Kinetics of Radiation-Induced Graft Copolymerization of 2-Hydroxyethyl Methacrylate onto Polyethylene Membranes

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Synopsis

The kinetics of radiation-induced graft copolymerization of 2-hydroxyethyl methacrylate onto polyethylene membranes in ethanol has been studied with radiation sources of cobalt-60. The influences of concentration of monomer, dose rate, and temperature on grafting rate were investigated. The results show the following functional relationship equations: $dG_0/dt \propto [M]_0$ and $dG_0dt \propto \dot{D}^{1/2}$. The apparent activation energy and the collision frequency factor of the grafting copolymerization are 8.0 kcal/mol and 1.505×10^7 $G\%$ $h^{-1/2}$ $Mrad^{-1/2}$ mol^{-1} L, respectively. The work established that the relationship of the grafting rate constant k with the temperature relational expression at arbitrary temperature: $\ln k = 16.5269 - 4026(1/T)$.

INTRODUCTION

The radiation-induced graft copolymerization is a well-known important method for modification of the chemical and physical properties of polymeric materials.

Odian et al.[1] studied the accelerating effect of methanol on the gamma-radiation-induced graft copolymerization of styrene to polyethylene. The kinetics of grafting in styrene–methanol mixtures for the hydrophobic polymers polyethylene and nylon have been reported in detail by Odian and co-workers.[2,3] Dilli and Garnett[4] investigated the kinetics of the radiation-induced grafting of styrene to cellulose in methanol in air at dose rates of 0.007, 0.014, and 0.078 Mrad/h in cobalt-60 and spent fuel element facilities.

Ishigaki et al.[5] studied low- and high-density polyethylene films irradiated by electron beams with doses of 2–50 Mrad and then immersed in an aqueous solution of acrylic acid (monomer concentration from 30 to 100 wt %) for 10 min–5 h at a temperature of 25–40°C. In the radiation grafting of acrylic acid onto polyethylene film, the effects of various factors on the grafting have been studied in detail and the results have been kinetically analyzed by Ishigaki and co-workers.[6]

The purpose of the present work was to study the kinetics of radiation induced graft copolymerization of 2-hydroxyethyl methacrylate (HEMA) onto polyethylene (PE) membranes.

Journal of Applied Polymer Science, Vol. 38, 821–828 (1989)

CCC 0021-8995/89/050821-08$04.00

EXPERIMENTAL

Materials

The PE membranes were supplied by the Shanghai Institute of Plastic Research. HEMA was manufactured in Germany.

Grafting Procedure

Samples were of 20 × 80 mm cut-out PE membranes, washed with soap, ethanol, and distilled water, and dried at 60°C under vacuum (10 mm Hg) for 7 h. The initial weight W_0 was then measured. The samples were immersed in grafting solution in grafting vessels, bubbled with N_2 gas (99.99%) for 20 min to remove oxygen, and then irradiated in a 60,000 Ci Co-60 source at different grafting conditions.

The grafted membranes were extracted in ethanol at 60°C for eight hours. The extracted membranes were then washed with distilled water and dried at 60°C under vacuum (10 mm Hg) for 7 h, and the dry grafted weight W_g was determined. The degree of grafting was calculated using the following equation:

