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Principal factors affecting sequential photoinduced graft polymerization

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Abstract

Gel permeation chromatography was used to show that poly(ethylene glycol 200) monomethacrylate (PEG200MA) is chemically bound to polystyrene by a sequential graft polymerization in liquid solution. For the graft polymerization on solid substrates, cellulose acetate has higher photografting reactivity and poly(vinylidene fluoride) shows lower photografting reactivity, compared to that of polypropylene. It was found that acrylic acid has higher photografting reactivity than either dimethyl aminoethyl methacrylate or PEG200MA. The rate of graft polymerization of AA increases linearly with increasing surface initiator concentration, as predicted by a kinetic model. The rate of the surface initiator formation follows a sequence of decreasing order in the following solvents: benzene > chloroform > hexane > methanol > cyclohexane > dimethyl sulfoxide due to the relative abstractability of hydrogen in the solvent and the wettability of the substrate by the solvent. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Photografting; Surface modification; Membranes

1. Introduction

There is significant interest among both academic and industrial scientific communities in developing methods for modifying the surfaces of solid substrates without altering the bulk properties. Various motivations exist for this type of modification, such as changing the surface composition and wettability properties, improving adhesion of metal and metal oxide films, protein immobilization, blood compatibility, etc. [1–7]. Numerous methods for surface modification have been published, e.g. irradiation of substrates with different sources (UV, cobalt, electron beam, etc.), graft polymerization of monomers on substrate surfaces, and binding of various materials to surfaces via different surface functional groups [3,8–11]. In our previous paper [12], a novel sequential photoinduced living graft polymerization technique was reported, using porous polypropylene (PP) membranes as the substrate and acrylic acid as the grafted monomer. Surface initiator formation and graft polymerization were verified by a series of experiments, and advantages of the sequential graft polymerization method compared with the conventional one-step photoinduced graft polymerization method were also demonstrated. Kinetic models of surface initiator formation and graft polymerization were presented. To understand the graft polymerization mechanism further and extend the applications of the sequential grafting method, gel permeation chromatography (GPC) is used here to characterize modified substrates, and the effects of several principal factors on the graft polymerization are investigated.

2. Materials and methods

2.1. Materials

The polymer films used as substrates are commercial, porous-disk microfiltration membranes with a diameter of 47 mm and nominal pore diameter of 0.22 μm. The materials studied included PP with a thickness of 110 μm (Micron Separations), cellulose acetate (CA) with a thickness of 120 μm (Sartorius), and poly(vinylidene fluoride) (PVDF) with a thickness of 100 μm. Acrylic acid (AA) (Aldrich), poly(ethylene glycol 200) monomethacrylate (PEG200MA) (Polyscience), and dimethyl aminoethyl methacrylate (DMAEMA) (Aldrich) were evaluated as the graftable monomers. All three monomers are hydrophilic; AA is negatively charged at pH above 4.2, DMAEMA is positively charged at pH below 11, and PEG200MA is neutral. Unmodified PP and CA membranes are hydrophobic and hydrophilic, respectively, and they are both essentially neutral. Benzophenone (BP) (Aldrich) was used as the photoinitiator, and benzene, acetone, toluene, tetrahydrofuran (THF), ethanol, and deionized water were

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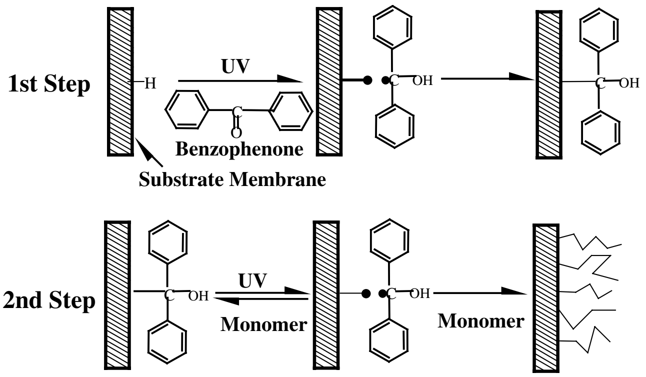


Fig. 1. Schematic diagram of the sequential photoinduced living graft polymerization method.

used as solvents. Low molecular weight polystyrene (PS) (Alfa Aesar, number-average molecular weight 2000) was used as the substrate in liquid-phase graft polymerization. All chemicals were used as received.

