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A Novel Sequential Photoinduced Living Graft Polymerization

Huimin Ma, Robert H. Davis, and Christopher N. Bowman*

Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309-0424

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ABSTRACT: A novel sequential ultraviolet (UV)-induced living graft polymerization method has been designed and investigated to modify polymeric materials. This method consists of two steps. In the first step, a surface initiator is formed on a substrate under UV irradiation in the presence of benzophenone (BP) solutions; in the second step, the monomers are grafted to the substrate by a living polymerization initiated by the surface photoinitiator. Hydrophobic porous polypropylene (PP) membranes were made hydrophilic and with negatively charged surface by grafting acrylic acid (AA). Experimental results demonstrated that grafting density and graft polymer chain length can be controlled by choosing the reaction conditions in the first step and in the subsequent step(s) independently. The amount of grafted polymer relative to the total amount of polymer from the novel sequential photoinduced graft polymerization method is 4-fold greater than that of the simultaneous grafting method for the system studied. In addition, a reaction mechanism was proposed and confirmed in the experiments. With regard to the surface initiator formation caused by hydrogen abstraction, the kinetic studies show that the reaction rate has a maximum value which depends on BP concentration. With regard to the graft polymerization in the second step, there is a linear relationship between the graft polymerization rate and the monomer concentration.

Introduction

It is widely known that the surface chemistry of solid substrates directly affects their behavior in many applications, such as dyeing, printing, adhesion, etc. Therefore, a variety of surface modification methods has been reported for a large number of different applications.[1−9] Photoinduced grafting is known to be a useful technique for the modification and functionalization of polymeric materials due to its significant advantages: low cost of operation, mild reaction conditions, selectivity to absorb UV light without affecting the bulk polymer, and permanent alteration of the membrane surface chemistry.

Photografting of polymers has been studied extensively since 1957.[10−17] The technique involves the initiation of the polymerization of vinyl or acrylic monomers at reactive sites generated on solid polymer surfaces using various methods. Previously, photografting has often resulted in production of significant amounts of homopolymer and cross-linked polymer if the initiator, benzophenone, abstracts hydrogen from monomer and reacted polymer. The relatively high levels of homopolymer formation associated with grafting are inconsistent with the idea of graft polymer formation resulting mainly from radicals formed on the substrate. The undesired homopolymer wastes expensive starting materials, and cross-linked polymer is detrimental to applications such as membrane filtration.

To circumvent the limitations above, a novel sequential photoinduced living graft polymerization method was designed (Figure 1) in the present work. In the first step, benzophenone abstracts hydrogen from the substrate to generate surface radicals and semipinacol radicals, which combine to form surface photoinitiators in the absence of monomer solutions. In the subsequent step(s), the monomer solutions are added onto the active substrate, and the surface initiators initiate the graft polymerization under UV irradiation. In this method, the homopolymer can be reduced significantly in polymerizations of monomers with abstractable hydrogens because semipinacol radicals have a very short lifetime and prefer to combine or terminate growing chains. Grafting density (number of grafting sites) and graft polymer chain length can also be controlled independently since initiator formation and graft polymerization occur independently in the successive steps.

Materials and Methods

Materials. The base substrates used in the experiments are commercial porous polypropylene microfiltration membranes, with a diameter of 47 mm, thickness of approximately 110 μm, pore diameter of 0.22 μm, and average weight of 0.06 g (Micron Separations Inc., M02WP04700). Acrylic acid (AA), (Aldrich, catalog no. 14,723-0) and poly(ethylene glycol 200) monomethacrylate (PEG200MA) (Polyscience, Inc., catalog no.16712) were used as the monomers. Benzophenone (BP) (Aldrich, catalog no. B930-0) was used as the initiator. Benzene, acetone, and deionized water were all used as solvents at different stages. All chemicals were used without purification.

Photografting Procedures. Both sequential and simultaneous photoinduced graft polymerization methods were used in the present work. First, the commercial PP membranes were soaked in benzene and dried to constant weight. Then, the membranes were weighed using an analytical balance that has an accuracy of 0.01 mg. For the sequential method, in the first step, 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), which was donated by 3M. The processor is equipped with two UV bulbs; each bulb is 400 W with a wavelength range of 232−500 nm. An optical multilayer dielectric interference filter (365 ± 5 nm), from Edmund Scientific (stock no. F43155), was used in the kinetic experiments. The quartz vessel was put on the conveyor, which carried the quartz vessel under the UV lamps. After irradiation

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* To whom correspondence should be addressed. Phone 303-492-3247, FAX 303-492-4341, e-mail bowmanc@colorado.edu.

