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In Situ Observation of Dithiocarbamate-Based Surface Photograft Copolymerization Using Quartz Crystal Microbalance

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ABSTRACT: A quartz crystal microbalance (QCM) technique which can detect weight increase in the nanogram order has been employed to continuously monitor the iniferter-based surface photograft polymerization behavior of vinyl monomers. The gold electrodes of the QCM were thinly coated with a photoreactive polystyrene partially derivatized with *N*,*N*-diethyldithiocarbamylmethyl groups acting as iniferters. A monotonic decrease in the resonance frequency of the vibrating oscillator of QCM, which was correlated with the weight increase via graft copolymerization initiated on the polystyrene, occurred immediately after ultraviolet light irradiation of the coated electrode surface in a methanolic or aqueous solution of vinyl monomers such as acrylamide (AAm), *N*,*N*-dimethylacrylamide (DMAAm), methacrylamide (MAm), methacrylic acid (MA), ethyl acrylate (EA), 2-hydroxyethyl methacrylate (HEMA), 2-(dimethylamino)ethyl methacrylate (DMAEM), *N*-vinyl-2-pyrrolidone (VP), and styrene (ST), except for vinyl acetate (VA). Upon cessation of irradiation, little frequency change was observed. The cycle comprising a decrease in resonance frequency under irradiation and no change under dark condition was repeated without appreciable fatigue. The polymer yield showed an almost linear increase with irradiation time up to 20 min. The apparent polymerization rate increased with concentration of monomer, light intensity, and surface density of dithiocarbamate groups. In addition, the rate was dependent on monomer's *Q* value and maximum at *Q* values of around 0.7−0.8 for EMA and HEMA.

Introduction

Surface design, which aims to provide surface functional values to fabricated devices, has become increasingly important since precise microarchitectural surface design is a fundamental requirement for advanced functional devices. For example, enhanced biocompatibility and function of biomedical devices such as artificial hearts, artificial grafts, and microbiosensors is essential. Since the biological responses upon implantation or blood circulation are determined by surface properties, chemical composition, and topology,[1−4] a surface micromanipulation technology that enables three-dimensional surface modification is essential for the development of these functional biomedical devices.

Among the various known surface modification techniques, photochemically driven processes can meet the above-mentioned requirements such as regional precision and dimensional precision, since photochemical surface modification occurs with micron-order precision only at the parts irradiated by light that is transmitted by a quartz crystal fiber.[5−10] In fact, our previous studies have shown that surface grafting of photoreactive polymers partially derivatized with phenyl azide groups resulted in the luminal surface modification of fabricated blood pumps.[11,12]

Well-defined polymers and copolymers (e.g., block, graft, tapered, or gradient) are usually prepared in a living polymeric system in which transfer and termination reactions are absent.[13−18] In regard to radical polymerization, the main difficulty in realizing a "living process" is the bimolecular reaction by radical coupling or disproportionation. Since termination is a second-order reaction and propagation is a first-order reaction of growing chain radicals, the degree of termination increases with the concentration of free radicals. A recent breakthrough in the development is "radical living" polymerization, the invention of the reversible deactivation of growing radicals by coupling with a stable free radical or a scavenger, enables more precise macromolecular design than using conventional radical polymerization.[19−27]

Photochemically driven radical polymerization using the iniferter technique (an iniferter acts as an initiator, transfer agent, and terminator), which has been extensively studied by Otsu et al., has a unique polymerization behavior.[19−25] When dithiocarbamate groups as the iniferter are irradiated with ultraviolet (UV) light, the iniferter dissociates into a radical pair: an alkyl radical that can polymerize vinyl monomers and a dithiocarbamate radical with much reduced reactivity to monomers, which tends to recombine with the former radical. The recombinant dithiocarbamate group undergoes dissociation to a radical pair upon UV irradiation; thus, monomer addition occurs, resulting in the elongation of the polymer chain. If neither transfer nor termination reactions occur, such photopolymerization proceeds only during UV irradiation in a quasi-living radical polymerization mechanism in which equilibrium exists between propagating (active) and nonpropagating (dormant) species. The quasi-living polymerization was classified as one of the living polymerizations according to the mechanistic feature of the equilibriums.[19−22] In fact, photopolymerization of styrene (ST) and methyl methacrylate (MMA) using *N*,*N*-diethyldithiocarbamate derivatives as the iniferter produced the respective polymers, the molecular weights of which increased with irradiation time under appropriate experimental conditions.[23−32] In addition, since the recombinant end

