Radiation graft-copolymerization kinetics of poly(ethylene terephthalate) fibres

F. Sundardi

Pasar Jumat Atomic Energy Research Centre, Polymer Section, PO Box 2 KBL, Jakarta, Indonesia
(Received 26 October 1978)

A theoretical analysis of radiation grafting kinetics has been made in terms of the quantitative inter-relationship between the degree of grafting (G_f), the grafting periods (t) grafting temperature (T) and the monomer content in the polymeric system (M). Poly(ethylene terephthalate) fibres and a number of hydrophilic monomers have been employed for these experiments. The grafting reactions were initiated by trapped radicals produced by irradiation of the polymeric system under vacuum at room temperature. Experimental results showed that the monomer content in the fibres obeyed the Arrhenius relationship. The overall activation energy of the grafting reaction has been calculated. Grafting reactions can proceed only if $\Delta E_t > \Delta E_p + \Delta E_M$. This termination activation energy ΔE_t is a function of the state of polymeric system.

INTRODUCTION

Radiation grafting has been known as an excellent tool for hydrophilization of synthetic hydrophobic fibres, such as poly(ethylene terephthalate) (PET) fibres. Radiation grafting of hydrophilic monomers on PET fibres for the purpose of dye ability improvement and antistatic improvements have been studied by a number of research workers[1-8], either using mutual irradiation or trapped radical initiation. However, the kinetic aspects of the grafting reaction have not been much studied.

It has been known that PET fibres are highly crystalline, hydrophobic and do not contain chemically reactive groups. Certain desirable properties can be imparted to PET fibres by grafting with hydrophilic monomers such as acrylic acid (AA), acrylonitrile (AN), N-vinyl-2-pyrrolidone (VP) and acrylamide (AM).
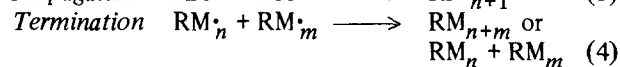
The purpose of this work was to study the kinetics aspects of the grafting reaction initiated by trapped radicals produced by irradiating PET fibres *in vacuo*. It has been shown that irradiation of polymeric systems will produce free radicals, trapped for a considerable time at room temperature[9,10]. Hydrophilic monomers such as AA, VP and AN have been employed for these grafting experiments. The influence of reaction time, monomer content and reaction temperature on the degree of grafting have been studied. A theoretical analysis has been made in terms of the quantitative relationship between these factors.

THEORETICAL ANALYSIS

According to Turner[11], irradiation of PET produces free radicals, $-O-C\cdot H-CH_2-O-$, which account for more than 90% of all the trapped radicals. G_R for these trapped radicals is only 0.02, very low compared with cellulose for which G_R lies between 1 and 6. This radiolysis reaction can be written as follows[12]:

$$\text{(1)}$$
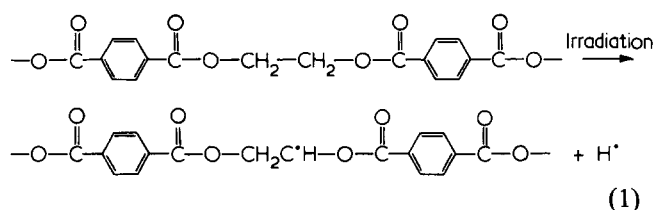
The number of trapped radicals produced will depend on the irradiation dose, the G_R value and the irradiation dose rate. In this analysis, we consider the case of the graft copolymerization reaction proceeding in PET fibres. By immersing irradiated PET fibres into a solution of monomers at a specific temperature, the monomer will diffuse into the fibres and reach the trapped radical site. These trapped radicals can initiate graft copolymerization reactions according to the following scheme:

Initiation	$R\cdot$ + M	$\longrightarrow$	$RM\cdot$	(2)
Propagation	$RM\cdot$ + nM	$\longrightarrow$	$RM\cdot_{n+1}$	(3)
Termination	$RM\cdot_n$ + $RM\cdot_m$	$\longrightarrow$	RM_{n+m} or	
			$RM_n + RM_m$	(4)

where $R\cdot$ = trapped radicals and $RM\cdot_m$ = growing radicals. The grafting rate can be assumed equal to the propagation rate and thus can be written as follows:

$$R_g = k_p \, (RM\cdot)(M) \qquad (5)$$

where ($RM\cdot$) is the concentration of all growing radicals at all stages; (M) is the monomer content in the PET fibres; R_g if the grafting rate; and k_p is the propagation rate constant.