$$\text{graft}(\%) = (W_g - W_0)/W_0 \times 100$$

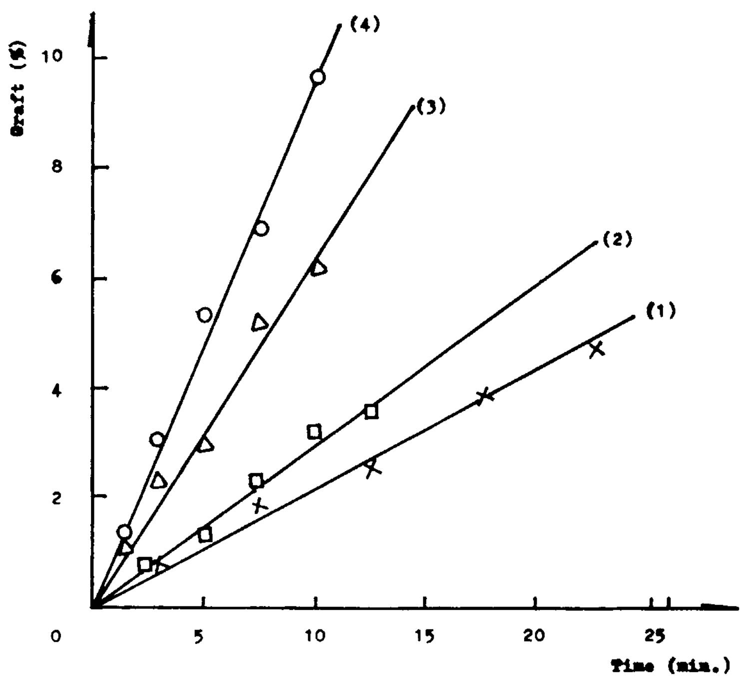

Fig. 1. Rate of grafting at varying monomer concentrations for PE membrane. HEMA concentrations (mol/L): (1) 0.411; (2) 0.617; (3) 1.233; (4) 1.987. Dose rate 0.219 Mrad/h; grafting temperature 25°C.

TABLE I
Effect of Monomer Concentration on Initial Rate of Grafting

Initial concentration $[M]_0$ (mol/L)	Initial rate of grafting dG_0/dt (%/h)
0.411	6.52
0.617	9.00
1.233	18.90
1.987	29.70

RESULTS AND DISCUSSION

Rate of Grafting

Concentration of Monomer. Figure 1 shows the initial rates of grafting (dG_0/dt) at varying concentrations of monomer for PE membranes. The results show that the initial rates are linear with time (0–25 min). As is clear from these results, the initial rates of grafting increase with increasing concentration of monomer for PE membranes. The initial rates of grafting, dG_0/dt, obtained graphically are shown in Table I.

Dose Rate

Figure 2 indicates the initial rate of grafting at different dose rates for grafting of HEMA onto PE membranes. The results show that initial rates

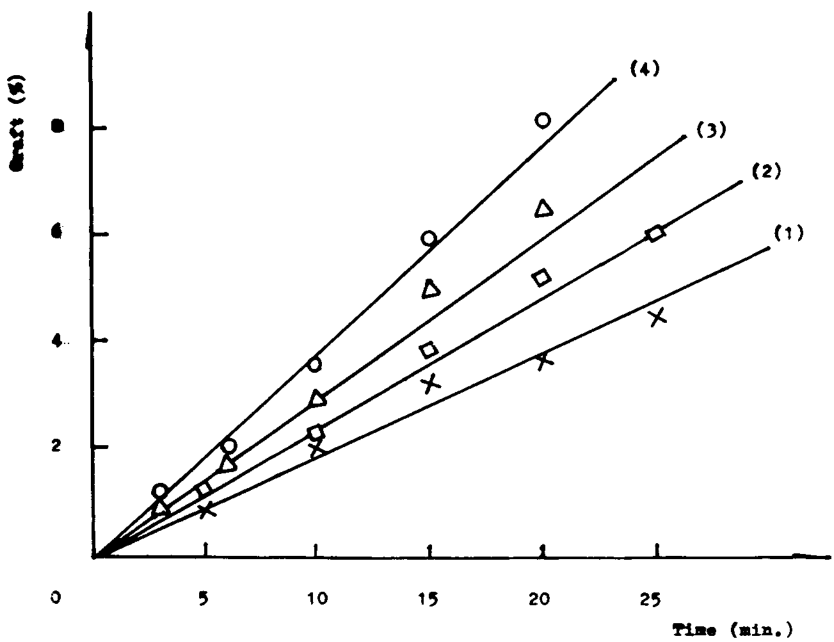

Fig. 2. The degree of grafting at different dose rates (Mrad/h) for grafting of HEMA onto PE membrane. Dose rate (Mrad/h): (1) 0.129; (2) 0.219; (3) 0.336; (4) 0.453. Concentration of monomer: $[M]_0 = 1.233$ mol/L; grafting temperature 25°C; membrane thickness 30 μm.