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as the dormant species can reinitiate polymerization in a solution containing another monomer, this method allowed the preparation of well-controlled block copolymers such as poly(styrene-*b*-methyl methacrylate) and poly(styrene-*b*-methyl methacrylate-*b*-styrene) both in solution and on microbeads surfaces.[28−30,33]

We utilized this method to prepare well-controlled, macromolecularly engineered surfaces of biomedical devices.[8−10,33] Our previous studies have shown that surface photopolymerization produced regionally precise, micropatterned surfaces onto which different polymers were regionally grafted,[8,10] a block copolymerized surface in which different polymer blocks were sequentially formed in graft polymers,[8,33] and a gradient surface in which the thickness of graft layer gradually varied in one direction.[8,10]

In this study, as an extension of our series of studies on photochemically driven dithiocarbamate-based surface macromolecular microarchitectural design,[8−10,33] we studied the in situ polymerization behaviors of various monomers, using the quartz crystal microbalance (QCM) technique,[34−39] in which polymer chains produced by graft copolymerization on the gold electrodes of QCM could be weighed in real time in nanogram order.

Experimental Section

Materials. Acrylamide (AAm), *N*,*N*-dimethylacrylamide (DMAAm), methacrylamide (MAm), methyl acrylate (MA), ethyl acrylate (EA), ethyl methacrylate (EMA), 2-hydroxyethyl methacrylate (HEMA), 2-(dimethylamino)ethyl methacrylate (DMAEM), vinyl acetate (VA), and *N*-vinyl-2-pyrrolidone (VP) were purchased from Wako Pure Chem. Ind., Ltd. (Osaka, Japan). Styrene (ST) was purchased from Ohken Co., Ltd. (Tokyo, Japan). AAm was used after recrystallization from methanol. The other monomers were used after distillation. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. Solvents and other reagents, all of which were of special reagent grade, were obtained from Wako and used after conventional purification.

Preparation of Photoreactive Copolymer (1). The photoreactive copolymer (**1**) was prepared by radical copolymerization of vinylbenzyl *N*,*N*-diethyldithiocarbamate (VD)[40] (obtained by condensation of vinylbenzyl chloride with sodium diethyldithiocarbamate) with ST in the presence of AIBN as an initiator in the dark at 60 °C. The details of the preparation method are described elsewhere.[8] The content of VD units in the copolymer (**1**) was calculated from ^{1}H NMR measurements and elemental analysis (C.H.N.).

In Situ Observation of Surface Photograft Polymerization. In situ continuous monitoring of photograft polymerization was performed using a quartz crystal microbalance (QCM) system (S-100, United System Integrators Co., Ltd., Fukuoka, Japan). The system is composed of a piezoelectric quartz oscillator, a dc source, a frequency generating circuit, a frequency counter (SC 7201, Iwatsu Electric Co., Ltd., Tokyo, Japan), and a personal computer (PC 9801E, NEC Corp., Tokyo, Japan). A 9 MHz AT-cut quartz crystal disk (Kyushu Dentsu Co., Ltd., Fukuoka, Japan) vacuum-plated with gold electrodes (0.198 cm^2) on each side was used as the piezoelectric quartz oscillator. The oscillator, in which one side of the electrodes was precoated with the photoreactive copolymer (**1**) (around 1 μm thick) by casting in toluene solution and the other side was sealed, was vertically immersed in a 30 mL quartz cell containing 20 mL of a vinyl monomer solution and was driven at 5 V dc. A stream of dry nitrogen was introduced through a gas inlet to sweep the cell for 5 min. The solvent used was methanol (except for AAm on which water was used). The oscillator was then UV irradiated by a 200 W Hg−Xe lamp (Hamamatsu Photonics, Ltd., L2859-01, Shizuoka, Japan) in an atmosphere of nitrogen from a distance of 20 cm. The light intensity, measured with a photometer (UVR-1, Topcon, Tokyo, Japan), was adjusted by the electric current. The temperature of the polymerization samples was maintained at 20−25 °C. The resonance frequency of the vibrating oscillator was measured using the frequency counter connected to the personal computer system. If the mass on the electrode is inelastic, then the following relation holds. That is, the decrease in frequency (ΔF) can be translated into the mass increase (Δm) on the electrode: $\Delta F = -1$ Hz corresponds to $\Delta m = 1.05$ ng.[39] On the basis of the linear decrease in frequency observed during the early period of photoirradiation, the apparent initial polymerization rate (R_p; mol/(min cm^2)) is as follows:

$$R_p = (\Delta F \times 1.05)/(t \times 0.196 \times \mathrm{Mw}) \qquad (1)$$

where t is the irradiation time (min) and Mw is the molecular weight of the monomer used.

Scheme 1. Chemical Structure of the Photoreactive Copolymers, 1: Poly(styrene-*co*-vinylbenzyl *N*,*N*-diethyldithiocarbamate)

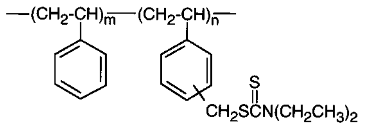
(**1**)

Table 1. Results of Copolymerization[a] of ST and VD

			copolymer			
	feed monomer ratio, VD/ST	yield[b]		M_n[c]	comp, VD/ST (mol %)	
run	(mol %)	(%)		(g mol^{-1})	^{1}H NMR	CHN
1	9/91	7.7	**1a**	36 700	11/89	10/90
2	20/80	8.5	**1b**	51 400	25/75	25/75
3	50/50	11.7	**1c**	37 000	49/51	53/47

[a] Polymerizations were performed in *N*,*N*-dimethylformamide at 60 °C for 3 h in the dark; [monomer] = 0.97 mol/dm^3, [initiator] = 9.5 mmol/dm^3. [b] Calculated from the weights of copolymers and monomers. [c] Determined by GPC analyses in chloroform at 40 °C.

Characterization. All ^{1}H NMR spectra were recorded in DMSO-d_6 solution using tetramethylsilane as the internal standard with a 270 MHz NMR spectrometer (JEOL, GX-270, Tokyo, Japan) at 30 °C. The compositions of the copolymers were determined from the signal intensities in the ^{1}H NMR spectra. Elemental analyses were performed at the Material Analysis Center of the Institute of Scientific and Industrial Research, Osaka University. Number-average molecular weights were determined by GPC analyses with a RI-8012 instrument (Tosoh, Tokyo, Japan) (column: Tosoh TSKgel G3000PW$_{XL}$ and G6000PW$_{XL}$) in distilled water and a HLC-8020 instrument (Tosoh, at Osaka National Research Institute, Osaka, Japan) (column: Tosoh TSKgel G5000H$_{XL}$, G4000H$_{XL}$ and G3000H$_{XL}$) in chloroform. Poly(ethylene glycol) standards samples were used for calibration. X-ray photoelectron spectroscopy (XPS) spectra were obtained with a Shimadzu ESCA 750 (Kyoto, Japan) using a magnesium anode (Mg Kα radiation) connected to an ESCAPAC 760 data processor, at room temperature and 2×10^{-7} Torr (8 kV, 20 mA).

Results

Preparation of Photoreactive Copolymer. Scheme 1 shows the chemical structure of the photoreactive copolymer, poly(styrene-*co*-vinylbenzyl *N*,*N*-diethyldithiocarbamate) (**1**), which was synthesized by radical copolymerization of styrene (ST) and vinylbenzyl *N*,*N*-diethyldithiocarbamate (VD) in the presence of AIBN in the dark. Table 1 summarizes the preparation conditions and the compositions of the copolymers obtained at the polymer yields of low conversions. The contents of VD units in the copolymers were 11 mol % for copolymer **1a**, 25 mol % for copolymer **1b**, and 49 mol