And the rate of termination can be written as follows:

$$R_t = -d(RM\cdot)/d(t) = k_t(RM\cdot)^2 \qquad (6)$$

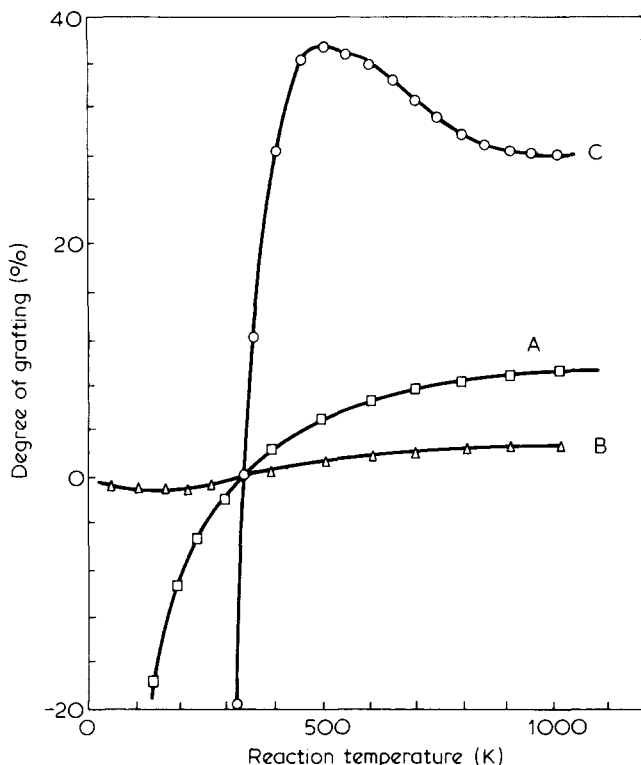where R_t is the termination rate and k_t is the termination rate constant.

Figure 1 Theoretical linear plot of G_f vs. T (equation 11). $\Delta E_t = 10$ kcal/(mol K)$^{-1}$; $A_p A_M/A_t = 1$; $\ln(RM_0^\cdot) A_t(t) = 15$: A, □——□, $\Delta E_a = 0$; B, △——△, $\Delta E_a = +2$kcal (mol K)$^{-1}$; C, ○——○, $\Delta E_a = -2$kcal (mol K)$^{-1}$

For a specified reaction temperature, the rate constant k_t can be assumed to remain constant throughout the grafting reaction and thus equation (6) can be integrated to yield:

$$(RM^\cdot) = (RM^\cdot)_0/[1 + k_t(RM^\cdot)_0(t)] \qquad (7)$$

where $(RM^\cdot)_0$ is trapped radical content at the beginning of the reaction. Rearrangement of equations (5) and (7) yields.

$$R_g = d(G_f)/d(t) = k_p(M)(RM^\cdot)_0/[1 + k_t(RM^\cdot)_0(t)] \qquad (8)$$

In the case of small diameter fibre, the grafting reaction can be regarded as a diffusion-free[13]. Under these conditions the rate of monomer diffusion into the PET fibres is much higher than the grafting rate. In a steady state, the monomer content in polymer (M) can be assumed constant during the grafting reaction because the monomer is in such abundant supply. Also if the rate constants k_p and k_t are assumed to remain constant throughout the grafting reaction, equation (8) can be integrated to yield:

$$G_f = k_p k_t^{-1}(M)\ln[1 + k_t(RM^\cdot)_0(t)] \qquad (9)$$

If the value of k_t $(RM^\cdot)_0(t)$ is much higher than 1, equation (9) can be simplified and becomes:

$$G_f = k_p k_t^{-1}(M)\ln[k_t(RM^\cdot)_0(t)] \qquad (10)$$

where G_f is the degree of grafting. Equation (10) describes the relationship between the degree of grafting and the grafting time. Theoretical semilogarithmic plots of G_f vs. t must be a straight line.