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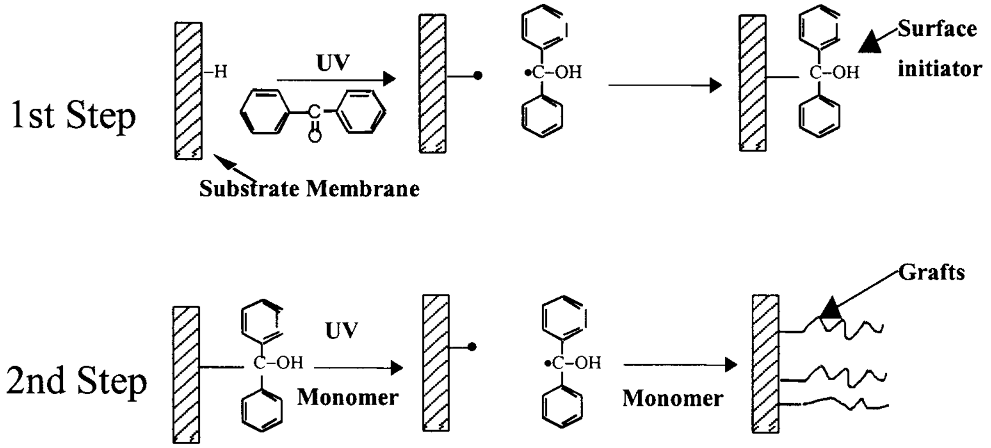

Figure 1. Schematic diagram of the novel photoinduced living graft polymerization method.

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 and that the membrane was put in a vacuum oven at 127 mmHg and 50 °C to evaporate the residual, unreacted solutions. The nongrafted poly(acrylic acid) was removed by soaking the membranes in deionized water for 24 h. Finally, the membranes were washed in acetone and dried to constant weight. For the simultaneous method, the procedures are similar to the procedures of the second step in the sequential method, except that both BP and monomer are present in the benzene solution.

The percent graft of BP, percent graft of monomer, grafting density, graft polymer chain length, and grafting efficiency are calculated by the following formulas:

$$\text{percent graft of BP} = (W_1 - W_0)/W_0 \times 100\% \quad (1)$$

$$\text{percent graft of monomer} = (W_2 - W_1)/W_0 \times 100\% \quad (2)$$

$$\text{grafting density, } D = (W_1 - W_0)/\text{MW}_{\text{BP}}/S \quad (3)$$

graft polymer length,

$$\gamma = [(W_2 - W_1)/\text{MW}]/[(W_1 - W_0)/\text{MW}_{\text{BP}}] \quad (4)$$

$$\text{grafting efficiency, } G_{\text{E}} = (W_2 - W_1)/(W_3 - W_0) \times 100\% \quad (5)$$

where W_0 is the weight of the blank membrane, W_1 is the weight of the membrane after the first step, obtained by weighing after extraction of unreacted BP solutions with proper solvents, W_2 is the weight of the membrane after the second step, obtained by weighing after extraction of homopolymer with proper solvents, S is the surface area of the membrane, MW_{BP} and MW are the molecular weight of BP and monomer, respectively, and W_3 is the weight of the membrane with both ungrafted and grafted polymer, obtained by weighing after vaporization of residual monomer and solvent solutions. The weight gain measurements were made using an analytical balance (Denver Instrument Co., A-200DS), which has an accuracy of 0.01 mg.

Results and Discussion

Verification of Surface Initiator Formation. It is well recognized that simultaneous photoinduced graft polymerization onto substrates occurs via hydrogen abstraction.[18-20] This principle suggests that excited benzophenone can abstract hydrogen in the absence of monomer to form the surface initiator, as proposed in Figure 1. A series of experiments have been conducted to provide evidence of the surface initiator formation in the first step of the process. The results are listed in Table 1. It is shown that the weight of the membranes did not change significantly without BP or without UV. However, the weight of the membranes did increase with BP coating and UV irradiation, and higher weight gain was obtained in nitrogen than in air. These results indicate that the reaction proceeded as desired and that the benzophenone (BP) was chemically bound to the substrate upon UV irradiation. Otherwise, the BP would be washed off from the substrate in a good solvent. There are two possible reasons for the weight gain. One is the formation of peroxide;[16,18,21] the other is the formation of graft BP through hydrogen abstraction. The formation of peroxide is excluded in our experiments, since oxygen is an inhibitor. Additional evidence about surface initiator formation is provided in later sections of this paper.