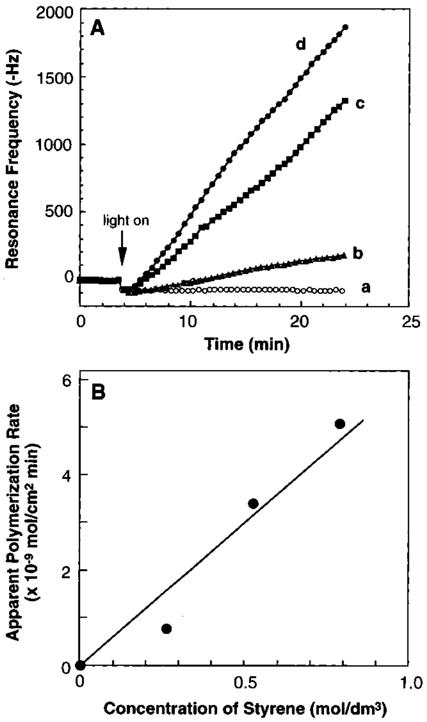

Figure 1. (A) Oscillator frequency changes with graft copolymerization of ST on the photoreactive copolymer **1b**-coated QCM in methanolic solution with UV irradiation (light intensity: 5 mW/cm^2). Concentration of ST: (a) 0, (b) 0.26, (c) 0.5, and (d) 0.76 mol/dm^3. (B) Relationship of oscillator frequency change calculated from (A) with concentration of ST.

% for copolymer **1c**, which were determined by ^{1}H NMR spectroscopy from the peak integration ratios of the aromatic protons (δ 6.3−7.2) to the remaining *S*-methylene protons (δ 4.2−4.6) of the dithiocarbamate moiety. The calculated compositions were nearly equal to those determined by the elemental analyses (mole percent of VD units in copolymers: **1a**, 10; **1b**, 25; **1c**, 53).

In Situ Observation of Surface Photograft Copolymerization. Continuous in situ monitoring of the weight increase by surface photograft copolymerization was carried out using the quartz crystal microbalance (QCM) systems. The photoreactive copolymer **1b** (thickness: around 1 μm) was coated on an electrode of the QCM and then immersed in a vinyl-containing monomer. The vinyl monomers used were acrylamide (AAm), *N*,*N*-dimethylacrylamide (DMAAm), methacrylamide (MAm), *N*-[3-(dimethylamino)propyl]acrylamide (DMAPAAm), methyl acrylate (MA), ethyl acrylate (EA), ethyl methacrylate (EMA), 2-hydroxyethyl methacrylate (HEMA), 2-(dimethylamino)ethyl methacrylate (DMAEM), vinyl acetate (VA), *N*-vinyl-2-pyrrolidone (VP), and styrene (ST). The solvent used was methanol except for AAm for which water was used.

Figure 1A shows the time-dependent changes in the resonance frequency of the vibrating oscillator of QCM in methanol containing different concentrations of ST. When the electrode was not irradiated by UV light, little change in the resonance frequency was observed. Upon UV irradiation under 20−25 °C, a small increase in resonance frequency was instantaneously observed, probably due to photoinduced electric noise. Upon further irradiation, although little change in resonance frequency was observed in the monomer-free solution (curve a in Figure 1A). In the presence of ST, a monotonic decrease in resonance frequency was immediately observed. A more profound decrease was observed at higher concentrations of ST (curves c and d in Figure 1A). The decrease in frequency can be translated into the mass increase on the electrode of QCM (−1 Hz = 1.05 ng). Few changes in frequency of the treated QCM were observed even after vigorous washing. On the other hand, in our previous paper,[8] XPS measurements and wettability studies showed that vinyl monomers such as DMAAm, MAA, ST, and *N*-[3-(dimethylamino)propyl]acrylamide can be photograft copolymerized on the polymer **1b**-coated film surface under the same conditions. In the XPS study, the sulfur signal was still observed even after photoirradiation in each monomer solution, indicating that dithiocarbamyl groups remained at the outermost layers even after photopolymerization. Thermally initiated polymerization was ruled out by the following experiment: no appreciable change in the resonant frequency was observed when QCM coated with the photoreactive copolymer in methanol solution containing ST was heated to 60 °C. It can be said that the increase in weight is due to the growth of polymers, possibly in the solvation state, which was produced by graft copolymerization on the photoreactive copolymer attached to the electrode surface. The polymer yield exhibited an almost linear increase with irradiation time up to 20 min. Figure 1B indicates that the apparent polymerization rate (R_p: mol/(cm^2 min)) calculated on the basis of eq 1 increased almost linearly with an increase in the monomer concentration.