The rate constant k_p and k_t, and the monomer content

in polymer (M) are functions of temperature T. If it be assumed that the Arrhenius relationship is applicable, equation (10) becomes:

$$G_f = A_p A_M A_t^{-1} \{-\Delta E_t/RT + \ln(RM^\cdot)_0 A_t(t)\} \exp(-\Delta E_a/RT) \qquad (11)$$

where $\Delta E_a = \Delta E_p - \Delta E_t + \Delta E_M$ is the overall activation energy for the grafting reaction.

Equation (11) describes the relationship between the degree of grafting (G_f), the grafting periods (t) and the grafting temperature (T). For a specified reaction period, the degree of grafting is only a function of reaction temperature (T). A plot of G_f vs T should be a curved line with a slope equal to dG_f/dT. Differentiating the equation (11) with respect to T we obtain:

$$dG_f/dT =$$

$$A_p A_M A_t^{-1} [-\Delta E_t/RT + \ln(RM^\cdot)_0 A_t t] [\Delta E_a/RT^2]$$

$$\times \exp(-\Delta E_a/RT)$$

$$+ A_p A_M A_t^{-1} [\Delta E_t/RT^2] \exp(-\Delta E_a/RT) \qquad (12)$$

The optimum value of the degree of grafting will be attained at $dG_f/dT = 0$. Thus the optimum temperature T_{op} of the grafting reaction can be calculated:

$$T_{op} = \Delta E_t \Delta E_a/R[\Delta E_t + \Delta E_a \ln(RM^\cdot)_0 A_t t] \qquad (13)$$

At a high reaction temperature $(T \to \infty)$, thus equation (11) becomes:

$$G_f = A_p A_M A_t^{-1} \ln(RM^\cdot)_0 A_t t \qquad (14)$$

Zero degree of grafting will be attained at temperature T_0:

$$\Delta E_t/RT_0 = \ln(RM^\cdot)_0 A_t t \qquad (15)$$

or

$$-\Delta E_a = RT_{op} T_0/[T_{op} - T_0] \qquad (16)$$

In practice, equation (15) is really a limiting condition for zero grafting. Zero grafting will presumably occur when

$$\Delta E_t/RT \geqslant \ln(RM^\cdot)_0 A_t t$$

since the degree of grafting cannot be negative. Theoretical plots of G_f vs T which fulfil the equation (11) can be seen in *Figure 1*.

Equations (15) and (16) show that the optimum reaction temperature, T_{op}, is not a function of monomer content in the polymer (M), but depends only on the overall activation energy ΔE_a, the trapped radical content and the reaction time. The degree of grafting at the optimum reaction temperature can be calculated by recombination of equations (16) and (11) to give:

$$G_{op} = (A_p A_M)(A_t e)^{-1}(\Delta E_t/\Delta E_a)\exp[(-\Delta E_a/\Delta E_t)\ln(RM^\cdot)_0 A_t t] \qquad (17)$$

or

$$G_{op} = (A_p A_M)(A_t e)^{-1}(\Delta E_t/\Delta E_a)[(RM \cdot)_0 A_t t]^{(-\Delta E_a/\Delta E_t)}$$

(18)

It can be calculated, according to the equation(18) that the optimum degree of grafting is much influenced by the overall activation energy ΔE_a. In the case:

(i) $\Delta E_a > 0$ then $G_{op} < 0$ and $G_0 = 0$
(ii) $\Delta E_a = 0$ then $G_{op} = 0$ and $G_0 = -\infty$
(iii) $\Delta E_a < 0$ then $G_{op} > 0$ and $G_0 = -\infty$

where G_0 is the degree of grafting at zero temperature.

It is seen that the shape of the curves are much influenced by the overall activation energy. In this case *Figure 1c* represents the curve for $\Delta E_a < 0$, *Figure 1a* for $\Delta E_a = 0$ and *Figure 1b* for $\Delta E_a > 0$. *Figure 1* shows that the grafting reaction can proceed only if $\Delta E_a < 0$.