2.2. Photografting procedures

In brief, the grafting is a sequential, two-step process as shown in Fig. 1 [12]. In the first step, BP abstracts hydrogen from the substrate to generate surface radicals and semipinacol radicals, which combine to form surface photoinitiators in the absence of monomer solutions. The unreacted benzophenone is then removed by a good solvent. In the subsequent step(s), the monomer solutions are added onto the active substrate, and graft polymerization is initiated by the surface initiators upon exposure to UV irradiation.

The procedures for graft polymerization in a liquid phase are described as follows. In the first step, both BP and PS are dissolved in benzene. Then, a thin liquid film of the sample is exposed to UV light, resulting in PS grafted with BP (PS-*g*-BP). After that, the sample is added to ethanol, and PS-*g*-BP precipitates from solution while the unreacted BP is removed by ethanol. In the second step, PEG200MA is added to the precipitated PS-*g*-BP, and the mixture is dissolved in toluene. After exposing the mixture of PS-*g*-BP and PEG200MA to UV light, PS grafted with PEG200MA (PS-*g*-PEG-BP) is precipitated by extracting unreacted PEG200MA and possible homopolymer using ethanol.

For grafting on solid subtrates, the commercial PP membranes were soaked in benzene and dried to constant weight. Then, the membranes were weighed using an analytical balance, which has an accuracy of 0.01 mg. In the first step of the sequential method, the presoaked and preweighed membranes were saturated with benzene solutions of BP (3 g of solution was added to the membrane) and then placed in a quartz reaction vessel, which was subsequently purged with nitrogen or air. The quartz vessel is an empty cylinder with a diameter of 25 cm and a height of 2.5 cm. UV irradiation was carried out in a commercial ultraviolet processor (model QC120244ANIRDR, manufactured by RPC Industries). The processor is equipped with two UV bulbs; each bulb is 400 W with a wavelength range of 232–500 nm. An optical multi-layer dielectric interference filter (365 ± 5 nm), from Edmund Scientific, was used in the kinetic experiments. The quartz vessel was put in the conveyor, which carried the quartz vessel under the UV lamps. After irradiation for a selected number of passes, the substrates were removed from the quartz vessel, and the residual, unreacted solutions were extracted by soaking and washing the membrane in acetone and drying the membrane at room temperature in air until constant weight. In the subsequent step, the procedures in the first step were repeated, except that monomer solutions were used instead of BP solutions. The residual, unreacted solutions, and nongrafted poly(acrylic) acid were removed by soaking the membranes in deionized water for 24 h. Finally, the membranes were washed in acetone and dried to constant weight.

Weight gain measurements are described in the previous paragraph and calculated using the following formulae:

$$\text{Percent of graft of BP} = \frac{W_1 - W_0}{W_0} \times 100\%, \qquad (1)$$

$$\text{Percent graft of monomer} = \frac{W_2 - W_1}{W_0} \times 100\%, \qquad (2)$$

where W_0 is the weight of the blank membrane, W_1 the weight of the membrane after the first step, obtained by weighing after extractions of unreacted BP solutions with proper solvents, and W_2 the weight of the membrane after the second step, obtained by weighing after extraction of homopolymer with proper solvents.

2.3. Equipment

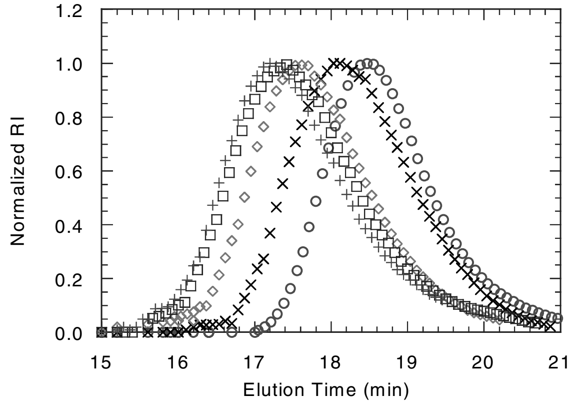
GPC analysis of the molecular weight distributions for both modified and unmodified PS was performed with a HPLC system (Beckman, System Gold) utilizing Styragel HR1 and HR3 columns (Waters) in series. The mobile phase is THF with a flow rate of 0.3 ml/min, and a refractive index detector was used. PS standards of varying molecular weight from 600 to 20000 (Polyscience) were used for HPLC calibration.