Table 1. Weight Percent Gain of PP Membranes and Standard Deviation for Six Repeats in Air or Nitrogen[a]

	without BP	without UV	with BP and UV
in air	0.01 ± 0.02	0.02 ± 0.03	0.17 ± 0.03
in N_2	0.03 ± 0.03	0.02 ± 0.02	0.34 ± 0.02

[a] "Without BP" means that blank membranes were irradiated 26.6 s (20 passes × 1.33 s). "Without UV" means that membranes were soaked in 5 wt % BP in benzene solution and then soaked and washed in acetone and dried until constant weight. "With BP and UV" means that the membranes were modified under the following conditions: 5 wt % BP in benzene, 26.6 s UV irradiation.

Table 2. Weight Percent Gain of PP Membranes and Standard Deviation for Six Repeats[a]

	blank membranes		membranes with surface initiator	
	without UV	with UV	without UV	with UV
in air	0.00 ± 0.00	0.02 ± 0.07	0.01 ± 0.01	0.01 ± 0.00
in N_2	0.01 ± 0.02	0.06 ± 0.04	0.02 ± 0.04	2.78 ± 0.32

[a] The monomer solution for all the membranes was 25 wt % AA in ethanol. UV irradiation time was 9.31 s (7 passes × 1.33 s). The grafted BP in the first step was 0.34 wt % of the blank PP membrane under the conditions of 5 wt % BP in benzene and 26.6 s UV irradiation.

Verification of Initiative Ability of Surface Initiator and Living Graft Polymerization. From Table 2, significant weight gain in the second step of the process was obtained on the membrane with surface initiator and UV irradiation in nitrogen. The weight

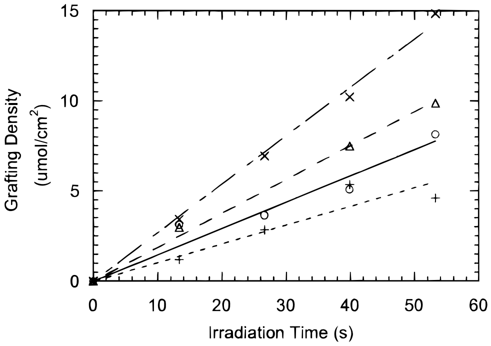

Figure 2. Grafting density versus irradiation time at different BP concentrations: (○) 0.5 wt % BP; (×) 10 wt % BP; (△) 30 wt % BP; (+) 70 wt % BP.

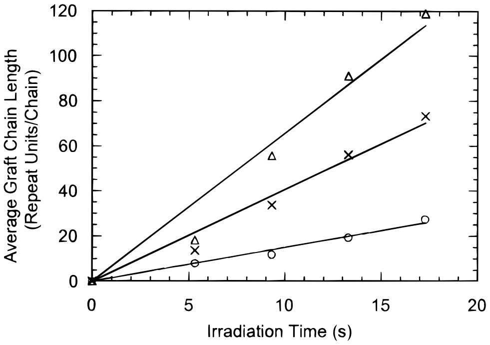

Figure 3. Average graft polymer chain length versus irradiation time at different AA concentrations: (○) 5 wt % AA; (×) 15 wt % AA; (△) 25 wt % AA. The amount of grafted BP in the first step was 0.34 wt % of the blank PP membrane under the conditions of 5 wt % BP in benzene and 26.6 s UV irradiation for all experiments.

change is relatively small or not significantly different from zero at all other conditions. These results indicate that the oligomer or polymer was indeed grafted on the membranes. Homopolymerization of AA can occur with or without surface initiator in the presence of UV irradiation. However, the homopolymer formed in the absence of surface initiator is washed off in a good solvent. Thus, the weight gain of the membrane is caused by graft polymerization that was initiated by the surface radicals. The membrane weight was nearly unchanged when the UV irradiation was performed in the presence of air. This result suggests that oxygen is a strong inhibitor of the second step of the graft polymerization process, as expected, since oxygen is an inhibitor of free radical polymerizations.