In the liquid state, however, the activation energy for termination of various vinyl monomers is less than 2 kcal $(mol K)^{-1}$. This value is much lower than the activation energy for propagation in the same monomer[16]. Thus grafting reactions cannot proceed in the liquid state. In the solid state, the rate constant for termination is very low, in agreement with the Trommodorf gel effect; hence ΔE_t in solid state must be greater than in the liquid state.

At low irradiation doses it can be assumed that the trapped radical content is proportional to the irradiation dose. Thus for an irradiation dose of 1 Mrad, the trapped radical content $(RM \cdot)_0$ can be calculated according to the following equation:

$$(RM \cdot)_0 = 10^{-3} \rho G_R \text{ mol } l^{-1}$$

(19)

where ρ is the polymer density and G_R is the radical yield/ 100 eV energy absorbed.

EXPERIMENTAL

Material

PET fibres used in this experiment were supplied by Indonesian Toray Synthetic (ITS). The fibres were washed with a solution of detergent, rinsed with water, dried in a drying oven and stored in a dessicator over silica gel. The average diameter of the fibres was about 0.01 mm.

Reagent grade AA, AN and VP monomers were purified by distillation under reduced pressure just before use. The other chemicals such as 1,1',2,2'-tetrachloroethane and 1,2-dichloroethane were chemically pure grade and were used without further purification.

The irradiation facility was a Gamma Cell 220, made in Canada with a dose rate of 2×10^5 rad h^{-1}.

Grafting technique

In this procedure, a PET fibre sample weighing about 1 g was put into a glass tube, evacuated and irradiated at room temperature. After a specified irradiation dose, the vacuum tube containing irradiated samples were filled with a solution of monomer (AA, AN or VP). The samples were then heated in a thermostatically controlled bath for a specified period and at a specific temperature. The grafting reaction proceeded at this stage. After heating for a specified period,

the samples were removed from the vacuum tubes, washed with hot water and dried to constant weight in an oven. The degree of grafting was calculated as % wt gain.

RESULTS AND DISCUSSION

Monomer absorption

The influence of reaction temperature T on the monomer content in the polymer (M) was studied. *Figure 2* shows the semilogarithmic plot of (M) vs. $1/T$. It is seen that the two curves are straight lines. Thus, for AA and AN monomers, the monomer content (M) obeys the Arrhenius relationship as follows:

$$(M) = A_M \exp(-E_M/RT)$$

where ΔE_M is the activation energy for monomer absorption. It could be deduced that $\Delta E_{M(AA)} = 5.34$ kcal $(mol K)^{-1}$ and $\Delta E_{M(AN)} = 1.10$ kcal$(mol K)^{-1}$. It is found that in the case of AA monomer, the monomer content in the PET fibres is much influenced by reaction temperature.

Monomer content in solution

Figure 3 shows that the degree of grafting, G_f, is a function of the monomer content in the solution. The higher the monomer content in the solution, the higher the degree of grafting. This experimental evidence can be explained by the assumption that the monomer content in the polymeric system at equilibrium is a function of the monomer content in solution. However, the increase of the monomer content in the solution will increase the possibility of the homopolymer formation. It can be reported that in the case of AA monomer, the formation of homopolymer can be avoided by using AA solutions with a concentration of less than 80% w/w and by the addition of 0.2% $FeSO_4 \cdot 7 H_2O$.

AN and VP monomers can be used in the pure state because the formation of homopolymer is not a serious problem. These homopolymers, such as polyacrylonitrile and poly(vinyl pyrrolidone) can be extracted easily.
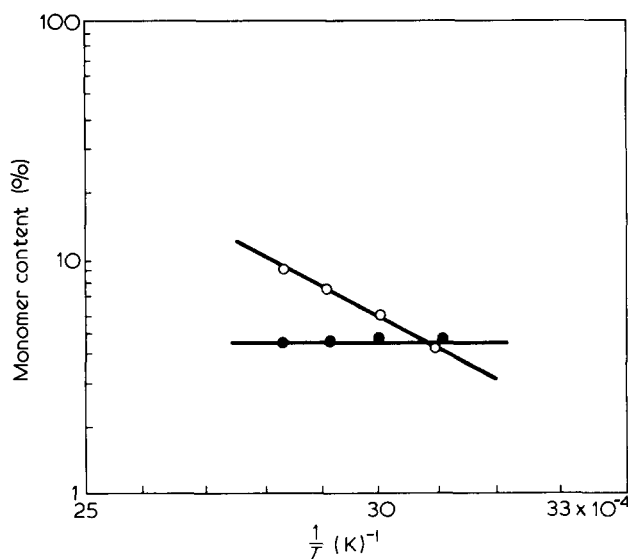