3. Results and discussion

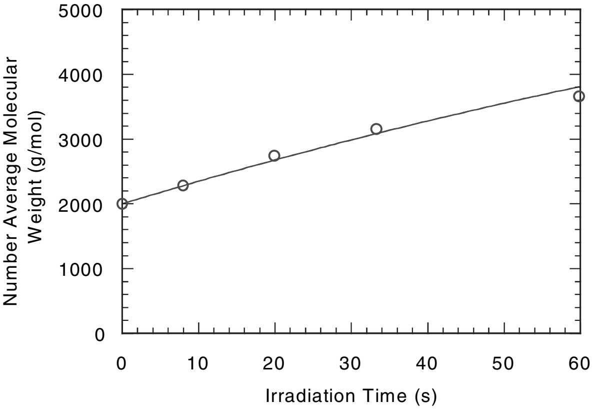
3.1. GPC studies with liquid-phase PS

Previously, evidence of weight gain of the substrate following application of the sequential grafting technique was obtained to demonstrate that monomers were grafted to PP substrates [12]. However, direct evidence is needed to demonstrate that the polymers are chemically bound to the substrate and that the grafted polymer chain length increases with increasing reaction time. In this work, graft polymerization of PEG200MA to PS was performed in solution using the sequential grafting method. The molecular weights of both unmodified and modified PS were measured using GPC. Control experiments were performed along with PS graft polymerization. It was found that the molecular weight distribution of controlled PS did not vary significantly when no BP was added to PS in the first step. However, increased molecular weights of modified PS were obtained when BP was used in the first step, with the same other procedures as those of control experiments. The results are shown in Fig. 2, indicating that poly(PEG200MA) was chemically bound to the PS. Further, the molecular weight of modified PS increases with polymerization time, demonstrating the reinitiating ability of the end groups of the grafted chains, as reported by Yang and Ranby [13].

The reaction mechanism and kinetic equations for solid-phase grafting were proposed in our previous paper [12].



(a)



(b)

Fig. 2. GPC results of liquid-phase polymerization for PS modified with PEG200MA. (a) Normalized refractive index versus elution time: (○) unmodified PS; (×) modified PS with irradiation time of 8 s; (◇) modified PS with irradiation time of 20 s; (□) modified PS with irradiation time of 33 s; (+) modified PS with irradiation time of 60 s. (b) Increase in molecular weight versus UV irradiation time: (○) experimental data; (—) model curve. The PS concentration was 6.7 wt% and the PEG200MA concentration was 20 wt% in toluene.

Similarly, the kinetic equation for liquid-phase graft polymerization is

$$\frac{\mathrm{d}[M]}{\mathrm{d}t} = k_\mathrm{P}[M]\{\phi I_0(1 - \mathrm{e}^{-\varepsilon b[\mathrm{BPHS}]})/k_\mathrm{t}\}^{1/2}, \tag{3}$$

where $[M]$ is the monomer solution concentration, ϕ the number of grafting chains produced per light photon absorbed, I_0 the intensity of incident UV irradiation, k_P and k_t the reaction rate constants, ε the molar absorptivity of the surface initiators, b the thickness of the solution layer in which the hydrogen abstraction reaction occurs, and [BPHS] represents the concentration of $(C_6H_5)_2OHC{-}PS$ (the initiator formed in the first step by hydrogen abstraction).

If we assume that [BPHS] is approximately constant due to its reinitiating ability, and let $[M^*] = \{\phi I_0(1 - \mathrm{e}^{-\varepsilon b[\mathrm{BPHS}]})/k_\mathrm{t}\}^{1/2}$, then Eq. (3) may be integrated to yield

$$[M] = [M_0]\,\mathrm{e}^{-k_\mathrm{P}[M^*]t}, \tag{4}$$

where $[M_0]$ is the initial monomer concentration and t the reaction time. Moreover,

$$\mathrm{MW}^{\mathrm{PS}} = \mathrm{MW}_0^{\mathrm{PS}} + \frac{[M_0] - [M]}{[M_0^{\mathrm{PS}}]} \times \mathrm{MW}, \tag{5}$$

where $\mathrm{MW}^{\mathrm{PS}}$ represents the molecular weight of the modified PS substrate, $\mathrm{M}_0^{\mathrm{PS}}$ the initial molecular weight of the PS, $[M_0^{\mathrm{PS}}]$ the molar concentration of the PS, and MW the molecular weight of the PEG200MA monomer. Substituting Eq. (4) into Eq. (5) yields