As mentioned earlier, the semipinacol radicals prefer to combine with growing polymeric chain radicals. So, the termination pattern produces a grafted copolymer that is rooted on the surface of the polymer substrates and carries end groups that were also found to be able to reinitiate polymerization, as reported by Yang and Ranby.[22] In fact, numerous experiments in our work also demonstrate that the growing chain radicals terminate the semipinacol radicals and then split off to initiate polymerization to increase the graft polymer chain length.

Control of Grafting Density and Average Graft Polymer Chain Length. Figure 2 shows the relationship between grafting density (mole of surface initiators per area) and UV irradiation time at different BP solution concentrations. As expected, grafting density increases with increasing UV irradiation time and has a maximum value with increasing BP concentration for a given UV irradiation time. Very low BP concentrations are undesired due to low surface initiation, whereas very high BP concentrations are undesired because BP absorbs the UV radiation. The results of Figure 2 indicate that the grafting density of the surface initiator can be controlled by controlling UV irradiation time and BP concentration.

In the second step of the novel photografting process, it is reasonable to assume that each surface initiator formed in the first step initiates polymerization to form one graft polymer chain since the surface initiator concentration is very low (0.34 wt % of the substrate) and the photoinitiation is very rapid. So, the average graft polymer chain length is calculated by eq 4. The results in Figure 3 demonstrate that the graft polymer chain length increases linearly with increasing UV irradiation time for a given grafting density and a given AA concentration, which is explained in the section Kinetics of Living Graft Polymerization. The graft polymer chain length also increases with increasing AA concentration in the ethanol solution. These results indicate that the graft polymer chain length can be controlled by adjusting irradiation time and monomer concentration, which is expected to have potential advantages in the membrane surface modification for controlling membrane fouling.

Comparison of Sequential and Simultaneous Grafting Methods. Both the simultaneous and novel sequential photoinduced grafting polymerization methods were used to modify PP membranes. With 0.34 wt % BP grafted in the first step and 50 wt % AA in ethanol in the second step, the grafting efficiency after 13.3 s of UV irradiation is 18 ± 3% for the simultaneous method and 83 ± 6% for the sequential method, at the 90% confidence level for three repeats. The conditions used for these experiments are ones that exaggerate the effects of lower efficiency in the simultaneous grafting case. Poly(acrylic acid) and monomer acrylic acid both are very capable of hydrogen abstraction. When other monomers with less labile hydrogens are grafted or at different grafting conditions, the grafting efficiency may be much higher for the simultaneous grafting method.[14,19]

For these studies, the grafting efficiency represents the percentage of grafted polymer relative to the total amount of polymer. It has been recognized that semipinocal radicals themselves rarely initiate bulk homopolymerization.[20] The significant percentage of homopolymer in the simultaneous method is attributed to the excited BP abstracting hydrogen from monomer to form monomer radicals, resulting in the formation of ungrafted homopolymer. Further, hydrogen abstraction from the graft polymer chain will result in the formation of branched or/and cross-linked polymer. In the novel sequential method, however, the homopolymer can be reduced significantly, and the formation of linear polymer chains is preferred, since there is no BP on the membrane surface or in the monomer solutions. The proposed reaction mechanism is confirmed by the fact that the grafting efficiency of the novel sequential method is 4-fold greater than that of the simultaneous method when AA was grafted to PP membranes in the present work. It is worth mentioning that the simultaneous grafting method is preferable when the hydrogen in the substrate is more readily abstracted by BP than is the hydrogen in the monomer and in the newly formed grafted polymer or homopolymer. Under these conditions, the polymerization can be more efficient and simpler for the simultaneous method. Clearly, the photoefficiency in the simultaneous graft polymerization will be dramatically higher than the overall photoefficiency in the proposed process. Thus, the proposed process is particularly useful only for monomers (and graft copolymers) which readily abstract hydrogen.

Reactions of a Novel Sequential Photoinduced Living Graft Polymerization. In this novel sequential photoinduced graft polymerization method, the grafting process can be divided into two steps: (1) synthesis of surface initiator and (2) graft polymerization of monomers. In the first step, a BP molecule absorbs a photon and then abstracts a hydrogen atom from the substrate. This abstraction process creates surface radicals and semipinacol radicals. Because there is no monomer present in this step, the recombination of the surface radicals and semipinacol radicals takes place readily and generates the surface initiators. The proposed reactions are described in eqs 6−8:

$$(C_6H_5)_2C{=}O + h\gamma \xrightarrow{k'_0} (C_6H_5)_2C{=}O^* \qquad \text{photoexcitation} \quad (6)$$

$$(C_6H_5)_2C{=}O^* + SH \rightarrow (C_6H_5)_2OHC^{\bullet} + S^{\bullet} \qquad \text{hydrogen abstraction} \quad (7)$$

$$(C_6H_5)_2OHC^{\bullet} + S^{\bullet} \rightarrow (C_6H_5)_2OHC{-}S \qquad \text{surface initiator formation} \quad (8)$$

where SH represents the substrate with hydrogen on the surface, * represents the excited state, and • stands for the radical.

