendy, E. H.; Kamal, H.; Hegazy, E. A. In *Proceedings of the Fifth Arab International Conference on Polymer Science and Technology*; The Egyptian Society of Polymer Science and Technology 1999; p 711.
6. El-Gendy, E. H. *Indian J Fibre Text Res* 2000, 25, 59.
7. El-Gendy, E. H. *Indian J Fibre Text Res* 2002, 27, 266.
8. El-Gendy, E. H. *Indian J Fibre Text Res* 2002, 27, 422.
9. El-Gendy, E. H. *J Appl Polym Sci* 2004, 94, 1070.
10. Vlagie, I.; Stannett, V. *J Macromol Sci Chem* 1973, 7, 1677.
11. Kaji, K.; Okada, T.; Sakurada, I. *JAERI* 1973, 5028, 52. *Chem Abstr* 1974, 80, 84518.
12. Shimano, Y.; Kaji, K.; Sakurada, I. *JAERI* 1971, 5027, 50. *Chem Abstr* 1974, 80, 84521.
13. Okada, T.; Kaji, K.; Katsuki, K. *JAERI* 1971, 5027, 50. *Chem Abstr* 1972, 76, 114582.
14. Aggour, Y. *Polym Int* 2001, 50, 347.
15. El-Gendy, E. H.; Eglal, H. K. *Indian J Fibre Text Res* 2004, 29, 129.

16. El-Gendy, E. H.; Marie, M. M.; Ali, N. M. *J Eng Appl Sci* 2005, 52, 163.
17. Chapiro, A. *Radiation Chemistry of Polymeric Systems*; Wiley: New York, 1962.
18. Shimano, Y.; Okada, T.; Sakurada, I. *JAERI* 1973, 1226, 43. *Chem Abstr* 1974, 80, 84521.
19. Rao, K. N.; Rao, M. H. *J Appl Polym Sci* 1979, 23, 2133.
20. Griskey, R. K. *Polymer Process Engineering*; Chapman & Hall: New York, 1995.
21. Bevington, J. C.; Eaves, D. E. *Nature* 1956, 178, 1112.
22. Collinson, E.; Dainton, F. S.; McNaughton, D. *J Chim Phys* 1955, 52, 556.
23. Restaino, A. J.; Mesrobian, R. B.; Morawetz, H.; Ballantine, D. J. *J Am Chem Soc* 1956, 78, 2939.
24. Burnette, G. M. *Mechanisms of Polymer Reactions*; Interscience: New York, 1954.
25. Fischer, H. *Z Naturforsch* 1956, 20, 428.
26. Burnett, G. M.; Evans, P.; Melville, H. W. *Trans Faraday Soc* 1953, 49, 1096.
27. Magat, E. E.; Miller, I. K.; Tanner, D.; Zimmerman, J. *J Polym Sci* 1963, 4, 615.
28. Rao, M. H.; Rao, K. N. *Radiat Phys Chem* 1985, 26, 669.
29. El-Gendy, E. H.; El-Shanshoury, I. A. *J Appl Polym Sci* 2004, 92, 3710.