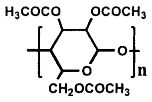
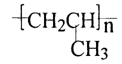
$$\mathrm{MW}^{\mathrm{PS}} = \mathrm{MW}_0^{\mathrm{PS}} + \frac{[M_0]}{[M_0^{\mathrm{PS}}]}(1 - \mathrm{e}^{-k_\mathrm{P}[M^*]t})\mathrm{MW}. \tag{6}$$

Based on the experimental data shown in Fig. 2, the best fit of Eq. (6) is shown in Fig. 2 as a solid line. The maximum likelihood estimate of the model parameter $k_\mathrm{P}[M^*]$ was obtained using KaleidaGraph™ based on the Levenberg–Marquardt [14] method by minimizing the sum of the squared errors. The confidence interval for the model parameter was calculated based on the work of Donaldson and Schnabel [15]. The best-fit model parameter is $k_\mathrm{P}[M^*] = 0.006 \pm 0.001\ \mathrm{s}^{-1}$, at the 90% confidence level. The experimental data are consistent with the best-fit equation, which is based on the proposed reaction mechanism, providing additional support for the proposed reaction mechanism. The slightly lower molecular weight obtained from the experiment relative to the molecular weight from the model prediction at 60 s of UV irradiation is likely caused by decreasing reactivity of radicals as graft chain length increases.

3.2. Different solid substrates

With AA as the monomer and BP as the photoinitiator, three types of commercial polymeric membranes were examined as solid substrates. The results are presented in Table 1. With respect to surface initiator formation (the first

Table 1
Photografting reactivity of polymeric membranes. Percent weight gain plus and minus one standard deviation for three repeats. BP solution was 5 wt% BP in benzene in the first step. The monomer solution was 15 wt% AA in ethanol in the second step. For the membranes used in the second step, the amount of grafted BP in the first step is 0.27 ± 0.04 wt% for both PP and CA

Substrate	Chemical structure	Surface initiator formation		Monomer graft polymerization	
		Irradiation time (s)	% Wt gain	Irradiation time (s)	% Wt gain
CA		11	1.0 ± 0.1	13	15.0 ± 0.2
PP	 $-[CH_2CH(CH_3)]_n-$	13	0.16 ± 0.02	13	7.3 ± 0.5
PVDF	$-[CH_2CF_2]_n-$	106	0.08 ± 0.05	N/A	N/A

step of the two-step process), CA has the highest reactivity due to the activating effect of the adjacent oxygen atoms. PP contains a large number of hydrogen atoms attached to tertiary carbons, which are easily abstracted by BP, and it therefore, has a higher reactivity than that of PVDF but a lower reactivity than that of CA. In fact, with regard to surface initiator formation on PVDF, BP concentrations of 1–30 wt% in benzene and irradiation times up to 106 s were tested, but no significant grafting onto PVDF was observed. In the graft polymerization (the second step of the two-step process), the carbon–carbon bond of the surface initiator species in CA is cleaved to form surface radicals and semipinacol radicals due to the activating effect of adjacent oxygen atoms. Thus, CA shows higher grafting reactivity than PP. The second step of the graft polymerization was not performed with PVDF because of the extremely small amount BP grafted in the first step.

In further studies, the effects of BP concentration on surface initiator formation for the CA membrane were examined using the sequential photografting method. A maximum reaction rate was observed with increasing BP concentration (see Fig. 3). The direct effect of higher BP concentration is to increase reaction rate, but the indirect effect of higher BP concentration is to increase light absorption, lowering the UV intensity at the interface of the BP solution and the membrane surface.