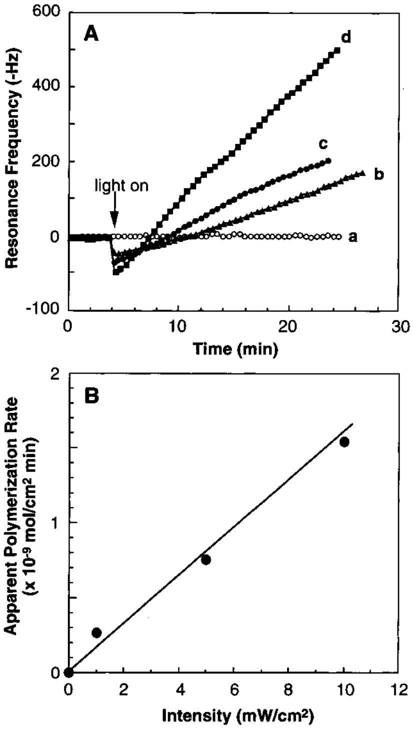

Figure 2. (A) Oscillator frequency changes with graft copolymerization of ST on the photoreactive copolymer **1b**-coated QCM in methanolic solution with UV irradiation (concentration of ST: 0.26 mol/dm^3). Light intensity: (a) 0, (b) 1, (c) 5, and (d) 10 mW/cm^2. (B) Relationship of oscillator frequency change calculated from (A) with light intensity.

The UV irradiation intensity dependence of the time-dependent change in the resonance frequency in photocopolymerization of ST in methanol is shown in Figure 2A. The resonance frequency decreased almost linearly

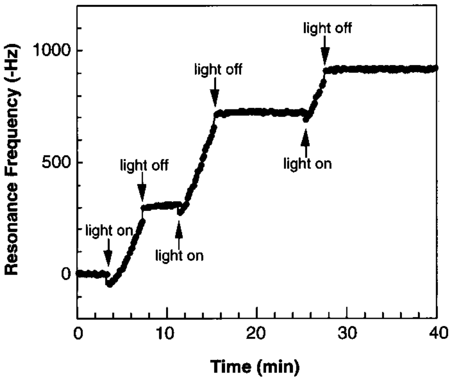

Figure 3. Oscillator frequency change of the photoreactive copolymer **1b**-coated QCM in a methanolic solution of ST (concentration of monomer: 0.5 mol/dm^3) with repeated UV irradiation (light intensity: 5 mW/cm^2) and cessation.

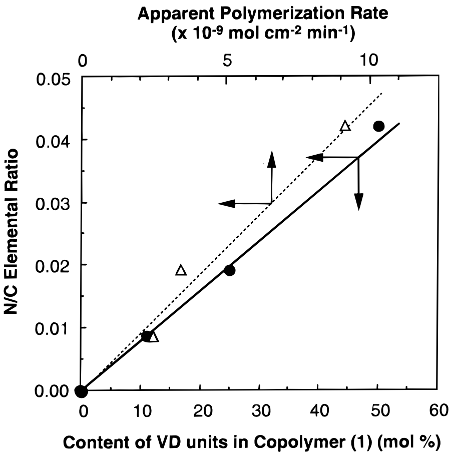

Figure 4. Relationships between the N/C elemental ratio of the photoreactive copolymer **1**-coated QCM surface and VD content in the copolymer **1**, as well as the apparent polymerization rate.