Figure 2 Influence of reaction temperature on the monomer content in polymer (PET fibres): O——O acrylic acid content; ●——● acrylonitrile content
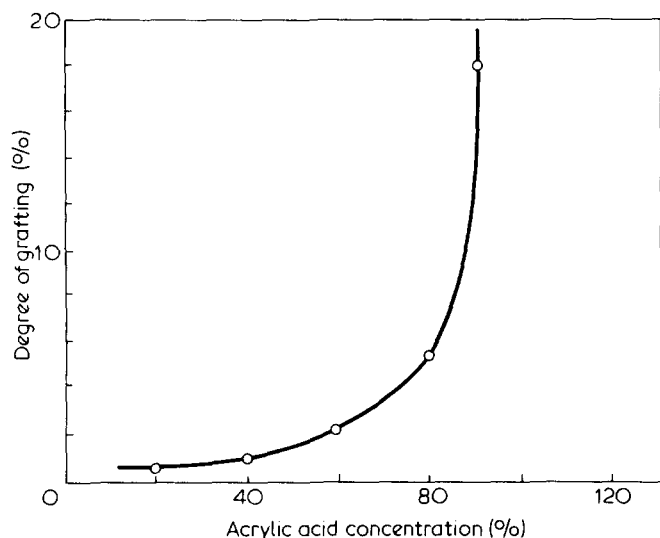
Figure 3 Influence of AA concentration on the degree of grafting G_f. Dose of irradiation = 1 Mrad, reaction time 1 h and reaction temperature 80°C

Reaction temperature

Figure 4 shows the plot of G_f vs. T at a constant reaction time. In the case of AA grafted onto PET fibres, with irradiation doses of 0.45 Mrad and the reaction time 2 h, the optimum degree of grafting G_{op} was attained at the reaction temperature of 75°C and the limiting conditions for zero grafting were attained at the reaction temperature of 45°C. Thus the overall activation energy can be calculated according to equation (16) giving:

$$\Delta E_a = -7.34 \text{ kcal(mol K)}^{-1}$$

or

$$\Delta E_t = \Delta E_p + \Delta E_M + 7.34 \text{ kcal(mol K)}^{-1}$$

According to equation (19) it can be calculated that:

$$\Delta E_t = 632.8 \ln 0.142 A_t$$

It can be noted that for many molecular reactions the collision factor A_t has been found to be close to the value 10^{10}.

In the case of grafting reactions of VP monomer onto PET fibres it was found that the optimum degree of grafting was attained at a temperature of 70°C and the limiting conditions for zero grafting were attained at 50°C. In this experiment, the PET fibres were extracted with tetrachloroethane before being used. The overall activation energy ΔE_a can be deduced:

$$\Delta E_a = -11.02 \text{ kcal (mol K)}^{-1}$$

and

$$\Delta E_t = 642.77 \ln 1.26 A_t \text{ cal(mol K)}^{-1}$$

If the PET fibres were used without extraction with tetrachloroethane before irradiation, the optimum degree of grafting was found to be lower compared with extracted fibres. However, the optimum temperature and the zero temperature appear to be the same. It was found that the optimum temperature $T_{op} = 70°C$ and the zero temperature $T_0 = 47°C$.

Then the overall activation energy for the grafting reaction can be deduced:

$$\Delta E_a = -9.5 \text{ kcal(mol K)}^{-1}$$

and

$$\Delta E_t = 636.8 \ln 1.26 A_t \text{ cal(mol K)}^{-1}$$

In the case of AN grafting on PET fibres, it was found that the optimum temperature $T_{op} = 70°C$ and the limiting condition for zero grafting was attained at a temperature of 50°C. The overall activation energy for the grafting reaction can be deduced:

$$\Delta E_a = -11.02 \text{ kcal(mol K)}^{-1}$$

and

$$\Delta E_t = 642.77 \ln 0.213 A_t \text{ cal(mol K)}^{-1}$$

Figure 4 has shown that the limiting condition for zero grafting was obtained at a temperature between 40° and 50°C. Calculations based on this curve and on the theroetical analysis led to the conclusion that the termination activation energy, E_t, for the grafting reaction of the three monomers (AA, VP and AN) onto PET fibres were not far different from each other. This means that the value of the termination activation energy, E_t, is specific for the polymer system and not for the monomer used for the grafting reaction.