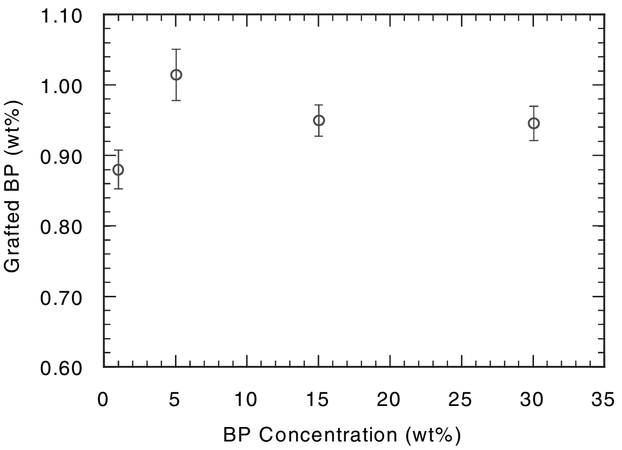


Fig. 3. Amount of grafted BP (weight percent gain of CA) versus BP concentration for an irradiation time of 10.6 s. The average weight of the unmodified CA membranes is 86 mg. The error bars represent plus and minus one standard deviation for three repeats.

In grafting AA onto CA, membranes with a surface initiator concentration of 0.27 ± 0.04 wt% were studied with variable AA concentration. For AA concentrations greater than 25 wt% and irradiation times greater than 13 s, significant crosslinking and homopolymer formation prevented the membranes from being removed from the glass substrate. For exposure times of 13 s, the weight gain of CA was found to be 5.8 ± 0.1 and 15.0 ± 0.2 wt% for 5 and 15 wt% AA in ethanol, respectively. The high degree of homopolymer formation and crosslinking likely results from chain transfer to the poly(AA) grafts that are being formed. Thus, though AA is a facile monomer to graft, it is difficult to control the amount and type of AA graft at large weight gains.

3.3. Monomers and solvents

The results are presented for three types of grafted monomers in Fig. 4. All of the experiments were performed with 25 wt% of monomer in ethanol, and the molar concentrations of AA, PEG200MA, and DMAEMA are 2.8, 0.7, and 1.3 mol/l, respectively. Under these conditions, it was found that AA exhibits the highest graft polymerization reactivity while PEG200MA and DMAEMA have lower graft polymerization reactivities.

The effects of different solvents on surface initiator formation were also examined. The solvent effect on surface initiator formation is largely related to the lability of hydrogen atoms in the solvent and the wettability of the substrate by

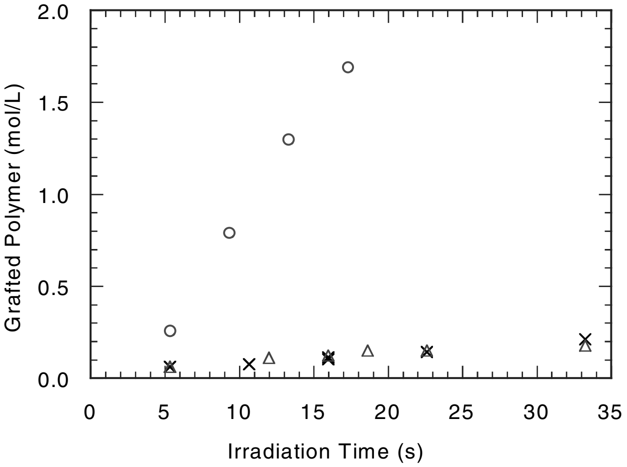


Fig. 4. Increase in polymer grafted onto PP membranes with irradiation time for different monomers with a concentration of 25 wt% monomer in ethanol: (○) AA; (×) PEG200MA; (△) DMAEMA.

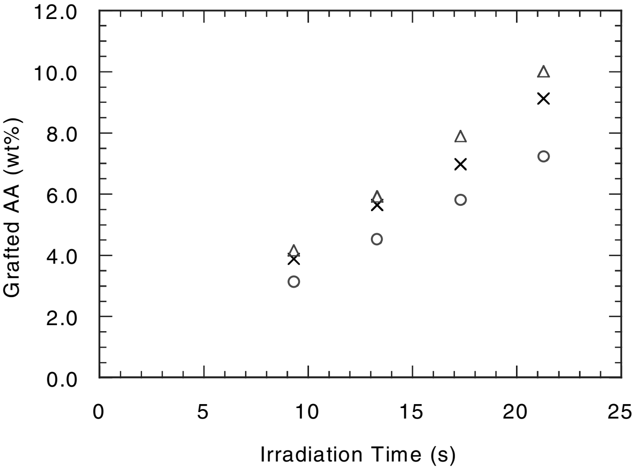


Fig. 5. Increase in AA grafted onto PP membranes with irradiation time at different surface initiator concentrations: (○) 0.007 mol/l; (×) 0.012 mol/l; (△) 0.017 mol/l. The AA concentration was 15 wt% monomer in ethanol.