TABLE II
Effect of Dose Rate on Initial Rate of Grafting

Dose rate (Mrad/h)	Initial rate of grafting dG_0/dt (%/h)
0.129	11.09
0.219	14.00
0.336	17.89
0.453	22.39

are linear with time (0–25 min). As is clear from result of Figure 2, the initial rate of grafting increases with increasing dose rate.

The initial rates of grafting, dG_0/dt, obtained graphically are shown in Table II. According to the data in Table I, a plot ln dG_0/dt against ln$[M]_0$, linear relationships are obtained in Figure 3. This result is expressed by the following relationship equation:

$$dG_0/dt \propto [M]_0 \quad (1)$$

Figure 4 indicates that the log–log plot of dG_0/dt against the dose rate is obtained with data in Table II. The linear relationships from Figure 4 are obtained from the following equation:

$$dG_0/dt \propto \dot{D}^{1/2} \quad (2)$$

It is found from eqs. (1) and (2) that the initial rates of grafting are proportional to the $[M]_0$ and $\dot{D}^{1/2}$. Combination of eqs. (1) and (2) yields, for

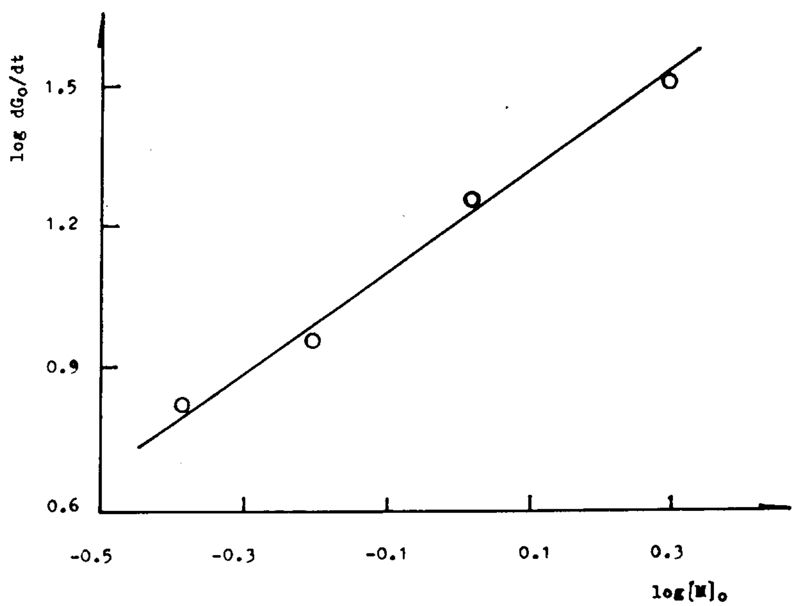

Fig. 3. Effect of $[M]_0$ on initial rate of grafting.

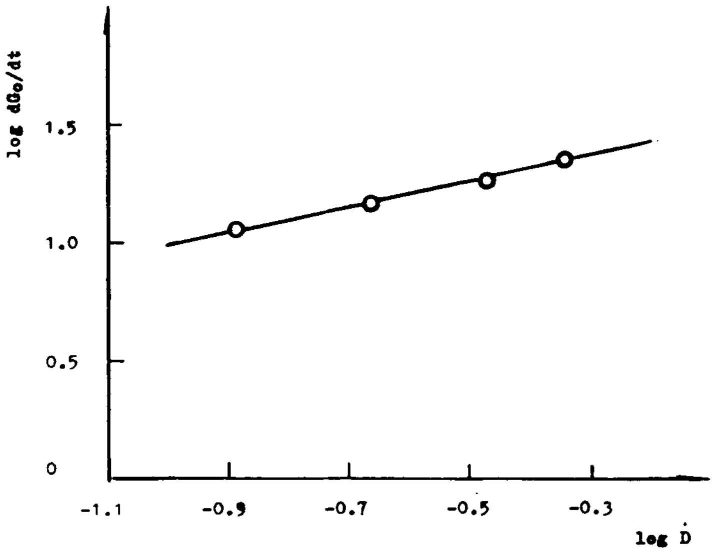

Fig. 4. Effect of $\dot{D}$ on the initial rate of grafting at different temperatures.

radiation graft of HEMA onto PE membranes,

$$dG_0/dt = k[\mathrm{M}]_0\dot{D}^{1/2} \tag{3}$$

where k is the apparent constant of the initial rate of grafting copolymerization.

