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NOTE
KINETICS OF RADIATION-INDUCED GRAFT COPOLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE ONTO SILICONE RUBBER FILMS

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INTRODUCTION

Radiation-induced graft polymerization of hydrogels onto polymeric substrates has been extensively investigated by several authors [1-6]. Comparatively little attention has been paid to the kinetics of the radiation-induced graft polymerization of hydrogels onto silcone rubber films.

The purpose of this paper is to probe further into the quantitative kinetics of the radiation-induced graft polymerization of 2-hydroxyethyl methacrylate (HEMA) onto silicone rubber film.

EXPERIMENTAL

Materials

The silicone rubber (SR) films were supplied by the Anqing Institute of Silicone Rubber Products Research. HEMA was manufactured in Germany. The HEMA content was >98%; it was used without further purification.

Radiation-Induced Grafting

The SR films were cut, washed with soap and ethanol, and dried at 60°C under vacuum (10 torr) for 7 h, and the intitial weight, W_0 (g), was measured. The sample was then immersed in the HEMA solution in a grafting reaction vessel, bubbled with 99.9% nitrogen for 10 min to remove oxygen, and irradiated in a 3600-Ci ^{60}Co source under various grafting conditions.

The grafted films were extracted in ethanol at 60°C for 8 h, washed with distilled water, and dried at 60°C under vacuum (10 torr). The dry grafted weight, W_g (g), was determined, and the grafting level G (mg graft/cm^2) was calculated as follows:

$$G = [(W_G - W_0)/A] \times 1000, \tag{1}$$

where A is the film area in cm^2.

RESULTS AND DISCUSSION

Figure 1 shows how the grafting level and rate increases with increasing HEMA concentration ([M]). The initial grafting rates, V_g (mg/cm$^2 \cdot$ h), obtained graphically, are shown in Table 1. Plots of ln V_g vs ln $[M]_0$ are linear with a slop of 2, i.e., the grafting rate varies as the square of the initial HEMA concentration..

Figure 2 shows that the rate of grafting increases with the radiation dose rate D. Plots of ln V_g (obtained graphically from Fig. 2 and shown in Table 2) vs ln D were linear with a slope of 1/2, i.e., the grafting rate varies as the square root of the radiation dose. Thus, one can express the grafting rate as follows:

$$V_g = k[\mathrm{M}]_0^2 D^{1/2}, \tag{2}$$

where k is the apparent rate constant. The values of k, calculated according to Eq. (2), are listed in Table 3.

Arrhenius plots of the rate constants reported above according to

$$\ln k = \ln Z - E_a/RT, \tag{3}$$

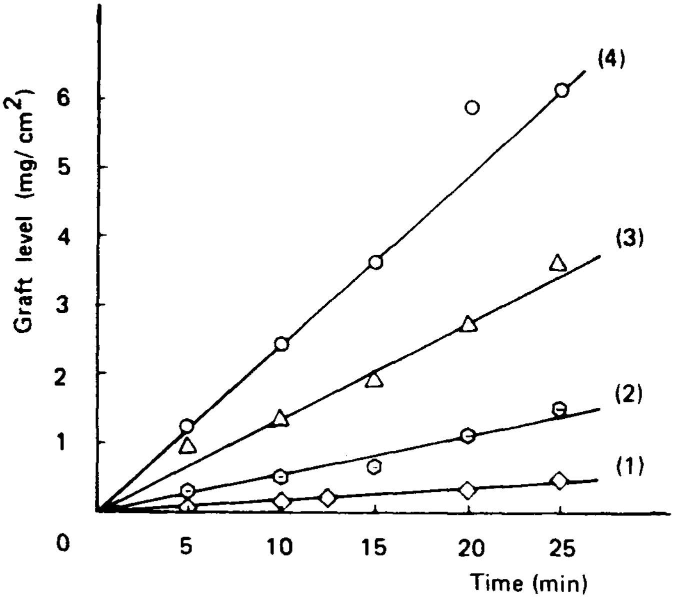

FIG. 1. Graft level at varying HEMA concentrations. HEMA concentration: (1) 0.62, (2) 1.23, (3) 1.99, (4) 2.47 mol/L. Dose rate: 0.57 Mrd/h. Temperature: 24°C. SR film thickness: 0.45 mm.

TABLE 1. Effect of HEMA Concentration on the Initial Grafting Rate

Initial HEMA concentration, $[M]_0$, mol/L	Initial grafting rate, V_g, mg/(cm^2 · h)
0.62	0.88
1.2	3.7
1.99	8.4
2.48	14.8