the solvent. It has been reported [16] that the photoreduction reactivity for different types of hydrogen typically follows tertiary H > secondary H > primary H > H in phenol ring. The use of benzene as a solvent resulted in the largest weight gain (see Table 2) because the benzene hydrogen is the least reactive to abstraction [17]. The photoreduction reaction for hexane is expected to occur in the secondary hydrogen, whose bond energy should be lower than 100 ± 1 kcal/mol.

3.4. Surface initiator concentration

Effects of surface initiator concentration on graft polymerization were also investigated. The different surface initiator concentrations were obtained by using different UV irradiation times for surface initiator formation (the first step of the two-step process). The amount of grafted polymer on the substrates at different surface initiator concentration is shown in Fig. 5. The increased amount of grafted AA with increasing reaction time at each surface initiator concentration confirms the reinitiatability of the polymer chain ends.

Based on the results presented in Fig. 5, the graft polymerization rate at each surface initiator concentration was obtained by taking the derivative of the amount of grafted AA with respect to irradiation time, calculated using linear regression in KaleidaGraph™. Confidence intervals for the model parameters were determined using the method reported by Walpole and Myers [18]. The best-fit slopes (reaction rate) and intercepts (grafted AA at time 0) and their 90% confidence intervals for each surface initiator concentration are presented in Table 3. As expected, the intercept is not significantly different from zero, and the reaction rate is nearly constant for each surface initiator concentration, which is because that the AA concentration is nearly constant due to low conversion, and the surface initiation remains really constant due to the reinitiatability of the terminated ends. In fact, this behavior is predicted by the following model, which was reported in our previous work [12].

$$\frac{\mathrm{d}[M]}{\mathrm{d}t} = (0.054\ \mathrm{s}^{-1})(1 - \mathrm{e}^{-34[\mathrm{BPHS}]})^{1/2}[M], \qquad (7)$$

where $[M]$ represents monomer concentration and [BPHS] the surface initiator concentration in mol/l. The kinetic equation of graft polymerization of AA on PP was obtained at a single surface initiator concentration of 0.012 mol/l.

The graft polymerization rates at different surface initiator concentrations were also calculated using the kinetic Eq. (7). The relationships between the graft polymerization rate and

Table 2
Effects of different solvents on surface initiator formation. BP concentration was 5 wt% in each solvent, and UV irradiation time was 26 s

Solvents	Chemical structure	Bond energy[a] (kcal/mol)	Weight gain percentage
Benzene	$H–C_6H_5$	110±2	0.37±0.03
Chloroform	$H–CCl_3$	96±1	0.25±0.05
Hexane	$H–C_6H_{13}$	100±1[b]	0.24±0.06
Methanol	$H–CH_2OH$	94±2	0.22±0.02
Cyclohexane	$H–C_6H_{11}$	96±1	0.2±0.1
DMSO	CH_3SOCH_3	N/A	0.16±0.03
45 wt% DMSO + 50 wt% acetone	$CH_3SOCH_3 + CH_3COCH_3$	N/A	0.14±0.01

[a] Bond strength data from Table 3 in the Handbook of chemistry and physics, 64th ed, 1983–1984.

[b] Data for $H–C_5H_{11}$, since data are not available for $H–C_6H_{13}$.

Table 3
The best-fit slopes (reaction rate) and intercepts (grafted AA at time 0) and their 90% confidence intervals at different surface initiator concentrations. The AA concentration was 15 wt% monomer in ethanol, and PP was the substrate

Surface initiator concentration (mol/l)	Slopes (mol/l/s)	Intercepts (mol/l)
0.007	0.037±0.001	0.00±0.02
0.012	0.05±0.01	0.0±0.2
0.017	0.053±0.005	−0.05±0.08

surface initiator concentration for both the experimental data and the model predictions are presented in Fig. 6. The experimental data fit the model curve well, further confirming the proposed reaction mechanism, although a better fit of the new data is achieved if the kinetic constant 0.054 s^{-1} is replaced by 0.049 s^{-1}.