Effect of Dose Rate

The effect of $\dot{D}$ on dG/dt at different temperature is shown in Figure 5. This figure shows such a plot of dG_0/dt against $[\mathrm{M}]_0\dot{D}^{1/2}$ yielding line relationships. The slopes of straight lines are the constants of the grafting reaction. These values are cited in Table III.

Apparent Activation Energy

Arrhenius equation:

$$d \ln k/dT = E/RT^2 \tag{4}$$

Because

$$dG_0/dt = k[\mathrm{M}]_0\dot{D}^{1/2}$$

$$\ln dG_0/dt = \ln k + \ln[\mathrm{M}]_0\dot{D}^{1/2}$$

Therefore,

$$(d \ln dG_0/dt)dT = d \ln k/dT = E/RT^2$$

$$(d \ln dG_0/dt)dT = E/RT^2 \tag{5}$$

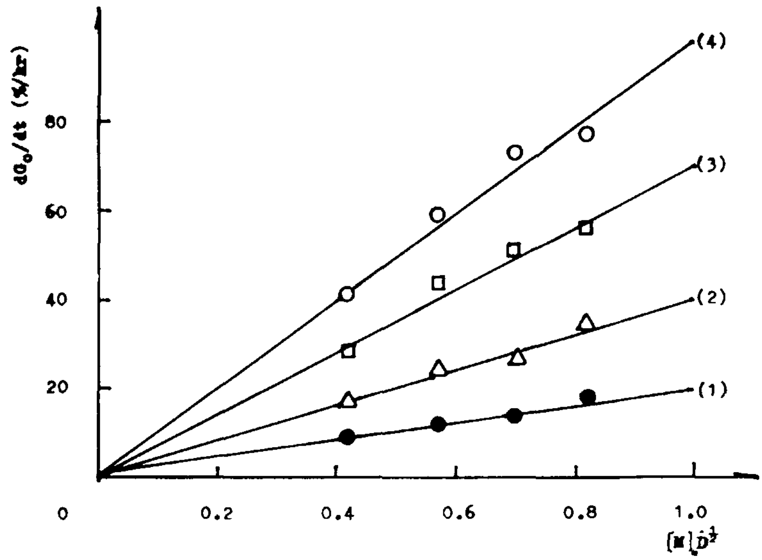

Fig. 5. Plot of the initial rate of grafting vs. dose rate $\dot{D}$. Grafting temperature (°C): (1) 25; (2) 41; (3) 54; (4) 66. Concentration of monomer: $[M]_0 = 1.233$ mol/L.

Integration of eq. (5) yields

$$\ln dG_0/dt = -E/RT + C \tag{6}$$

or

$$\log dG_0/dt = -E/(2.303 \times RT) + C \tag{7}$$

The plot of $\log dG_0/dt$ against $1/T$ is shown in Figure 6. The slope of the straight lines in Figure 6 is $A = -E/2.303R$. Therefore, $E = -2.303AR$.

The apparent activation energy was calculated. These values are shown in Table III.

Apparent Collision Frequency Factor

The apparent rate constants for grafting copolymerization can be expressed by an Arrhenius type relationship:

$$k = Ze^{-E/RT}$$

Values of Z, the collision frequency factors of grafting copolymerization at different temperatures, were calculated by the k and E are known from Table III. These values are shown in Table IV.

It is interesting to note tnat, in the variations in the values of Z, the frequency factor for graft copolymerization, the steric effects are probably the more important factor. Thus, the more hindered monomers (e.g., HEMA) have lower Z values than the less hindered ones.