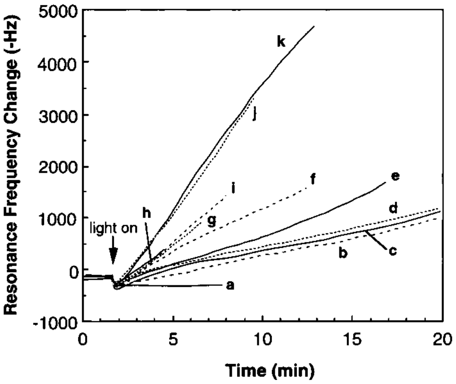

Figure 5. Resonance frequency change with graft copolymerization of various vinyl monomers on the photoreactive copolymer **1b**-coated QCM surface in methanol (except for AAm for which water was used) (concentration of monomer: 0.5 mol/dm^3). Light intensity: 5 mW/cm^2. a, VA; b, ST; c, MAm; d, VP; e, AAm; f, MA; g, DMAAm; h, DMAEM; i, EA; j, EMA; k, HEMA.

Table 2. Apparent Polymerization Rates of the Dithiocarbamate-Initiated Surface Photograft Polymerization[a] of Vinyl Monomers

monomer	*Q* value[b]	*e* value[b]	$R_p \times 10^{-9}$ (mol cm^{-2} min^{-1})[c]
VA	0.026	−0.220	0
VP	0.140	−1.140	4.4 ± 0.5
MA	0.42	0.600	8.8 ± 1.3
EA	0.520	0.220	14.5 ± 0.8
EMA	0.730	0.520	21.1 ± 1.6
HEMA	0.80	0.20	22.3 ± 4.0
ST	1.00	−0.800	3.4 ± 0.2
DMAAm	1.08	−0.500	11.9 ± 1.1
AAm	1.12	1.190	7.8 ± 1.9
MAm	1.460	1.240	4.6 ± 0.6
DMAEMA	2.080	0.420	7.5 ± 0.7

[a] Polymerizations were performed on the photoreactive copolymer **1b**-coated QCM surfaces; [monomer] = 0.5 mol/dm^3, irradiation intensity = 5 mW/cm^2. [b] Data from: *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York. [c] $R_p = (\Delta F \times 1.05)/(t \times 0.196 \times Mw)$, where ΔF is the frequency change per irradiation time (*t*, min) and Mw is the molecular weight of the monomer used.

with irradiation time, irrespective of the light intensity (curves b, c, and d in Figure 2A). The apparent polymerization rate increased almost linearly with light intensity (Figure 2B).

Figure 3 shows the change in the resonance frequency with or without UV irradiation in a methanolic solution of ST. The irradiation resulted in an immediate monotonic decrease in the resonance frequency, but on cessation of irradiation, little change in frequency was observed. Repeated cycles of irradiation and cessation produced very similar changes in the resonance frequency without appreciable fatigue.

The dependence of resonance frequency change on surface density of the iniferter was studied (Figure 4). Photoreactive copolymers (**1a, 1b,** and **1c**) with different contents of photoreactive dithiocarbamate groups were coated onto the QCM electrodes. N/C elemental ratios of the coated QCM surface, determined from the respective peak areas of the C_{1s} and N_{1s} signals in XPS spectra, were 0.009 for copolymer **1a**, 0.019 for copolymer **1b**, and 0.042 for copolymer **1c**, which are similar to those calculated from the elemental ratios of the copolymers (0.013, 0.026, and 0.045, respectively), suggesting that iniferter groups are homogeneously distributed on the outermost layer of the coated surfaces. Photograft copolymerization of ST on these coated QCM electrodes shows that the rate of resonance frequency change at the initial stage of photopolymerization (within 5 min) increased linearly with an increase in the N/C elemental ratios of the photoreactive copolymer **1**-coated QCM surfaces, indicating that the photopolymerization rate is proportional to the surface density of the iniferter.

Figure 5 shows the time-dependent change in the resonance frequency for the copolymer **1b**-coated QCM electrodes in methanolic solutions of various vinyl monomers (except for AAm for which water was used). Irrespective of the monomer type, a linear resonance frequency change was noted during the early period of photoirradiation. The total weight increase after graft copolymerization was less than 5 μg per the coated electrode surface (0.198 cm^2) for all monomers. The conversion was approximately 5−10 × 10^{-4}%. The rates of resonance frequency change per unit time (Hz/min) were as follows: 540 ± 98 for HEMA, 504 ± 37 for EMA, 308 ± 18 for EA, 242 ± 21 for DMAEM, 219 ± 20 for DMAAm, 164 ± 24 for MA, 103 ± 25 for AAm, 91 ± 11 for VP, 73 ± 10 for MAm, 66 ± 3 for ST, and nearly zero for VA. The apparent average initial polymerization rates of various vinyl monomers, calculated on the basis of eq 1, are tabulated in Table 2.