4. Conclusions

The novel sequential photoinduced living graft polymerization reported previously [12] was further characterized and applied to several new monomer–substrate combinations. The increased molecular weight of liquid-phase PS with increasing UV irradiation time provides, for the first time, direct evidence that grafted polymer was chemically bound to the substrate. The chemical composition of the substrate, monomer, and solvent were all known to be a key factor affecting the photografting reactivity. Among the solid substrates used in the experiments, CA was found to have the highest photografting reactivity, while the reactivity of PP is higher than that of PVDF, but lower than that of CA. AA was found to be more reactive than either PEG200MA or DMAEMA. The hydrogen lability and the wettability of solvents play important roles in the surface initiator formation, and experiments demonstrate that the surface initiator formation rate on PP goes as benzene > chloroform > hexane > methanol > cyclohexane > DMSO. The experimental data obtained at different surface initiator concentrations fit the kinetic model well, providing further characterization of the graft polymerization mechanism.

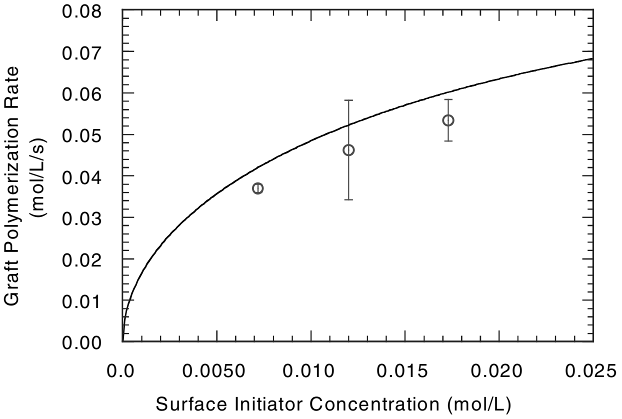


Fig. 6. Increase in the graft polymerization rate with surface initiator concentration: (○) experimental data; (—) model curve. The AA concentration was 15 wt% monomer in ethanol, and PP was used as the substrate.

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References

[1] Bunker BC, Rieke PC, Tarasevich BJ, Campbell AA, Fryxell GE, Graff GL, Song L, Liu J, Virden JW, Mcvay GL. Science 1994;264:48–55.
[2] Margel S, Vogler EA, Firment L, Watt T, Haynie S, Sogah DY. J Biomed Mater Res 1993;27:1463–76.
[3] Badley RD, Ford WT, McEnroe FJ, Assink RA. Langmuir 1990;6:792–801.
[4] Keszler B, Kovacs G, Toth A, Bertoti I, Hegyi M. J Membr Sci 1991;62:201–10.
[5] Yamagishi H, Crivello JV, Belfort G. J Membr Sci 1995;105:237–47.
[6] Ma H, Bowman CN, Davis RH. J Membr Sci 2000;173:191–200.
[7] Ma H, Nielsen DR, Bowman CN, Davis RH. Sep Sci Technol 2000 (in press).
[8] Brandriss S, Margel S. Langmuir 1993;9:1232–40.
[9] Kim KJ, Fane AG, Fell CJD. Desalination 1988;70:229–49.
[10] Jonsson AS, Jonsson B. J Membr Sci 1991;56:49–76.
[11] Ulbricht M, Oechel A, Lehmann C, Tomaschewski G. J Appl Polym Sci 1995;55:1707–23.
[12] Ma H, Davis RH, Bowman CN. Macromolecules 2000;33:331–5.
[13] Yang W, Ranby B. Macromolecules 1996;29:3308–10.
[14] Press WH, Teukolsky SA, Vetterling WT, Flannery BP. Numerical recipes in C. 2nd ed. Cambridge: Cambridge University Press, 1992.
[15] Donaldson JR, Schnabel RB. Technometerics 1987;29:67–82.
[16] Yang W, Ranby B. J Appl Polym Sci 1996;62:533–43.
[17] Beckett A, Porter G. Trans Faraday Soc 1963;59:2039.
[18] Walpole RE, Myers RH. Probablity and statistics for engineers and scientists. 3rd ed. New York: Macmillan, 1985.