In the second step, the substrate with the surface initiators grafted on its surfaces is exposed to the solution of monomer to be grafted and UV irradiation. The UV light cleaves the carbon−carbon bond of the surface initiator to form surface radicals and semipinacol radicals. The monomer reacts with surface radicals preferentially because of steric effects. Thus, the desired polymer chains can be grafted onto the substrate. The proposed reactions are listed in eqs 9−12:

photoexcitation:

$$(C_6H_5)_2OHC{-}S + h\gamma \xrightarrow{k_0} (C_6H_5)_2OHC^{\bullet} + S^{\bullet} \qquad \text{surface radical formation} \quad (9)$$

initiation:

$$S^{\bullet} + M \xrightarrow{k_i} SM_1^{\bullet} \qquad \text{grafted monomer radical} \quad (10)$$

propagation:

$$SM_n^{\bullet} + M \xrightarrow{k_p} SM_{n+1}^{\bullet} \qquad \text{grafted polymer radical} \quad (11)$$

termination:

$$SM_n^{\bullet} + (C_6H_5)_2OHC^{\bullet} \xrightarrow{k_i} SM_nC(C_6H_5)_2OH \qquad \text{grafted polymer} \quad (12)$$

where • stands for the radical and M represents monomer.

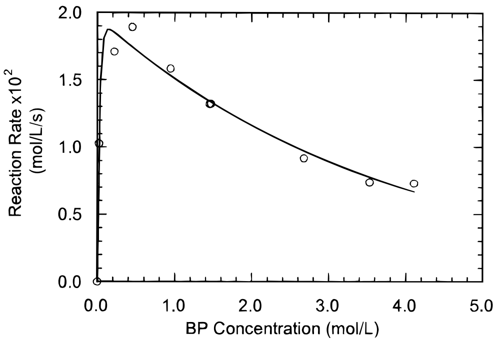

Figure 4. Reaction rates of initiator formation versus BP concentration: (○) experimental data; (—) model curve. UV irradiation time is 26.6 s for all experiments.

Kinetics of Surface Initiator Formation. In terms of eqs 6−8 and the Lambert−Beer law, the kinetic equation of surface initiator formation is written as

$$d[BPHS]/dt = f\phi_S I_0 e^{-\epsilon c[BP]}(1 - e^{-\epsilon b[BP]}) \qquad (13)$$

where BPHS represents $(C_6H_5)_2OHC{-}S$ (the surface initiator formed in the hydrogen abstraction), f is surface initiator formation efficiency, ϕ_S is the quantum yield of surface initiator formation, I_0 is the intensity of incident UV irradiation, c is the thickness of a BP solution layer through which UV irradiation must pass to reach the substrate surface, and b is the thickness of the membrane where the hydrogen abstraction reaction occurs.

To determine the parameters in eq 13, experiments were performed using different BP concentrations at different irradiation times. The surface initiator formation rate can be obtained by taking the derivative of the amount of grafted BP with respect to irradiation time. It was found that the reaction rate is a constant for a given initial BP concentration. This behavior is predicted by eq 13 because the conversion of BP is very low and the BP concentration can be considered to be nearly constant.

The relationship between reaction rate and BP concentration is shown in Figure 4. As explained previously, there is an optimum BP concentration that maximizes the reaction rate, due to the reduction in UV transmittance to the membrane surface at high BP concentrations. The circles represent the experimental data while the solid line represents the best fit of eq 13. The maximum likelihood estimate of the model parameters is obtained using KaleidaGraph based on the Levenberg−Marquardt[23] method by minimizing the sum of the squared errors. The confidence intervals for the model parameters were calculated on the basis of the work of Donadson and Schnabel,[24] as suggested by Young et al.[25] The best-fit model parameters and their 90% confidence intervals are $f\phi_S I_0 = 0.020 \pm 0.001$ mol/(L s), $\epsilon c = 0.26 \pm 0.01$ L/mol, and $\epsilon b = 34 \pm 10$ L/mol.