Discussion

Recent studies have reported fairly good control of radical polymerization, including chain architecture, end groups, molecular weight, and distribution of the polymers.[23−32] To develop a controlled polymer system, the concentration of radicals must be low to prevent bimolecular termination. This has been realized by creating equilibrium between propagating (active) and nonpropagating (dormant) polymer end by the addition of additives to the polymerization system. The additives include iniferters,[23−30] stable nitroso radical species,[31,32] various organometallic species,[41−44] or catalyzed atom-transfer radicals.[45−48] All systems except the iniferter system are driven thermally; therefore, a relatively high temperature is required. Since the iniferter system proceeds photochemically at room temperature, surface graft copolymerization using this system is best suited for surface modification of fabricated devices. As a continuation of our series of studies[8−10,33] focusing on iniferter-driven surface microarchitectures, iniferter-based polymerization behaviors were studied using the QCM technique.

Benzyl *N*,*N*-diethyldithiocarbamate, first synthesized by Okawara et al. as a radical polymerization initiator,[49] was extensively studied by Otsu and his colleagues as a photoiniferter (photoradical polymerization initiator-transfer agent terminator).[23−30] According to the iniferter concept proposed by them, living radical polymerization occurs as follows. At first, photolysis of benzyl *N*,*N*-diethyldithiocarbamate (R−S) by UV irradiation reversibly yields a pair of radicals: a benzyl radical ($R^\bullet$) and a dithiocarbamate radical ($S^\bullet$) (eq 2). The former radical can react with a vinyl monomer (M) to yield a radical polymer end ($R{-}M^\bullet$) (eq 3), and continuous repetition of this reaction leads to chain elongation (eq 4). The latter dithiocarbamate radical, whose reactivity to a monomer is much lower than that of the former benzyl radical, preferentially recombines with a propagating polymer end, resulting in a bimolecular termination reaction (dormant end) (eq 5). The dithiocarbamate end-capped chain thus formed can be reversibly dissociated into a radical pair by UV irradiation (eq 6). If only the reactions shown in eqs 2−6 are involved in the polymerization process, then quasi-living polymerization occurs with equilibrium between propagating (active) and nonpropagating (terminated) species in the absence of permanent termination.[19−22]

$$R{-}S \overset{h\nu}{\rightleftharpoons} R^\bullet + S^\bullet \tag{2}$$

$$R^\bullet + M \rightarrow R{-}M^\bullet \tag{3}$$

$$R{-}M_n{}^\bullet + M \xrightarrow{k_p} R{-}M_{n+1}{}^\bullet \tag{4}$$

$$R{-}M_n{}^\bullet + S^\bullet \xrightarrow{k_t} R{-}M_n{-}S \tag{5}$$

$$R{-}M_n{-}S \overset{h\nu}{\rightleftharpoons} R{-}M_n{}^\bullet + S^\bullet \tag{6}$$

Here, $M_n{}^\bullet$ denotes a polymer radical with n monomer units, and k_p and k_t are rate constants for propagation and recombination, respectively.

Otsu et al. have extensively studied the conditions that leads to quasi-living polymerization, such as the species of monomer and iniferter and their concentrations, solvent, polymerization temperature, and wavelength for irradiation.[25,28] ST, MMA, MA, VA, acrylonitrile, and methacrylonitrile were studied for this purpose. Among the monomers, ST and MMA showed living radical polymerization behavior under appropriate polymerization conditions. Both the monomer conversion and number-average molecular weight (M_n) of the resultant polymers increased with photoirradiation time, and the plots of molecular weight vs conversion gave linear relationships through the origin. The number of polymer chains per iniferter molecule remained almost unity during the entire course of polymerization.