Theoretical analysis has concluded that the grafting reaction can proceed only if the termination activation energy is much higher than the sum of propagation and absorption activation energies. Experimental results were found to be in agreement with this statement.
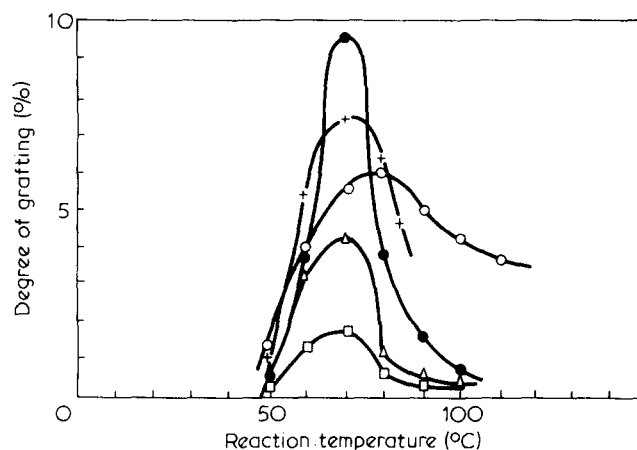
ACKNOWLEDGEMENT

Figure 4 Influence of reaction temperature on the degree of grafting. O———O, AA 80%, irradiation dose 0.45 Mrad and reaction time 2 h; + ——— +, AN pure,irradiation dose 0.45 Mrad and reaction time 3 h; ●———●, VP pure-irradiation dose 2 Mrad and reaction time 4 h. The PET fibres were extracted with tetrachloroethane before use, 1 h at 75°C; △———△, VP monomer, irradiation dose 2 Mrad and reaction time 4 h; □———□, VP monomer irradiation dose 1.18 Mrad and reaction time 4 h

REFERENCES

1   Kale, P. D. and Lokhande, H. T. *J. Appl. Polym. Sci.* 1975, **19**, 461
2   Sakurada, I. and Okada, T. *JAERI* 1969, **74**, 5022
3   Huglin, H. G. and Zlatev, V. B. *Eur. Poly. J.* 1974, **10**, 199
4   Magat, E. E. and Tanner, D. US Pat. 3 670 046 (1972)
5   Sakurada, I., Kyotoshi, Kyotofu and Okada, T. US Pat. 3 649 494 (1972)
6   Veb Textilekombinat Cottbus; Brevet Francaise, No 2.220.546 (1974)
7   Bonnefis, J. C. and Puig, J. R. *J. Appl. Polym. Sci.* 1971, **15**, 553
8   Liepins, J., Surles, J. R., Morosoff, N. and Stannett, V. T. *J. Appl. Polym. Sci.* 1977, **21**, 2529
9   Ohniski, S., Kashiwagi, M., Ikeda, Y. and Mitta, I. *Proc. on 'Large Radiation Sources in Industry I' IAEA*, 1960, 291
10 Chapiro, A. 'Radiation Chemistry of Polymeric Systems' 1962, p 361
11 Turner, D. T., Adv. Chem. Ser. 1967, **66**, 127
12 Guthrie, J. T. *Polymer* 1975, **16**, 134
13 Odian, G., Henry, R., Koenig, R., Mangaraj, D., Le Doan Trung, Bou Cho and Arif Derman *J. Polym. Sci. (Polym. Chem. Edn)* 1975, **13**, 623
14 Hayakawa, K. and Kawase, K. *J. Polym. Sci. (A-1)* 1967, **5**, 439
15 Nicolais, C., Drioli, E., Hopfenburg, H. B. and Tidone, D. *Polymer* 1977, **18**, 1137
16 Chapiro, A. 'Radiation Chemistry of Polymeric Systems', 1962, p 50