Kinetics of Living Graft Polymerization. According to eqs 9−12, the kinetic equation can be written as

$$R_m = k_p[M]\{\phi I_0(1 - e^{-\epsilon b[BPHS]})/k_t\}^{1/2} \qquad (14)$$

where R_m represents the rate of monomer consumption, ϕ is the number of grafting chains produced per light photon absorbed, k_P and k_t are reaction rate constants, and [M] stands for monomer solution concentration. To determine the quantitative relationship between reac-

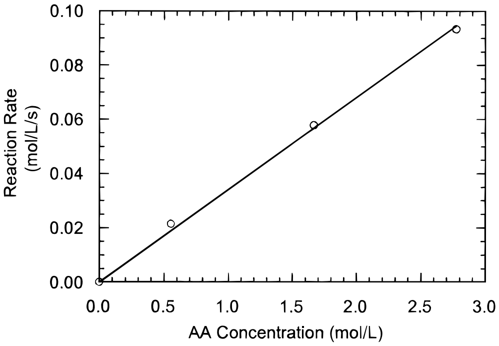

Figure 5. Reaction rates of graft polymerization versus AA concentration: (○) experimental data; (—) model curve. The amount of grafted BP in the first step was 0.34 wt % of the blank PP membrane under the conditions of 5 wt % BP in benzene and 26.6 s UV irradiation for all experiments.

tion rate and monomer concentration, we used different monomer concentrations at different irradiation times in the experiments. The monomer consumption rate was obtained by taking the derivative of the amount of grafted AA with respect to irradiation time. It was found that the reaction rate is a constant for each initial AA concentration. This behavior is predicted by eq 14, because the conversion of AA is very low, and the AA concentration can be considered to be nearly constant. The linear relationship between monomer consumption and reaction time further verifies the living graft polymerization.

The relationship between reaction rate and AA concentration is shown in Figure 5. The linear relationship of reaction rate and AA concentration confirms the proposed kinetic eq 14. The parameters in the graft polymerization rate equation were obtained using linear regression in KaleidaGraph. Confidence intervals for the model parameters were calculated using the method reported by Walpole and Myers.[26] The best-fit slope and intercept as well as their 90% confidence intervals are $0.033 \pm 0.002\ \mathrm{s}^{-1}$ and 0.001 ± 0.003 mol/(L s), respectively. As expected, the intercept is not significantly different from zero.

The parameters in eq 14 were obtained using the following method. The value of ϵb is 34 L/mol from the surface initiator formation kinetics, and [BPHS] is 0.014 mol/L in the kinetic study of graft polymerization. The value of $k_\mathrm{p}\{\phi I_0(1 - \mathrm{e}^{-\epsilon b[\mathrm{BPHS}]})/k_\mathrm{t}\}^{1/2}$ is $0.033\ \mathrm{s}^{-1}$ from the slope of the best-fit line in Figure 5. Therefore, $k_\mathrm{p}\{\phi I_0/k_\mathrm{t}\}^{1/2}$ is $0.054\ \mathrm{s}^{-1}$, and the final kinetic equation for graft polymerization is $R_\mathrm{m} = 0.054(1 - \mathrm{e}^{-34[\mathrm{BPHS}]})^{1/2}[\mathrm{M}]$, with [BPHS] and [M] having units of mol/L and R_m having units of mol/(L s).

Conclusions

A novel sequential photografting technique was developed for utilization in grafting monomers with abstractable hydrogens to polymer supports. For the first step, the surface initiator formation via hydrogen abstraction was verified. The initiative ability of the surface initiator and living graft polymerization were also demonstrated. The kinetic study of the initiator formation shows that there is a maximum reaction rate depending on BP concentration. The kinetic study of the graft polymerization indicates that there is a linear relationship between the monomer consumption rate and monomer concentration. The kinetic study of initiator formation and graft polymerization confirmed the proposed reaction mechanism. The grafting efficiency of the novel method is 4-fold greater than that of the simultaneous method for grafting acrylic acid to polypropylene membranes. The novel method also substantially eliminates undesired homopolymer and cross-linked or branched polymer formation. The grafting density and graft polymer chain length can be determined and controlled independently. Hydrophobic PP microfiltration membranes can be made hydrophilic with grafted poly(acrylic acid) and/or PEG200MA and may be multifunctionalized by grafting different polymers using the novel sequential photoinduced living graft polymerization method.

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