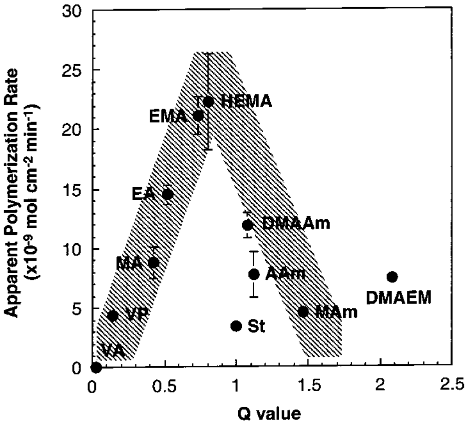

Figure 6. Relationship between the monomer's *Q* value and the apparent polymerization rate.

In this study, using the QCM technique which can measure mass change on the electrode in the nanogram order as a decrease in resonance frequency shift,[37−39] continuous in situ monitoring of propagation behavior of surface graft copolymerization on a benzyl *N*,*N*-diethyldithiocarbamate-derivatized electrode surface was carried out in monomer-containing methanol or aqueous solutions. The following results were obtained.

The resonance frequency change is strongly correlated with the weight increase of the solvation state of the polymers produced by graft copolymerization on the photoreactive copolymers coated on the QCM electrode surface. However, an approximate polymerization behavior quantified in eq 1 can be discussed as follows. The resonance frequency change of QCM exhibited an almost linear decrease during the early period of polymerization (within 15 min) irrespective of the species of monomer used, except for VA which did not induce polymerization. The apparent initial polymerization rate (R_p) increased almost linearly with an increase in monomer concentration (Figure 1), intensity of irradiation (Figure 2), and surface density of dithiocarbamate groups (Figure 4). These photopolymerization characteristics fulfill the requirements of iniferter-based living polymerization. On the other hand, initial R_p depended on the species of monomer used (Figure 5 and Table 2). A relatively large R_p was observed for HEMA and EMA compared to that for ST.

It would be of interest to correlate the apparent initial R_p in this iniferter-based polymerization with the monomers' Q values that were obtained for radical polymerization initiated by conventional initiators.[50] As shown in Figure 6, for monomers with relatively low Q values, very small R_p's were observed. With an increase in Q values, R_p also increases. Maximum R_p's were observed for EMA and HEMA (Q values around 0.7−0.8), and the R_p's decreased as the Q values were increased further. This is in contract to conventional radical polymerization behavior where very high propagation rate constant k_p's are experimentally observed for monomers with very low Q values and an increase in Q value tends to decrease in k_p value, whereas monomer reactivity to various radicals such as methyl, styryl, and oxyl radicals tends to increase with an increase in Q value.[51,52] The smaller the Q value of monomers is, the higher reactivity of the radical produced from the monomers is. The k_p dependence on Q values for conventional radical polymerization appears to be determined by the reactivity of a radical. Thus, the Q value can be used as an apparent index of reactivity of a radical. On the other hand, in iniferter-based radical polymerization, there is a bell-shape dependence between Q values and the obtained R_p's which can be translated into a k_p value in this experimental condition (Figure 6). This relation may account for the balance between k_p and radical recombination rate constant (k_r) as follows. A high radical reactivity should provide a larger k_r between propagating polymer radical and dithiocarbamate radical. This gives a higher probability of the formation of the dormant state of polymer chain end than the radical state, resulting in lower R_p. On the other hand, a low radical reactivity may reduce k_r, which may provide an increase in R_p. It can be said that R_p can be estimated by the Q value of the monomer.

Although quasi-living radical copolymerization techniques, including stable nitroso radical species[31,32] that react with a growing polymer chain radical to form a relatively stable C−N covalent bond and act as potent polymerization inhibitors, have been developed for controlled (co)polymerization, our previous studies have shown that iniferter-based surface graft copolymerization provides microarchitectural surfaces with controlled polymer or block lengths and regional precision.[8−10,33] This allows us to utilize this technique to provide surface functionality for the improvement of biomedical devices and microdevices. Such studies will be reported in the near future.

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