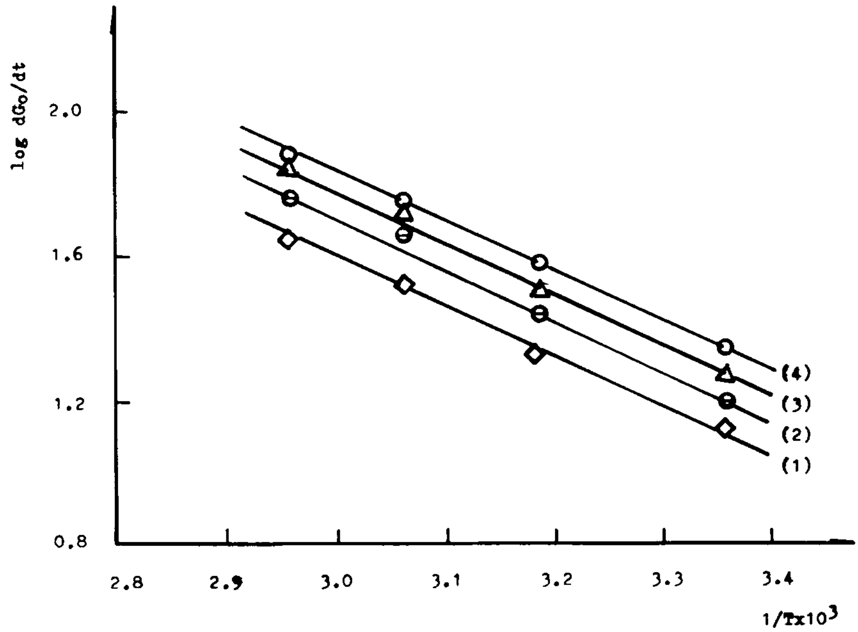

Fig. 6. Effect of temperature on initial rate of grafting for graft of HEMA onto PE membrane. Dose rates (Mrad/h): (1) 0.121; (2) 0.219; (3) 0.336; (4) 0.453.

TABLE III
The Apparent Rate Constant of Grafting Reaction and Apparent Activation Energy of Grafting Reaction

Dose rate (Mrad/h)	k (G% h$^{-1/2}$ Mrad$^{-1/2}$ Mol^{-1} L	E (kcal/mol)
0.129	21	7.7
0.219	41	8.4
0.336	70	8.4
0.453	97	7.4
Average value		8.0

TABLE IV
The Apparent Collision Frequency Factors of Grafting Copolymerization at Different Temperature

Temperature (°K)	$Z \times 10^{-7}$ (G% h$^{-1/2}$ Mrad$^{-1/2}$ mol^{-1} L)
298	1.548
314	1.518
327	1.557
339	1.395
Average value	1.505

The substitution of average apparent activation energy and average apparent collision frequency factor into $k = Z \times e^{-E/RT}$ yields

$$k = 1.505 \times 10^7 \times e^{-8000/RT} \tag{10}$$

Therefore, this work has established the relationship of the apparent rate constant of grafting copolymerization with the absolute temperature at arbitrary temperature:

$$\ln k = 16.5269 - 4026(1/T) \tag{11}$$

The apparent rate constant of grafting copolymerization, k, is calculated by eq. (11), if T, the Kelvin temperature, is known. It is the same the other way round.

References

1. G. G. Odian, A. Rossi, and E. N. Trachtenberg, *J. Polym. Sci.*, **42**, 575 (1960).
2. G. G. Odian, M. Sobel, A. Rossi, and R. Klein, *J. Polym. Sci.*, **55**, 6632 (1961).
3. G. G. Odian, M. Sobel, A. Rossi, R. Klein, and R. Acker, *J. Polym. Sci. A*, **1**, 639 (1963).
4. S. Dilli and J. L. Garnett, *J. Appl. Polym. Sci.*, **11**, 859 (1967).
5. I. Ishigaki, T. Sugo, K. Senoo, T. Okada, J. Okamoto, and S. Machi, *J. Appl. Polym. Sci.*, **27**, 1033 (1982).
6. I. Ishigaki, T. Sugo, T. Takayama, T. Okada, J. Okamoto, and S. Machi, *J. Appl. Polym. Sci.*, **27**, 1043 (1982).

Received March 17, 1988
Accepted August 2, 1988