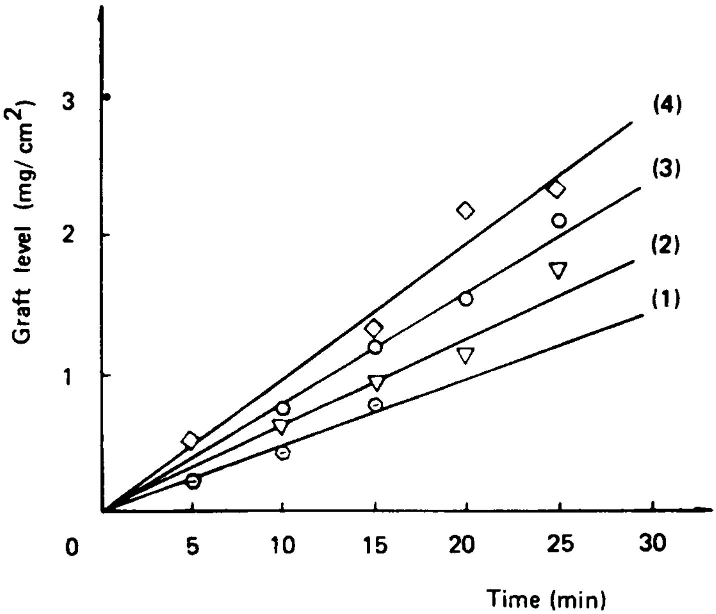

FIG. 2. Graft level at different radiation dose rates. Dose rate: (1) 0.225, (2) 0.439, (3) 0.532, (4) 0.904 Mrd/h. HEMA concentration: 1.5 mol/L. Grafting temperature: 24°C. Film thickness: 0.68 mm.

TABLE 2. Effect of Dose Rate on the Initial Grafting Rate

Dose rate, Mrd/h	Initial grafting rate, V_g, mg/(cm$^2\cdot$h)
0.227	2.9
0.439	3.7
0.532	4.9
0.904	5.8

TABLE 3. The Apparent Rate Constants for Graft Copolymerization at Different Temperatures

Dose rate, Mrd/h	k, mg·cm^{-2}·h$^{-1/2}$·Mrd$^{-1/2}$·mol^{-2}·L^2			
	16°C	37°C	52°C	62°C
0.227	1.34	3.16	4.97	5.23
0.313	1.32	3.09	5.15	5.89
0.439	1.35	2.94	4.80	5.43
0.532	1.30	3.10	5.59	5.91
0.904	1.25	3 .21	4.69	5.85
Average value	1.31	3.10	5.40	5.66
From plot of V_g vs $[M]_0{}^2D^{1/2}$	1.29	3.24	4.73	5 .71

gave E_a, the apparent activation energies, and Z, the frequency factors, as shown in Tables 4 and 5. Thus, the rate constant is given by

$$k = 7.54 \times 10^4 \exp(-6200/RT), \tag{4}$$

and this leads to an equation that summarizes all the kinetic results:

$$V_g = 7.5 \times 10^4 \exp(-6200/T)[M]_0{}^2D^{1/2}. \tag{5}$$

Now, whenever $[M]_0$, D, and T are known, the grafting rate can be predicted. (See Fig. 3.)

TABLE 4. The Apparent Activation Energies of Graft Copolymerization

Dose rate, Mrd/h	E_a, kcal/mol
0.227	6.31
0.313	6.21
0.439	6.21
0.532	6.24
0.904	6.24
Average value	6.24

TABLE 5. The Collision Frequency Factors Graft Copolymerization at Different Temperatures

Temperature, K	$Z \times 10^{-4}$, $mg \cdot cm^{-2} \cdot h^{1/2} \cdot Mrd^{-1/2} \cdot mol^{-2} \cdot L^2$
289	7.77
310	7.41
325	7.56
335	7.43
Average value	7.54

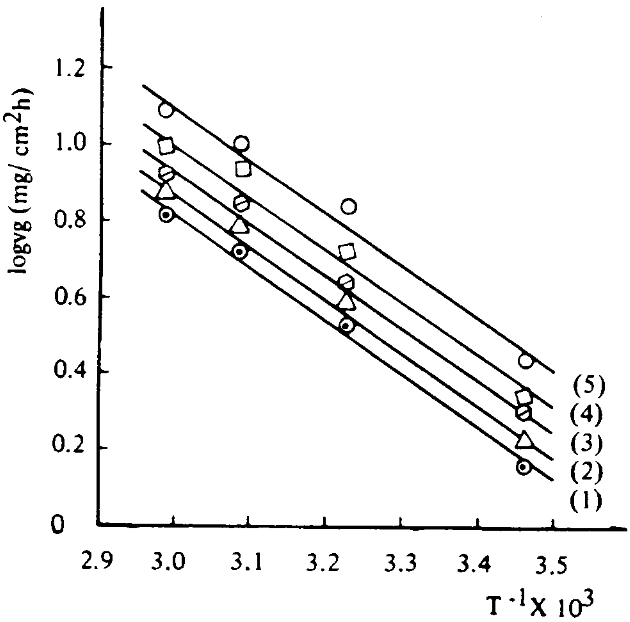

FIG. 3. Effect of grafting temperature on V_g. Dose rate: (1) 0.227, (2) 0.313, (3) 0.440, (4) 0.532, (5) 0.904 Mrd/h.

Further experimental results indicated that 0–5% ethylene glycol dimethacrylate (EDMA) has no effect on the grafting rate, but when the initial EDMA concentration is above 5%, V_g is reduced, perhaps due to a crosslinking reaction. Traces of methacrylic acid in HEMA have no effect on V_g.

Variation of the SR film thickness from 0.4 to 2.20 mm has no obvious effect on V_g because all the grafting occurs at the surface of the SR film.

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